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Synthesis and Thermo-Physical Characterization of Graphene Based Transformer Oil

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Abstract

Transformer oils are used to serve as coolants and an insulation medium to avoid overheating in transformers. Due to low thermal conductivity of transformer oils which may result in overheating, nanoparticles has been introduced to overcome this matter. In this research, graphene nanoparticles (GNPs) with a high thermal conductivity of 5000W/mK were dispersed in transformer oil at a concentration of 0.01-0.1 wt% respectively. The stability of the graphene-transformer oil nanofluids (GTNFs) produced is studied using UV-Vis spectrophotometer in which the concentrations of suspensions were assessed. An optical microscope is used to study the dispersion quality and the uniformity of clusters formed at different weight fractions qualitatively. Thermal conductivity and viscosity of the samples were measured over a range of temperature from 20-100 °C. The thermal conductivity and viscosity of GTNFs were observed to be strongly dependent on the temperature and concentration of GNPs. The enhancement in thermal conductivity obtained was from 2.63-69.31 % as the temperatures varies from 20-100 °C, for 0.01-0.1 wt% of GNPs. It was also further observed that the viscosities of the GTNFs were reduced by 8.33-23.97% as the temperature rises allowing more convectional heat flow. It is thus concluded that the increase in thermal conductivity and decrease in viscosity as temperature rises enhances the overall performance of the transformer oil.

Keywords- transformer oil, graphene nanofluids, thermo-physical properties, thermal conductivity, viscosity

1. Introduction

Nanotechnology has been expanding widely over the years and was predicted to have the usage of 1 trillion per year starting from year 2015 [1]. It is a technology which comprises microscopic particles known as nanoparticles with size ranging from 1-100nm. The five major types of nanoparticles are Carbon Nanotubes (CNT) and Fullerenes, Semiconductors, Metals, Ceramics, and Polymeric. These nanoparticles are exceptionally prominent for its thermal, mechanical, electrical and optical properties. In terms of heat transfer, the thermal properties of the nanoparticles play an important role in enhancing the performance of heat transfer fluids. Heat transfer fluids such as water, transformer oil and ethylene glycol (EG) which are widely used in heating systems, transportation, electronic cooling, petroleum refineries and many more. However, these conventional fluids have considerably low thermal conductivities which causes them to have limited range of applications. Hence, nanoparticles with higher thermal conductivities are dispersed into the heat transfer fluids producing nanofluids with higher heat transfer capabilities [2]. Nanofluids in general are suspensions of nanoparticles dispersed in a base fluid. The addition of micro-sized particles into base fluids is not efficient due to its heavier weight and the gravitational force which causes the sedimentation of particles leading to a degradation in thermal properties [3]. The sedimentation can be significantly reduced or even prevented with nanoparticles which are lighter and smaller in size and thus enhancing the thermal properties of the fluid [4].

Nanostructured carbon materials such as GNPs have been attracting attention due to its high thermal conductivity of 5000 W/mK which is much higher than that of CNT (3000 W/mK) and diamond (2000 W/mK) [5-6]. Graphene is a monolayer graphite which consist of one-atom-thick planar sheet with bonded carbon atoms densely packed together in a honeycomb crystal lattice [7]. Due to the ability of GNPs to enhance the thermo-physical properties of heat transfer fluids, it can be added to transformer oil to increase the overall performance of the transformer. Transformers are used to regulate the voltage supply to homes, processing plants, factories and all other places which use electricity. While performing its duty, transformers also generate electricity which causes an increase in temperature which leads to overheating and failure to operate. Transformer oil which is stored in the transformer tank is used as a source of cooling and electrical insulation of the electrical appliances inside the tank. Thus, it is highly desirable for the oil to have a higher thermal conductivity to enhance the cooling effect. The addition GNPs into base oil has high potential to increase the thermal conductivity which in turn increases the heat transfer rate from the electrical appliances to the oil. Consequently, overheating which causes transformers failure can be prevented.

As of today, there are generally two methods of producing nanofluids. The methods used to prepare nanofluids is vital as the thermo-physical properties of the nanofluids can only be studied if the nanoparticles are well dispersed in the base fluid. The one-step method can be divided into chemical methods and physical methods respectively. In 2001, Eastman et al.[8] developed a one-step physical vapour condensation method to reduce agglomeration by direct condensation of metallic vapor into nanoparticles by allowing contact with a low vapour pressure liquid. However, this method is not appropriate for large scale synthesis of nanofluids due to its high cost. Hence, a one-step chemical method is developed. Zhu et al.[9] prepared copper

nanofluids using the one-step chemical method by reducing Copper(II) Sulfate Pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) using Sodium Hypophosphite Monohydrate ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$) in EG under microwave irradiation. The copper nanofluids produced were well dispersed and stable. Despite its stability, it has a major disadvantage in which the residues of reactant left in the nanofluids due to incomplete reaction. Apart from the one-step methods, the two-step method is the more widely used to prepare nanofluids. The nanoparticles are first prepared as dry powders by mechanical or chemical exfoliation before dispersing the nano-sized powders into a base fluid. The second processing step of dispersing the powder into the fluid is aided with agitation, ultrasonic agitation, homogenizing or ball milling. The two-step method is considered as the most economic method in producing large scale nanofluids. Rashmi [10] prepared CNT-water nanofluid using the two step methods where CNT was obtained in powder form before dispersing it into water in the presence of dispersant. The CNT-water nanofluids were homogenized at 28000 rpm and sonicated for four hours at room temperature. Gum Arabic (GA) was used to aid the dispersion of CNT and the nanofluids produced were found to be stable for more than 6 months.

With a stable nanofluid produced, its thermo-physical properties such as the thermal conductivity and viscosity are important properties of nanofluid to be studied. It is generally expected to show high thermal conductivity enhancement and lower viscosities. In 2010, Weiyu et al.[11] developed graphene-EG nanofluid which resulted in a thermal conductivity enhancement of 86% with 5.0 vol% of GNPs proving significant increase in thermal conductivity compared to a conventional EG fluid. Choi et al. [12] work showed 20% enhancement in thermal conductivity at 4 vol% of Al_2O_3 nanoparticles. GNPs which has a thermal conductivity of 5000 W/mK is much higher than that of Al_2O_3 (30 W/mK) has a high potential to further enhance the thermal conductivity. In the work done by Madhusree et al. [13], the viscosity of copper oxide (CuO)-gear oil nanofluid decreases significantly with the increase in temperature. Similar observations were also reported by Praveen et al. [14] on CuO-EG nanofluids. The viscosity of an ideal transformer oil should be kept low so that it has less resistance to the convectonal flow of oil allowing higher rate of heat transfer.

This study aims to synthesize and evaluate the stability of GTNFs with concentration of GNP ranging from 0.01 to 0.1 wt%, respectively. The thermo-physical properties (thermal conductivity and viscosity) of the stabilized GTNFs were also investigated as a function of temperature and GNPs concentration. Enhanced thermo-physical properties could considerable extend the lifetime and performance of transformer.

2. Research Methodology

2.1 Chemical

GNPs is obtained from Graphene supermarket, USA with purity of 99.2% with average flake thickness of 12 nm and average particle (lateral) size of 4500 nm, respectively. Complimentary naphtha based transformer oil was obtained with the collaboration of Lube World Holdings Sdn. Bhd. Naphtha based oil was also chosen as the oil allows natural convection circulation as sludge present (if any) will not precipitate at the bottom and obstruct the transformer cooling system [15].

2.2 Synthesis of Nanofluids

GTNFs were prepared using the two-step method in which a measured amount of dry GNPs were dispersed into measured amount of transformer oil. Different amount of GNPs ranging from 0.01 to 0.1 wt% were selected based on the similarity of weight percentage used by other researchers on other GNPs or other carbon-based nanofluids[10, 16-17]. The GNPs of different weight percentage were dispersed into transformer oil to produce nanofluids with the total weight of 40 grams. Table 1 shows the amount (in wt. %) of GNPs in each sample.

Table 1. Amount of GNP and transformer oil used in the present study.

Samples	GNPs (wt%)	Transformer Oil (g)
G1	0.01	39.996
G2	0.02	39.992
G3	0.04	39.984
G4	0.08	39.968
G5	0.10	39.960

After the GNPs were dispersed in the transformer oil, the samples were sonicated for 4 hours using a water bath sonicator (Elma Transsonic TI-H-15) at room temperature and 35 kHz. The sonication time was set as a fixed variable based on the stability studies done by Rashmi et al.[18] in which 4 hours of sonication time can maintain the stability of nanofluids for over six months signifying its high stability. Sonication helps to entangle the nanoparticles which are in clusters to prevent agglomeration by means of physical vibrations. Despite that, prolonged sonication may cause deformation of the natural GNPs structure which leads to the inability to fully utilize the properties of the structure [18].

2.3 Stability Studies on Nanofluid

In this research, the stability of nanofluids prepared was studied using a UV-Vis spectrophotometer (Shimadzu UV-1800, Japan) in which the concentration measurement is based on Beer–Lambert’s law that states that the absorbance is directly proportional to the concentration of the sample. Stability studies were performed for a period of 3 weeks. This method used evaluates the stability of nanofluids prepared quantitatively by measuring the concentration of nanoparticles in the suspension versus sedimentation time. Before the start of the stability tests, the UV-Vis absorbance curve and a linear calibration curve were obtained as shown in Figures 1 and 2 respectively by exposing light energy with wavelength between 190 nm to 900 nm to the samples. Part of the molecules absorbs the light energy from the UV-Vis spectrophotometer and create peaks in the spectrum. The UV-Spectra obtained for this research was at 570 nm (highest peak). With the wavelength of 570nm for the GTNF, a linear calibration curve was obtained. For the next 3 weeks, the concentrations of samples were measured and the consistency of the concentration readings indicates how well the GNPs dispersed in transformer oil.

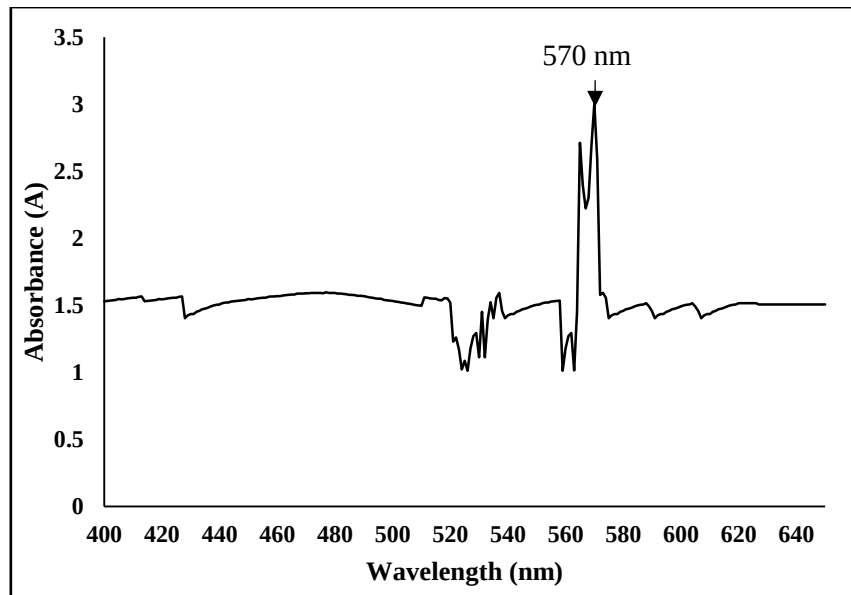


Figure 1. UV-Vis absorbance curve.

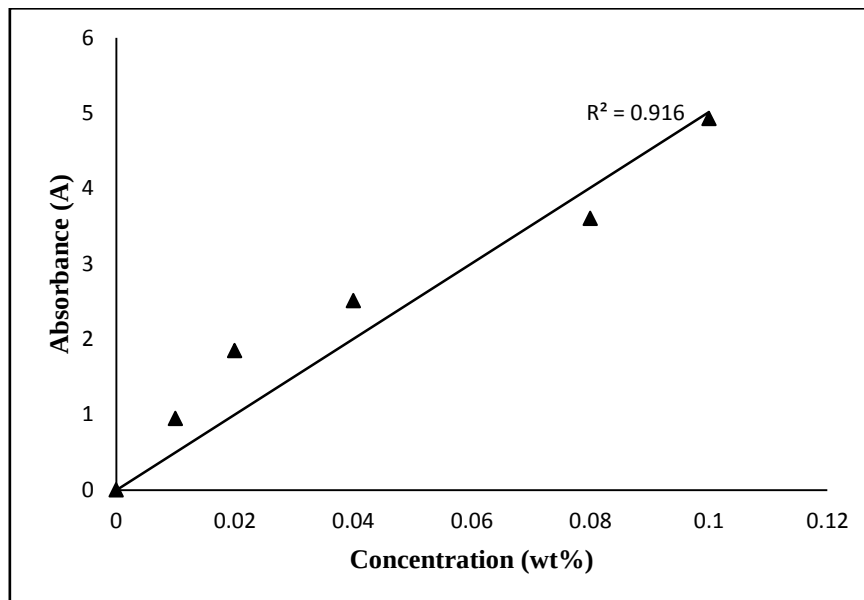


Figure 2. Calibration curve for different GNPs concentration at 570 nm.

2.4 Characterization of Nanofluids

The dispersion of the GTNFs were further studied using an optical microscope (Swift M10D Series Digital Microscope) using 40X magnification lens. The usage of the optical microscope is limited as it is an ordinary light microscope and thus it does not give accurate image of the clusters formed. However, it allows qualitative assessment to be done in which the uniformity of clusters formed can be observed.

2.5 Thermo-Physical Properties

2.5.1 Thermal Conductivity Measurements

A thermal conductivity analyzer (KD2 Pro Decagon Device, USA) was used to measure the thermal conductivity of the stable nanofluids of different GNPs

concentration (0.01-0.1 wt%) against different temperature. The variation of temperature (20-100°C) of the nanofluids are done by immersing the nanofluids into an oil bath at 20°C intervals. This range of temperature was chosen based on the operating temperature of transformer oil at 65 °C which may go up to 95 °C. The thermal conductivity meter was first calibrated using the standard glycerine at room temperature. The probe (60mm long single needle) from the meter was inserted into the nanofluid samples prepared. The readings are automatically taken at a 15 minutes interval. Only readings with the error with value less than 0.01 were recorded. Approximately 10 readings results were recorded per sample and the average readings were then obtained. The percentage enhancement in thermal conductivity of each sample compared to pure transformer oil was calculated using Eq (1) below [18]:

$$\text{Percentage Enhancement (\%)} = \frac{k_{\text{nanofluid}} - k_{\text{base fluid}}}{k_{\text{base fluid}}} \times 100\% \quad (1)$$

2.5.2 Viscosity Measurements

The viscosities of the nanofluids were measured using the viscometer (Brookfield DV-II+ Pro EXTRA) for G1, G3 and G5 against different temperature of GTNFs. Spindle model LV-1 (61) was used based on its wide range of viscosity. Similarly to the measurements taken for the thermal conductivity, the temperatures were varied between 20-100°C at 20°C interval. All results obtained from the experiments were analysed using graphs plotted of different concentration of GNPs against temperature of the nanofluids.

3. Results and Discussion

3.1 Stability of Nanofluid

The stability of the GTNFs is measured based on the GNPs concentrations which corresponds to the absorbance at 570 nm as shown in Figure 1. The stability of each sample (G1-G5) is shown in Figure 3. From Figure 3, it is clear that all the samples prepared were stable in the three weeks of UV-Vis measurement. It is also observed that the stability of G5 was slightly decreased with increasing sedimentation time. This is due to the higher amount of GNPs added to the oil forming a denser solution. It is a distinguished fact that denser particles tend to sediment quicker than less dense particles. However, even the largest change in concentrations of G5 is very small of about 5.1% which occurred at 170 hour before the concentrations of G5 stabilizes again.

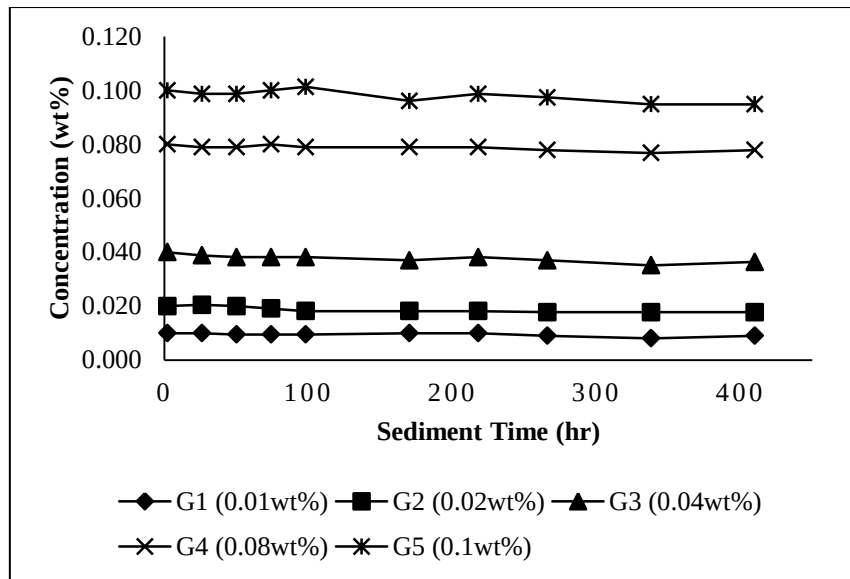
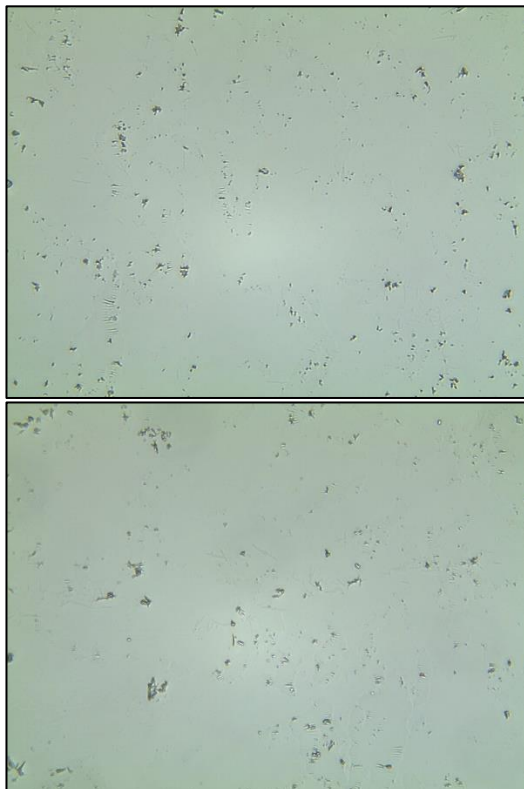


Figure 3. Effect of concentration and sediment time on the stability of GTNFs.

3.2 Optical Microscope

Figure 4 shows images of the dispersion of GNPs in transformer oil as captured using 40X magnification lens of the optical microscope. It is observed that there are good dispersions as the small clusters formed are uniform. GTNFs with higher concentrations such as G5 (0.1 wt%) show more distinct image of the clusters formed as the weight fraction of GNPs is higher causing the nanofluid to have more clusters. All images were taken after two months from the preparation of nanofluid in which agglomerates tend to form.



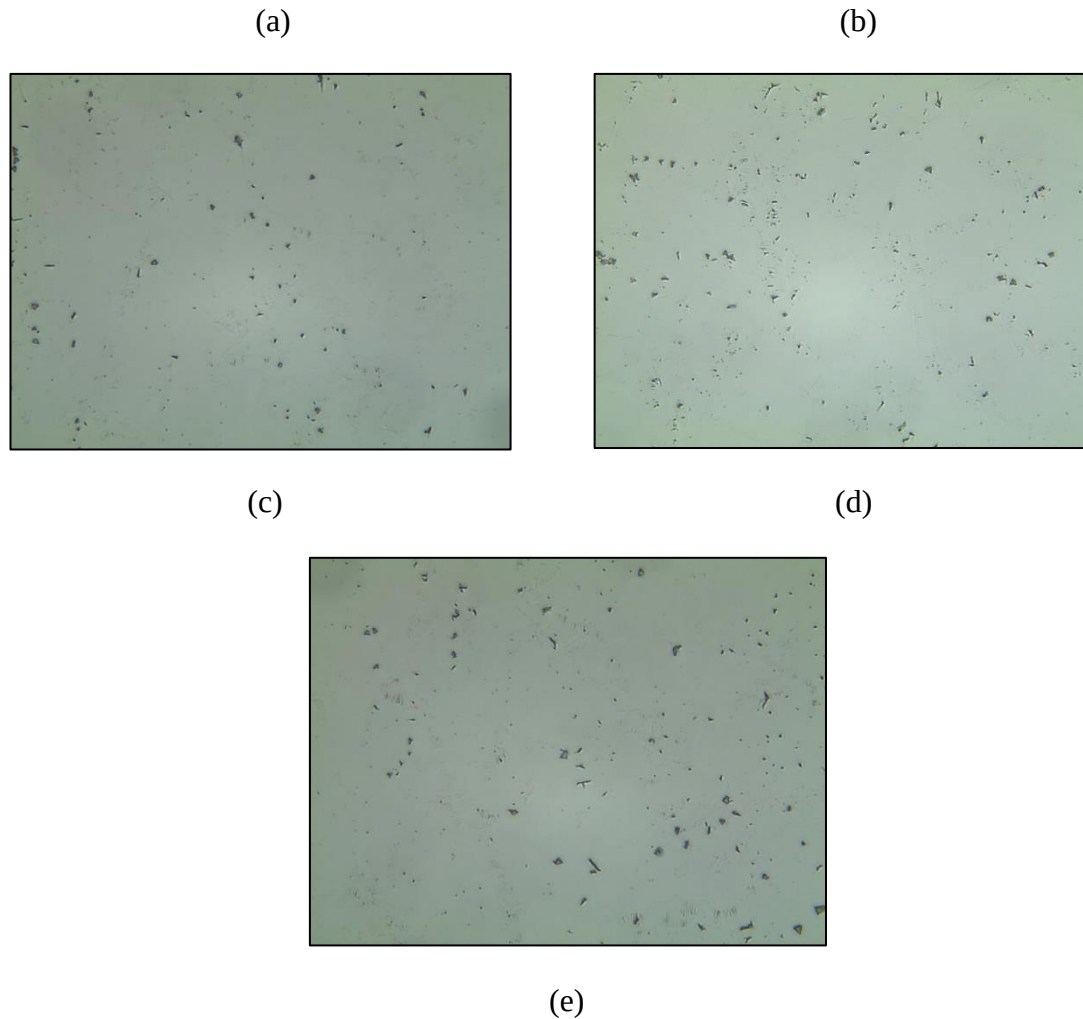


Figure 4. Optical Microscope Images of (a) G1 (0.01 wt %) (b) G2 (0.02 wt %) (c) G3 (0.04 wt %) (d) G4 (0.08 wt %) (e) G5 (0.1 wt %).

3.3 Thermo-Physical Properties

3.3.1 Thermal Conductivity

Effects of different GNPs concentrations and temperature are studied on the effective thermal conductivity of GTNFs as shown in Figure 5. It is depicted that the thermal conductivity increase notably with the increase of GNPs concentrations and temperature. The enhancement in thermal conductivity with respect to concentration obtained at 60 °C for 0.01-0.1 wt % of GNPs as shown in Figure 6 was from 5.66-29.25 %. The enhancement obtained with respect to temperature for G5 (0.1 wt%) at 20-100 °C was from 13.86-69.31 %.

However, there is a drop in thermal conductivity at 40 °C because of the nature of naphthenic based transformer oil in which its thermal conductivity decreases with increasing temperature [19-20] which is also observed from Figure 5. After 40 °C, the effect of Brownian motion of GNPs which is a strong function of temperature overtook the effect of the decreasing thermal conductivity nature of transformer oil. The collision of nanoparticles due to Brownian motion is a slow process which occurs after the thermal diffusion of the nanoparticles suspended in the base fluids [21]. Thus, the effect of Brownian motion is only significant after 40 °C.

The perfect structure and properties of GNPs being two-dimensional and has low thermal interface resistance attributed the excellent thermal conductivity enhancement at such low concentrations. Also, the thermal conductivity is enhanced due to the large surface area available on the GNPs for heat transfer which is the major contribution of the increase in effective thermal conductivity of the nanofluids prepared.

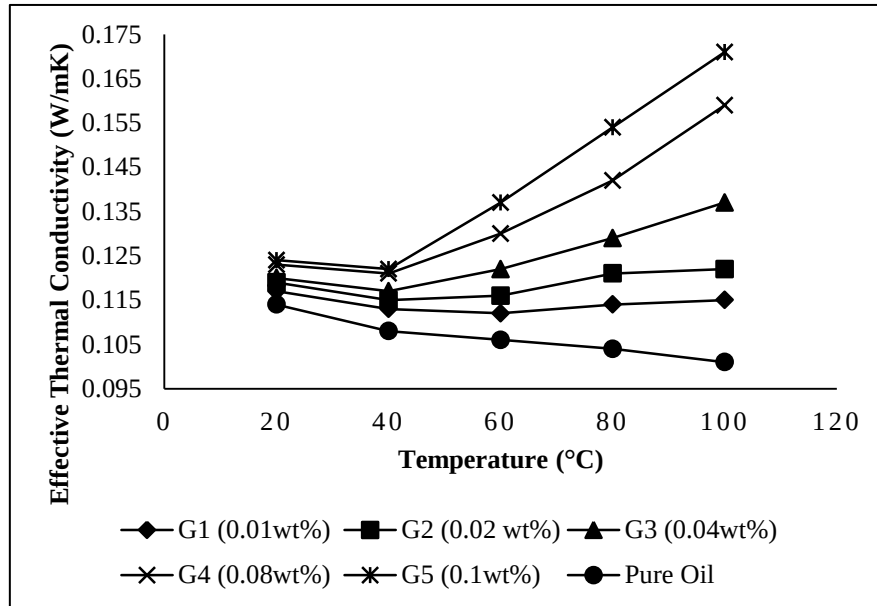


Figure 5. Effective thermal conductivity of GTNFs.

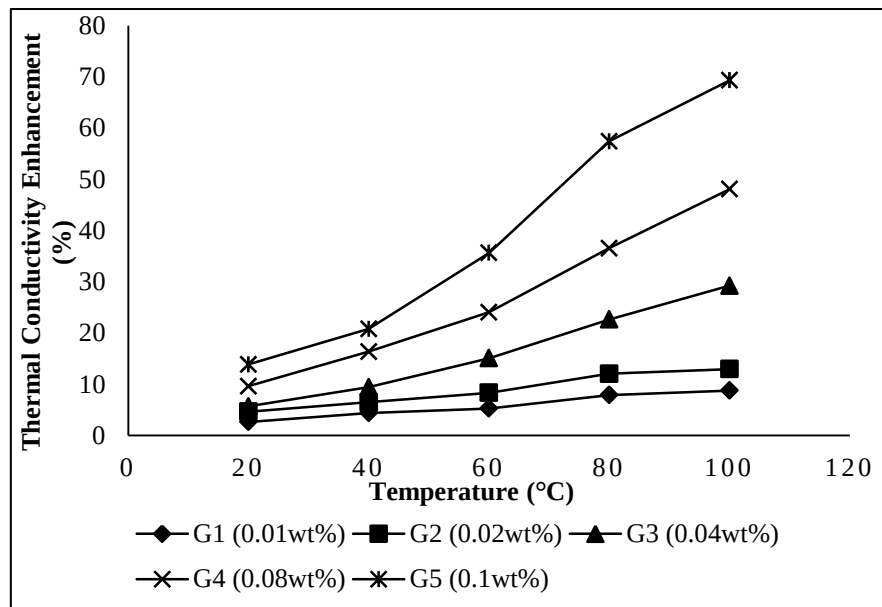


Figure 6. Percentage thermal conductivity enhancement of GTNFs.

3.3.2 Viscosity

Viscosity of the GTNFs were measured as function of with GNP concentration and temperature as shown in Figure 7. It can be seen from Figure 7 that over the measured temperature range, the viscosity of pure oil and GTNFs decreases with increasing

temperature. The viscosity of the GTNFs were reduced by 8.33-23.97% as the temperature rises and thus allowing more convectional heat flow. The increasing temperature reduces the intermolecular forces of the particles and fluid and thus decreasing the viscosity [10]. It is also observed that the viscosity of the GTNFs decreases with the increase in GNPs concentration. This is due to the self-lubricating effect of GNPs which increases with increasing concentration. GNPs which is well known as a self-lubricating composite has low shear strength which lowers the viscosity of the GTNFs [22-23].

The decrease in viscosity as an effect of increasing temperature and concentration of GNPs increases the average velocity of Brownian motion of the nanoparticles [24]. The increase in Brownian motion of the GNPs increases the kinetic energy of the particles and thus increases their collision for heat transfer.

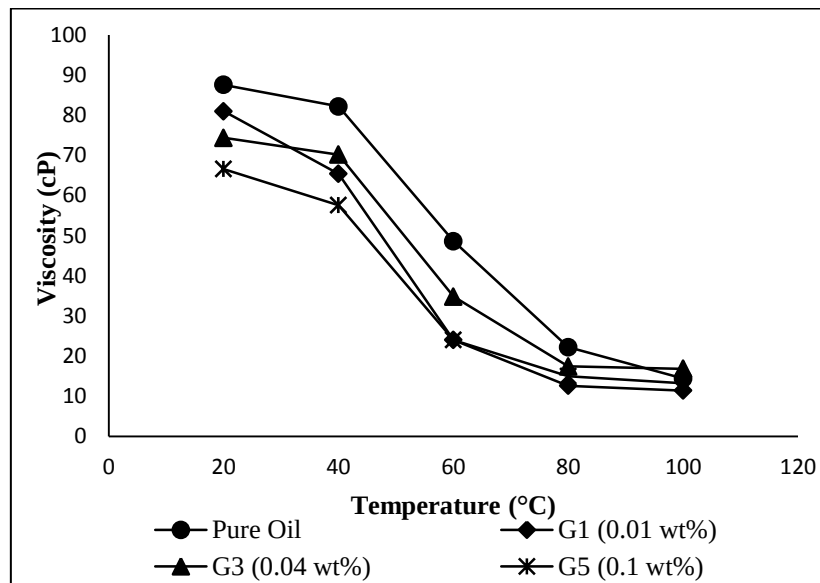


Figure 7. Viscosity of GTNFs.

4. Conclusion

Transformer oil is used as a source of cooling to prevent overheating in transformers. However, transformer oil being a conventional heat transfer fluid has a low thermal conductivity which leads to low heat transfer rate. GNPs which are widely known for its thermal properties have provided an alternative solution to enhance the thermo-physical characteristics of the fluids. In this work, the GTNFs with GNPs concentration of 0.01-0.1 wt % were stable for more than 3 months after a 4-hour sonication. The thermo-physical properties such as thermal conductivity and viscosity of the nanofluids were proven to increase the heat transfer capability of the oil. From the results obtained, temperature and concentration of GNPs play significant roles in the enhancement of thermo-physical properties. The enhancement in thermal conductivity obtained was from 2.63-13.86 % and 8.77- 69.31 % as the temperatures varies from 20-100 °C, for 0.01 wt% and 0.1 wt% of GNPs. The viscosity of GTNFs were reduced by 8.33-23.97% as the temperature rises allowing more convectional heat flow. The increase in thermal conductivity and decrease in viscosity as temperature rises enhances the overall performance for heat transfer of the transformer oil. Thus, it can be concluded that GNPs can successfully enhance thermo-physical

properties of a transformer oil which can be further applied in transformer cooling technologies saving cost and energy.

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Production of Activated Carbons Derived From Coffee Wastes for the Adsorption of CO₂ Gas

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Abstract

One of the Grand Challenges for engineering is the development of efficient carbon sequestration methods. Adsorption using activated carbons aims to undertake this challenge to reduce CO₂ gases in the environment in order to reduce the adverse effect of global warming. Hence, in this present work, the adsorption of carbon dioxide gas was studied on the production of activated carbons which are derived from coffee wastes by physiochemical activation which includes the combination of chemical activation with K₂CO₃ and physical activation with CO₂ gas. Coffee wastes are first carbonized under a flow of N₂ gas (1 L/min) for 1 hour and heated to a carbonization temperature of 800^oC to produce char. The char is then impregnated with a concentration of 20 wt% and 50 wt% of K₂CO₃ using an impregnation ratio (K₂CO₃/raw coffee wastes) of 1:1. Finally, the char is activated by a flow of N₂ (1 L/min) for one hour, and heated to a final activation temperature of 700^oC with CO₂ gas (1 L/min) for 1 hour. The results from the various FTIR spectra showed that various functional groups are present on the activated carbons which increases the CO₂ adsorption capacity which include N-H, O-H, C-H, C=O, C=C and C-O functional groups. Besides that, the BET surface area and total micropore volume attained by activated carbons CWAC 0.5 are 189 m²/g and 0.07491 cm³/g respectively. Based on the Density Functional Theory (DFT) and the Horvath-Kawazoe pore size distribution plot, which showed that a maximum pore size distribution of activated carbon CWAC 0.5 occurred at a pore width of 0.50 nm and exhibited a micropore distribution. Lastly, the CO₂ adsorption capacity of activated carbon CWAC 0.5 attained by the CO₂ adsorption isotherm corresponded to 0.4401 mmol/g.

Keywords: Activated carbon, Coffee wastes, Potassium Carbonate, Carbon dioxide gas, Adsorption of CO₂ gas.

1. Introduction

Activated carbon is an amorphous solid which possesses very large internal surface areas and pore volumes [1]. Activated carbons have gained a massive attention due to its usage, advantages which it possess and also play an important role in various liquid and gas phase applications due to their association with high adsorptive capacities [1]. There are many kinds of activated carbon precursors which are available throughout the world. These activated carbons can be divided into synthetic or natural carbon precursors. Examples of synthetic precursors include polymers, coals, carbon nanotubes and also carbon nanofibers [2]. On the other hand, natural carbon precursors include carbonaceous materials which have major advantages such as high amount of carbon contents, a very low amount of inorganic materials and lastly they are relatively cheap and readily available worldwide. Agriculture by products or wastes have caught the attention of many researches worldwide and proved to be used as a carbon precursor for the production of activated carbons, mainly due to their low cost price. Besides that, agriculture wastes have distinct advantages such as a high amount of mechanical strength, a large adsorption capacity and lastly they contain ash contents which are very low [3]. In addition, these agriculture wastes which are made from lignocellulosic materials have other advantages such as they act as a source which are renewable and also will not cause major environmental impacts [2]. In the past, many types of carbon precursors had been investigated and researched upon. These include bagasse, cherry stones, bamboo, olive stones, apricot stones, oil-palm stones, nutshells, wall-nut shells, acorn shells, pine cone, peanut shells, palm shell, coconut shells, groundnut shells, tobacco residues, cotton stalk, tea leaves and lastly coffee husks [3].

In this research paper, coffee wastes are chosen as a carbon precursor for the adsorption of carbon dioxide gas. The reasons are as follows. The largest commodity which is placed second after petroleum and is traded globally is coffee. According to the International Coffee Organization, in the year 2008, the production of coffee accounts to a total of 680 million tonnes. Due to the massive amount of coffee produced around the world, approximately 30 million tonnes of coffee wastes are generated as a consequence [4]. Unfortunately, only a small percentage of coffee wastes discharged are utilized for several applications such as health supplement, animal food additive, synthesis of fuel and lastly a feedstock in order to synthesise other chemical compounds [5]. Besides that, coffee wastes are also utilized for the manufacture of compost, as a fuel in boilers and lastly for the production of biodiesel [6], [7]. The presence of large quantities of coffee wastes will evidently impose environmental impacts such as land, air and water pollution. However, due to the fact that coffee wastes possess high economic values and also obtained from renewable resources strongly justify that coffee wastes represent an excellent candidate for the manufacture of activated carbons as it evidently reduces environmental impacts. Based on all the reasons which are stated above, the motivation of this research is to investigate the viability of producing activated carbons which are derived from coffee wastes for the adsorption carbon dioxide gases.

It is essential to understand the various methods for the production of activated carbons. Basically, the activation process can be performed by three methods, which are chemically, physically or the combination of both chemical and physical method (physiochemical method) [8]. The first type of activation method is the chemical activation. Generally, the chemical activation process consists of the impregnation of the biomass precursors with a chemical agent and finishing it by heat treatment. The main purpose of the dehydrating agent is to influence the pyrolytic decomposition of the raw biomass material. There are many types of dehydrating agents used in studies performed in the past. They include zinc chloride [9], potassium carbonate [10], phosphoric acid [11], potassium hydroxide [12] and sulphuric acid [13]. In this research, potassium carbonate, K_2CO_3 is used as an activating agent due to the fact that the usage of NaOH and KOH chemicals are substances which are deleterious, hazardous, expensive, corrosive in nature and environmentally unfriendly [14], [15], [16], [17]. In contrast, K_2CO_3 is not deleterious as it is used as food additives, not detrimental, does not have adverse environmental impacts, non-toxic, easily removed by washing it with water, good operating conditions and lastly exhibits weak corrosion [17], [16], [14], [15], [18]. Lastly, the usage of phosphoric acid will impact the environment as it increases the acidity of water which consequently affect aquatic lives.

On the other hand, the physical activation method for the production of activated carbons mainly consist of 2 steps. The first step is the pyrolysis of the biomass material at high temperatures in an inert atmosphere. The main purpose of undergoing this step is to eradicate most of the oxygen and hydrogen molecules in the biomass precursor. The preceding step is the activation of the char at high temperatures ($900^{\circ}C - 1000^{\circ}C$) with the presence of an oxidizing gas. Examples of oxidizing gases used are carbon dioxide gas, steam, air or a mixture of one or more components [19], [20]. In this research, CO_2 gas is used in the physical activation method. The process of physical activation allows the production of activated carbons which exhibit pore size distributions which are narrower [21]. Besides that, the usage of physical activation method for the production of activated carbons can be applied in a wide array of applications such as in food and pharmaceutical industries [22].

There are many advantages which are associated with the usage of chemical activation methods. These advantages include obtaining higher carbon yields as opposed to physical activation [10], [23] and having lower energy costs, since chemical activation process normally proceeds with a lower activation temperature as compared to physical activation [23], [24], [19]. Consequently, lower energy costs translate to higher economic values [25]. The carbon yield by utilizing chemical activation method are usually higher than physical activation due to dehydrogenation properties which are associated with chemical agents which prevent tar formation and reduce the liberation of various volatile compounds [19]. Besides that, chemical activation produces better developed porosities and pore sizes which are more uniformly formed as opposed to physical activation [10], [23], [26], [25], [24], [19].

On the other hand, physical activation also exhibits advantages over the usage of chemical activation. For example, physical activation allows better control over the production of microporous structures which are desired. At higher temperatures, pore diameters will increase and as a consequence, pore volume increases significantly [27]. However, the main attraction of physical activation as opposed to chemical activation is that it prevents the incorporation of any impurities which originate from the

activation agent used. In addition, due to the physical activation step, a certain percentage of the carbonized material mass is lost mainly due to the liberation of gaseous carbon oxides [27]. Besides that, the pore structure of activated carbons can be further increased mainly caused by partial oxidation of the carbonized char by the action of oxidizing agents such as steam and CO₂ gas [27].

As can be deduced from the various advantages which are associated with chemical and physical activation methods, it would be logical that the combination of both activation methods would entail the various advantages which are exhibited by both activation methods. The combination of chemical and physical activation methods are termed as physiochemical method [8]. The physiochemical activation method would obviously incur higher costs and also longer preparation period as opposed to chemical or physical activation methods. However, these small drawbacks are compensated with attractive advantages which are associated with physicochemical activation. These include the production of activated carbons which are high in quality and also surface area which are larger [8].

Based on the observations made in this field area, there are scarce studies which are being researched upon which utilizes the physiochemical method [28], [29]. Hence, due to the scarcity of research using the physiochemical method reported in the literature, this led to the motivation of this research. To emphasize further, as far as the authors' knowledge, no research had been made in the production of activated carbons derived from coffee wastes using physiochemical method which comprises of chemical activation of K₂CO₃ and physical activation using CO₂ gas for the adsorption of CO₂ gas. Hence, the objective of this research is to investigate the CO₂ adsorption capacity of activated carbons derived from coffee wastes using physiochemical activation and to determine the ideal concentration of K₂CO₃ and CO₂ gas using physiochemical activation which would yield the highest CO₂ adsorption capacity of activated carbons derived from coffee wastes.

2. Materials and methods

2.1 Coffee wastes

The carbonaceous precursor which is used for the production of activated carbons (AC) are coffee wastes which are the by-products of coffee beans. The production of coffee wastes are obtained after the contents in the beans are extracted. The coffee wastes used in this research is obtained from an outlet in Starbucks at Taylor's University Lakeside Campus, Subang Jaya, Malaysia. Prior to the usage of the coffee wastes, the samples are first separated from any refuse or debris which might be mixed with the coffee wastes. After the separation process, mud and other impurities which are present on the surface of the coffee wastes are removed by washing the samples with distilled water.

2.2 Preparation and characteristics of activated carbons

2.2.1 Preparation of activated carbons

Firstly, the coffee wastes are washed thoroughly with distilled water to remove any impurities or debris which might be present. After the washing process is completed, the coffee wastes are then passed through a mesh size 20-35 sieve to obtain evenly sized coffee wastes samples [30]. The coffee wastes are grounded and sieved in order to achieve particle sizes which are uniform and measures between 1 and 3 mm in diameter [31], [32], [33], [34]. Next, the coffee wastes are then placed in a metal tray and spread evenly. The purpose for spreading the coffee wastes evenly in the tray is to ensure that all the samples are being heated in the oven evenly. The coffee wastes are then placed into an oven and heated to a temperature of 110°C for a total duration of 24 hours. The function of heating the coffee wastes in an oven is to remove any moisture which are present in the samples. After the coffee wastes are dried for a day, the samples are then removed from the oven and stored in a desiccator [30]. The purpose of the desiccator is to ensure that no further moisture would be adsorbed by the coffee wastes by providing a moisture free environment. The desiccator is filled with silica beads which will absorb all moisture which are present in the vicinity of the desiccator. The samples are stored in the desiccator prior to any further treatments. The process of physiochemical activation consists of three steps which are carbonization of coffee wastes, impregnation of coffee wastes with K_2CO_3 and finally the activation of the resultant char with CO_2 gas.

2.2.2 Proximate analysis on raw coffee wastes

Many types of physical and chemical characterizations of activated carbons which are derived from coffee wastes are carried out. Throughout the process for the production of activated carbons, measurements had been carried out on the mass loss after undergoing the activation process, after rinsing and washing with distilled water and lastly after completing the process of drying [35].

The proximate analysis on raw coffee wastes consist of carbon yields, volatile contents, moisture contents and finally ash contents [35]. The volatile and moisture contents for each coffee wastes samples are analysed using the thermogravimetric (TGA) method. The proximate analysis integrated with TGA is used to determine the total amount of volatile matter (VM), moisture content, fixed carbon (FC) and finally the total amount of ash content [38]. The total amount of fixed carbon content is calculated by the differences in values obtained from the total mass of moisture, volatile and ash contents [37]. The procedure to determine the various proximate analysis parameters are as follows. Approximately 10 mg of the raw coffee wastes, the resultant char and activated carbon samples are placed into a crucible made from

aluminium. The samples are then placed inside the TGA furnace. The total amount of volatile matter (VM) and moisture content are obtained from the TGA furnace. The furnace is continuously heated from room temperature until it reaches a final temperature of 950°C. The heating rate of the furnace is 10°C min⁻¹ and the total flow of nitrogen gas is 75 ml min⁻¹. On the other hand, the total fixed carbon (FC) content can be determined by first increasing the heating rate until it reaches 950°C with a heating rate of 75°C/min and a nitrogen flow of 10 ml min⁻¹. The total amount of ash content which are present in the samples are represented by the mass of residue obtained [38].

2.2.3 *FTIR (Fourier transform infrared spectroscopy) analysis on raw coffee wastes, carbonized char and activated carbons derived from coffee wastes*

The function of infrared (IR) spectroscopy is to identify all types of functional groups which are attached on the surface of activated carbons. The FTIR spectrum from the various carbon samples are obtained by using a PerkinElmer-2000 FTIR spectrometer [40]. The carbon samples tested using this equipment are samples obtained from raw coffee wastes, carbonized chars and finally activated carbons derived from coffee wastes. All data acquisitions was performed automatically by the connection of the FTIR machine to an interface computer using a standard software package [40]. Prior to using the FTIR equipment, the carbon samples are dried in an oven for 24 hours at a temperature of 110°C and placed in a desiccator. The carbon samples are first mixed with potassium bromide (KBr) solids with a ratio of 1:99 (mass of carbon samples: mass of KBr solids). After mixing the samples and the solid KBr together, the mixture is compressed between two stainless steel cylinders with a total pressure of 10 tonnes/cm² for 10 minutes in order to form a solid film which is very thin and transparent [41], [40]. This thin film is called a pallet. Besides that, a pallet made from pure KBr is used as a reference to account for any background measurements. Lastly, the IR spectrum is recorded from 4000 to 400 cm⁻¹ by using a resolution of 4 cm⁻¹ [40]. A total of 4 scans are taken for each FTIR spectrum. However, there are limitations which exist by using this method. Since the activated carbons are black in colour, a very small sample size must be used in order to ensure that the light beams emitted from the FTIR machine can penetrate the activated carbon samples and to ensure the accuracy of all the FTIR spectra obtained.

2.2.4 *Textural characterization of activated carbons*

In order to obtain physical characterizations of activated carbons, two types of physical adsorption analysis are used, which are N₂ and CO₂ adsorption. These physical adsorptions are carried out at temperatures of -196°C for N₂ and 0°C for CO₂ [32]. Before performing the various adsorption measurements, all the carbon samples are outgassed for a total duration of 24 hours at a temperature of 100°C under vacuum condition [31], [33]. These adsorption are carried out in a volumetric apparatus named Micromeritics Tristar 3000 [31], [33]. The main reason for the usage of both types of adsorption isotherms is to obtain complementary information about textural

characterizations of all carbon samples. Firstly, the adsorption of CO₂ at a temperature of 0°C and a pressure of up to 1 bar is only permissible to pores which are narrower than 1 nm in width. On the other hand, N₂ adsorption at a temperature of -196°C is assessable to a wider range of pore sizes. However, the adsorption of N₂ have some drawbacks. The main disadvantages of using N₂ adsorption is that diffusion limitations exist in the narrowest pores due to cryogenic temperatures [33]. The usage of CO₂ molecules at 0°C is preferred over N₂ molecules in order to avoid the underestimation of the total pore volume which are calculated from the N₂ adsorption at a temperature of -196 °C [42].

The apparent surface area (S_{BET}) of all the carbon samples are calculated from the N₂ adsorption isotherms by utilizing the standard Brunauer, Emmett, and Teller (BET) equation which exists in the linear form using a relative pressure (P/P₀) which ranged from 0.05 to 0.3 [40], [43]. Besides that, the narrow micropore volume (W₀) (pore widths less than 0.7 nm) are obtained from the CO₂ adsorption isotherms at a temperature of 0°C by using the Dubinin-Radushkevich equation [42]. The micropore surface area (S_{DR}) are determined by using the Dubinin-Radushkevich equation. The assumptions made for the usage of the DR equation are that the density of adsorbed phase equals to 1.023 cm³ g⁻¹, cross sectional area of 0.187 nm² and finally an affinity coefficient of 0.36 [42]. The total pore volume (V_T) is obtained from the total amount of nitrogen molecules being adsorbed at a relative pressure of 0.99. Next, the micropore volume (V_{DR}) is also obtained by the N₂ adsorption isotherm by using the Dubinin-Radushkevich (DR) equation [31]. Relative pressures ranging from 10⁻⁵ to 10⁻¹ are used to evaluate the micropore volume using the DR equation of the activated carbon samples [40].

2.2.5 CO₂ adsorption/desorption measurement

The adsorption/desorption measurements of the activated carbons derived from coffee wastes are obtained using a TGA/SDTA851 thermogravimetric analyser (TGA) [30]. The adsorption capacity is performed under atmospheric pressure. A total of 15 mg of activated carbons are heated from 25°C to 60°C with a flow of pure nitrogen gas. The gas flow rate of nitrogen gas is 75 cm³/min and the sample is heated at a rate of 2°C/min. The sample is heated isothermally for a total of 30 minutes. Next, the nitrogen gas flow is switched off and CO₂ gas is switched on with a total flow rate of 75 cm³/min at a temperature of 60°C for 90 minutes. The CO₂ gas flow is then switched off and the nitrogen gas flow is switched on with a flow rate of 75 cm³/min and at a temperature of 60°C for a total of 30 minutes. All data points for weight of activated carbon samples and temperatures for the whole analysis duration are recorded. The CO₂ adsorption capacity have units of (mg CO₂/g adsorbent) and the CO₂ desorption capacity have units of (%). Both parameters are calculated based on Eq. (1) and Eq. (2).

$$\text{CO}_2 \text{ adsorption capacity (mg CO}_2\text{/g adsorbent)} = \frac{m_1 - m_0}{m_0} \times 1000 \quad (1)$$

$$\text{CO}_2 \text{ desorption capacity (wt \%)} = \frac{m_1 - m_2}{m_1 - m_0} \times 100 \quad (2)$$

where m_0 , m_1 , and m_2 represent the weight of the activated carbon (mg) immediately after the initial heat treatment using N_2 flow is completed, after the CO_2 adsorption process is completed and after the desorption process under N_2 flow is completed, respectively [30].

3. Results and discussion

3.1 Proximate Analysis of Raw Coffee Wastes

The proximate analysis of raw coffee wastes is illustrated in Fig 1. The devolatilization of raw coffee wastes using a heating rate of $10^\circ\text{C}/\text{min}$ is shown terms of weight percentage of raw coffee wastes (wt %) against temperature ($^\circ\text{C}$). When the temperature is increased from room temperature at 30°C to 950°C , the effect of the increase in temperature on the weight percentage of raw coffee wastes are interpreted with the description as follows.

Firstly, based on Zone I in Fig. 1, at a temperature range from 30°C to 261°C , the removal of moisture from the raw coffee wastes sample occurred which corresponded to a weight reduction of 7.76 wt %. The results for moisture removal from raw coffee wastes sample are in good agreement with the results obtained by Wen-Tien, Sii-Chew et al. [44], in which they obtained a total moisture removal of approximately 5 wt %. The main material which is evaporated from the sample is water molecules or moisture content. The temperature of 110°C in the TGA furnace caused a complete evaporation of water molecules from the sample which is in complete agreement with other papers published in the literature [45].

The next temperature range represented in zone II occurred from 261°C to 500°C and a very significant reduction of weight percentage of raw coffee wastes which equates to 66.87 wt % occurred. The drastic decrease in weight percentage of raw coffee wastes in Zone II is mainly due to the eradication of volatile matters which are present in the raw coffee wastes after the removal of moisture content. The reduction of weight percentage of volatile contents on raw coffee wastes are in good agreement with the results published by Wen-Tien, Sii-Chew et al. [44] who reported a total removal of volatile contents of approximately 60 wt%. There are two main factors which contributed to the significant reduction of weight percentage of raw coffee wastes (66.87 wt %) at a temperature range of 261°C to 500°C . First and foremost, the first factor is contributed by the elimination of light volatile components primarily consisting of carbonyl $\text{C}=\text{O}$ functional groups which are present in aldehydes, acetyl derivatives, ketone groups and esters. The next factor for the reduction of weight percentage of (66.87%) is due to decompositions of cellulose and hemicellulose components which are present in the raw coffee wastes samples. The decompositions of hemicellulose and cellulose macromolecules occurred due to a rearranged and altered polysugar structure which exist in the raw coffee wastes sample [44], [46]. Besides that, all the carbon atoms in a carbon-rich coffee wastes sample are reduced to

a sample which contained pure carbon atoms. This process is crucial for the production of activated carbons. The carbon atoms formed a mechanically strong structure which permeates over the entire surface area of the sample and contained many voids or pores on the surface.

The final zone which is represented by zone III occurred at a temperature range from 500°C to 950°C which resulted in a total weight reduction of 13.67 wt % of the raw coffee wastes sample. During the thermal treatment temperature ranging from 500°C to 950°C, the total reduction of weight percentage of 13.67 wt % is mainly due the decomposition of heavier tar components which are embedded in the raw coffee wastes sample. These tar components are identified as lignin molecules. The decomposition of lignin macromolecules require very high thermal energy due to their large cross-linked structures and hence only decompose at a temperature ranging from 500°C to 950°C. The total decrease of weight percentage of approximately 10 wt % of raw coffee wastes obtained by the results published by Wen-Tien, Sii-Chew et al. [44] due to the decomposition of lignin macromolecules are in very close agreement with the total reduction of 13.67 wt % of raw coffee wastes obtained in this research.

Finally, the only impurities which reside in the structure of the sample represent the total ash content. The ash content represents the inorganic, amorphous, inert and an unusable part which are present in the sample [47]. It is clear that the lower the ash content which are present in the sample, the higher the efficiency of activated carbons produced. The total ash content of 3.361 wt % is present in the raw coffee wastes sample. Although the total ash content is slightly higher as compared to other coffee wastes samples found in the literature, the total volatile contents contained in the sample are much higher than the volatile contents found in the literature. A higher volatile content would translate to a lower carbon yield of activated carbons produced. A slightly higher ash content in the raw coffee wastes can be attributed towards the highly hygroscopic nature of the coffee sample. The high hygroscopic nature of the sample would tend to absorb a higher amount of impurities such as ash compounds and moisture much more easily as opposed to other carbonaceous materials. The total amount of ash content in this sample is slightly higher than the ash content found in the literature [48], [49].

The total fixed carbon represents the solid residue which are combustible and which remained in the raw coffee wastes after the sample had undergone the heating process and the total volatile matter had been expelled from the sample. The total fixed carbon content in raw coffee wastes are of major importance as the total fixed carbon gives an estimation of the total amount of coke which would be yielded from a solid sample [49]. The total fixed carbon content obtained in this research (22.01 wt %) from the raw coffee wastes are much higher than the fixed carbon content obtained from other journals in the literature. As an example, the total fixed carbon derived from coffee wastes reported by Tsai, Liu et al. [49] are 8.230 wt %. It is very essential to ensure that the total fixed carbon in the raw coffee wastes are very high. The reason behind this statement is due to the fact that a high fixed carbon content will ensure that the production of activated carbons would exhibit a large percentage of micropores on the surface of the activated carbon. The higher the total fixed carbon, the lower the amount of volatile matter and moisture content which are embedded in the raw coffee wastes. In addition, the lower the amount of volatile matter and moisture content the higher the adsorption of CO₂ molecules as there are less impurities on the surface of activated carbons which would block the CO₂ molecules from being adsorbed in the micropores

of the activated carbons. The results obtained for the total ash content in raw coffee wastes are in close agreement with the results obtained in the literature which registered a value of 3.92 wt % and 1.7 wt % respectively [48], [46].

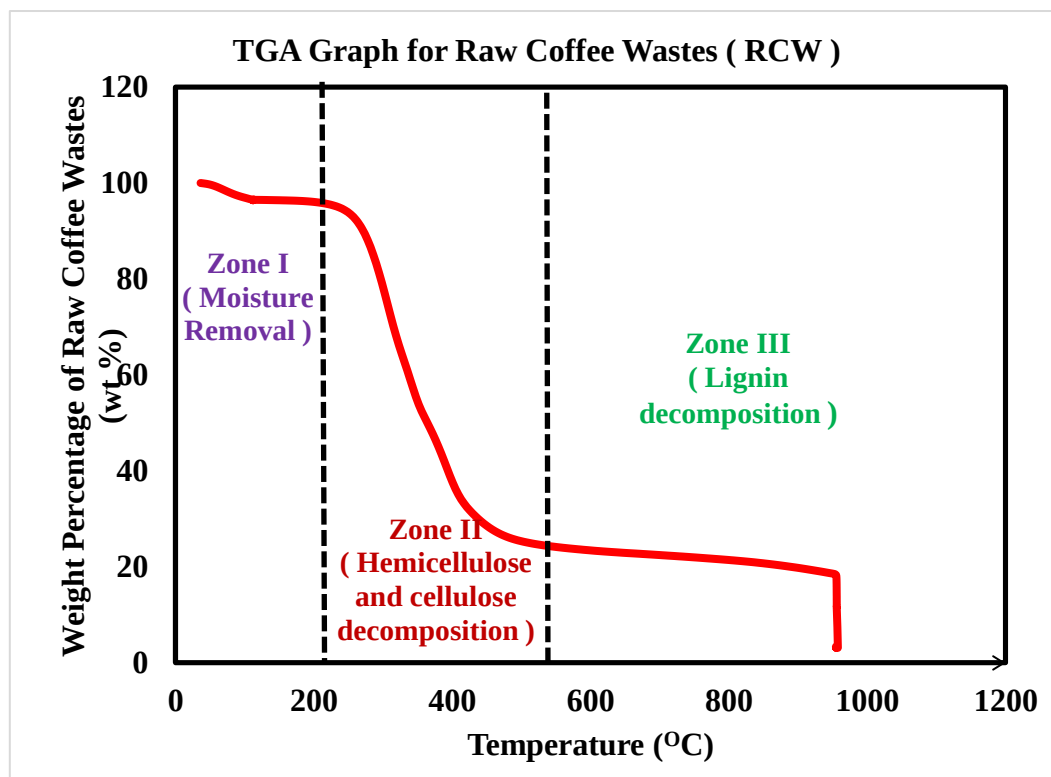


Figure 1. TGA Graph for Raw Coffee Wastes (RCW)

3.2 Effect of concentration of K_2CO_3 on surface functional groups of raw coffee wastes, carbonized char and activated carbons from coffee wastes

Functional groups played a major role in determining the characteristics of activated carbons. Hence, Fourier transform infrared spectroscopy (FTIR) analysis is carried out in this research in order to study the nature of the functional groups which are present on the surface of activated carbons derived from coffee wastes which had undergone the process of physiochemical activation.

Based on Fig. 2, there exist many kinds of functional groups on the surface of raw coffee wastes (RCW). These functional groups consist of O-H stretching vibration band (3368 cm^{-1}) which can be ascribed towards the presence of hydroxyl functional groups. Besides that, the C-O adsorption band (1163 and 1061 cm^{-1}) indicates the presence of oxygen functional groups. These findings are in good agreement with the results obtained by Virote, Chaian et al. [52] in which they obtained similar functional groups on coffee residues. In addition, the presence of distinct peaks on the FTIR spectra at a wavenumber of 2924 , 1745 and 1654 cm^{-1} respectively give a good indication of the presence of C-H, C=O and lastly C=C functional groups. These

results obtained in this research are in line with similar results obtained from other researches using coffee wastes as a biomass precursor [52], [53].

The FTIR spectra in Fig. 2 illustrates the various functional groups which exist on the surface of carbonized coffee wastes after undergoing the process of carbonization at a temperature of 800°C (CWC). The presence of O-H and also N-H functional groups are detected on the FTIR spectra which represent adsorption bands located at 3225 and 3681 respectively. On the other hand, the methylene and methyl functional groups are which are attributed towards the C-H and $\text{-CH}_2\text{-}$ stretching vibration modes originated from aliphatic chains can be clearly seen at wavenumber 2926 and 2853 cm^{-1} . In addition, the adsorption bands at 1629 cm^{-1} can be ascribed towards the presence of C=C aromatic ring stretching on indication of quinone of quinine functional groups. Lastly, the presence of carboxyl functional groups can be deduced from the adsorption bands located at 1436 cm^{-1} . All the functional groups which exist on the surface of the char produced are in total agreement with the result obtained from Karifala, Cesar et al. [54] in which they obtained the same functional groups after undergoing the process of carbonization on spent coffee wastes. The C-O stretching vibration band at 969 and 941 cm^{-1} indicates the presence of C-O functional group as a result of carbonization in this work. When comparing both spectra obtained from the raw coffee wastes and the one obtained from the carbonized char, it is evident that the C=O functional group which exists on the surface of raw coffee wastes had vanished after undergoing the process of carbonization. It can be inferred that the disappearance of carbonyl C=O functional groups found in aldehydes, acetyl derivatives, ketone groups and also esters indicates that the char produced contains a very minute amount of carboxylic functional groups [14].

Based on Fig. 2, the FTIR spectra for sample CWAC 0.2 are analysed. The O-H functional group located at 3181 cm^{-1} suggested the presence of hydroxyl functional group. The presence of the O-H functional groups are in good agreement with other research which obtained the stretching vibration band at 3400 cm^{-1} which is attributed towards the O-H stretching vibration band in hydroxyl groups [10], [55]. Besides that, the bands which are located at 2884 cm^{-1} are assigned to the presence of symmetric C-H bands and also asymmetric C-H bands, which gives a clear indication for the presence of alkyl functional groups such as methylene and methyl groups. However, these bands exhibit very low intensity peaks for the spectra of activated carbons [14]. Similarly, the presence of C-H functional groups are also obtained from other research paper after completing the chemical treatment of K_2CO_3 [55]. On the other hand, the peak which occurs around 2251 cm^{-1} is ascribed towards the presence of $\text{C}\equiv\text{C}$ stretching vibration which gives a clear indication for the presence of aromatic rings or the presence of N-H functional groups. Next, the stretching adsorption band at wavenumber 1741 cm^{-1} is assigned towards carbonyl C=O functional groups found in aldehydes, acetyl derivatives, ketone groups and also esters. However, as can be observed based on Fig. 2, the C=O bands are relatively small and does not exhibit a sharp and distinct peak. Hence, it can be concluded that the activated carbon treated with K_2CO_3 and physically activated by CO_2 gas at 700°C contains a small amount of carboxylic functional groups [14]. This observation is in good agreement with results obtained by Gurten, Ozmak et al. [14], in which they obtained the similar results. Lastly, the presence small peaks of stretching bands at 1300-1000 cm^{-1} which are ascribed to C-O stretching in alcohols, acids, phenols, esters and ethers gave a distinct reasoning that the C-O functional groups had decreased during the physiochemical treatment on char [14].

The FTIR spectra shows the functional groups which exist on activated carbons CWAC 0.5. As can be inferred, all the functional groups which exist in the FTIR spectra of 0.2 wt % K_2CO_3 are the same as the functional groups which exist in FTIR spectra of 0.5 wt % K_2CO_3 . However, the only difference is the absence of $C\equiv C$ stretching vibration functional group and the introduction of $C=C$ when compared to utilizing 50 wt% K_2CO_3 as opposed to using 20 wt % of K_2CO_3 . The explanation to this phenomenon is that when the concentration of K_2CO_3 increased from 20 wt % to 50 wt%, the decomposition of $C\equiv C$ to $C=C$ occurred due to an electrophilic addition which occurred on carbon triple bonds and changed them into carbon double bonds. In addition, the introduction of $C=O$ functional groups onto the surface of activated carbons had also occurred. The stretching adsorption band at wavenumber 1735 cm^{-1} which is ascribed towards carbonyl $C=O$ functional groups are found in aldehydes, acetyl derivatives and also ketone. Hence, the presence of these functional groups are mainly due to the physiochemical activation on char derived from coffee wastes.

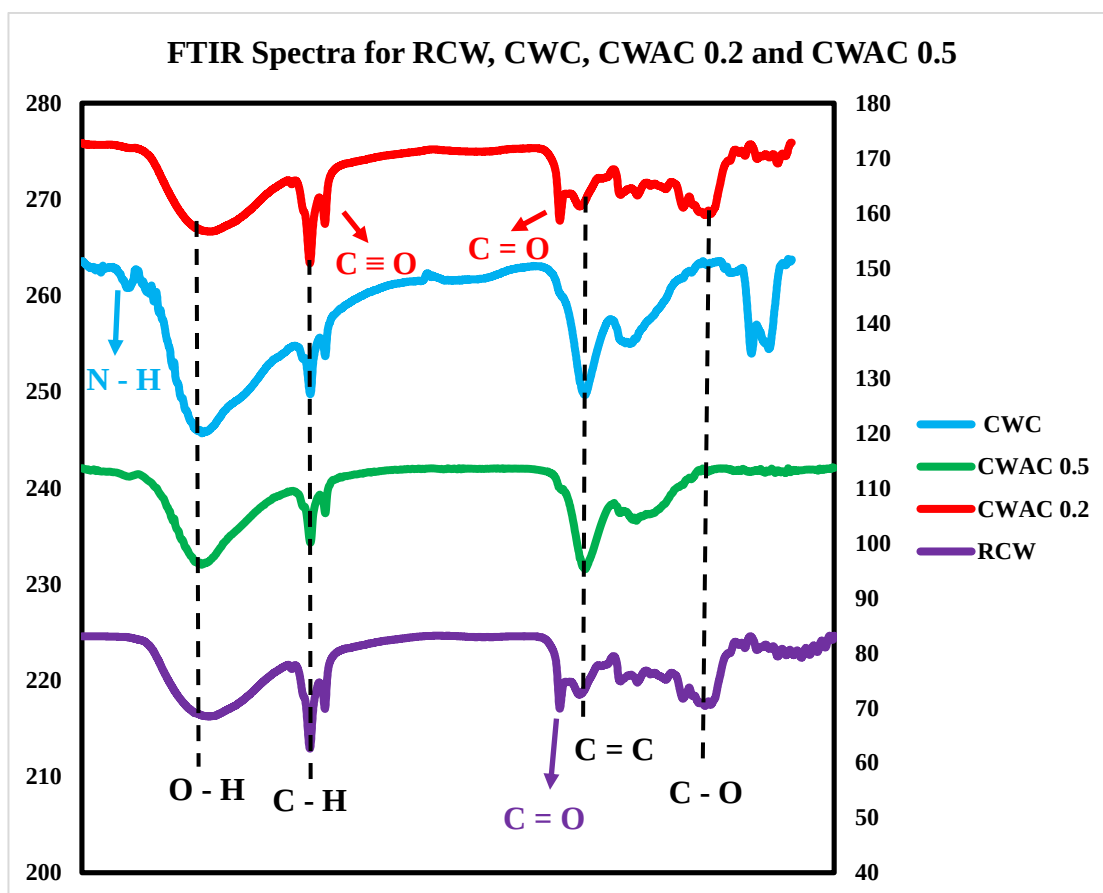


Figure 2. FTIR spectra for RCW, CWC, CWAC 0.2 and CWAC 0.5

3.3 Effect of Physiochemical Activation on BET Surface Area and Pore Volume

In this section, the effect of physicochemical activation on the total BET surface area and also pore volume will be discussed thoroughly. Based on the results obtained, it is evident that a relationship between the concentration of K_2CO_3 used and the BET

surface area of activated carbons exists. As the concentration of K_2CO_3 increases from 20 wt % to 50 wt %, the total BET surface area of activated carbons increases as well. The results showed that the highest BET surface area attained by activated carbons occurred using a concentration of K_2CO_3 at 50 wt % which registered a total BET surface area of $189 \text{ m}^2/\text{g}$. Besides the importance of concentration of K_2CO_3 for the production of high BET surface area activated carbons, carbonization temperature also plays an equally important role. Based on a study conducted by Irem, Selhan et al. [88], as the carbonization temperature was raised from 600°C to 800°C , the total BET surface area of activated carbons also increased, reaching a maximum BET surface area at a carbonization temperature of 800°C . These results obtained by Irem, Selhan et al. [88] are in excellent agreement with the results obtained in this research as the maximum BET surface area is achieved at a carbonization temperature of 800°C .

Besides discussing about the importance of BET surface area, porosity development on the surface of activated carbons are of equal importance. The porosity development on activated carbons refers to the total pore and micropore volume. The activated carbon CWAC 0.2 have a total pore and micropore volume of $0.001095 \text{ cm}^3/\text{g}$ and $0.001138 \text{ cm}^3/\text{g}$ respectively. On the other hand, the activated carbon CWAC 0.5 registered a total pore and micropore volume of $0.09751 \text{ cm}^3/\text{g}$ and $0.07491 \text{ cm}^3/\text{g}$ respectively. It is interesting to point out the total micropore volume on activated carbon CWAC 0.5 occupied 76.8% of the total pore volume on the activated carbon. Hence, a relationship can clearly be deduced from the results obtained in which as the concentration of K_2CO_3 increased from 20 wt % to 50 wt %, the total pore and micropore volume of activated carbons also increased. Based on a research performed by Irem, Selhan et al. [88], when the concentration of K_2CO_3 increased from 25 wt % to 50 wt % at a carbonization temperature of 800°C , the total micropore volume obtained from the activated carbons derived from grape seeds also increased from $0.35 \text{ cm}^3/\text{g}$ to $0.47 \text{ cm}^3/\text{g}$. The results obtained in this research are in good agreement with the results obtained by Irem, Selhan et al. [88].

After determining the effects of physiochemical activation of activated carbons on total BET surface area and pore volume, another important test which represents the nitrogen adsorption isotherm of activated carbon samples are obtained. Basically, the porosity of activated carbon can be determined based on the nitrogen adsorption isotherm graph. As can be deduced from the nitrogen isotherm graph, the activated carbon CWAC 0.5 isotherm represents a type 1 isotherm based on the Brunauer, Deming, Deming and Teller (BDDT) adsorption isotherm classifications [80]. Based on the nitrogen adsorption isotherm of activated carbon CWAC 0.5, it can be inferred that the knee of its adsorption isotherm represents a sharp curvature at a relative pressure of less than 0.1. This observation suggests a highly microporous structure of activated carbon CWAC 0.5, in which almost all the micropores which are smaller than 2 nm are filled up very quickly at a very low relative pressure of less than 0.1. Besides that, the major nitrogen gas uptake occurred at a very low relative pressure for activated carbon CWAC 0.5 which corresponded to a partial pressure of less than 0.1. In addition, the adsorption isotherm of activated carbon CWAC 0.5 reached a plateau which ranged from a relative pressure of 0.05 to 1 and there exists no hysteresis loop on its adsorption isotherm. These characteristics which are exhibited by the CWAC 0.5 adsorption isotherm gave a clear indication which suggest that activated carbon CWAC 0.5 is essentially microporous.

On the other hand, the activated carbon CWAC 0.2 represents a type IV isotherm based on the Brunauer, Deming, Deming and Teller (BDDT) adsorption isotherm classifications [80]. One of the main differentiating factor between adsorption isotherm CWAC 0.2 and CWAC 0.5 is the isotherm of CWAC 0.2 exhibits a hysteresis loop on the desorption stage. As can be reasoned from the isotherm of CWAC 0.2 sample, the maximum uptake of nitrogen gas occurred at a relative pressure of approximately 1, which implied that the structure of activated carbon CWAC 0.2 are predominantly mesoporous. The pore widths of the mesoporous structure spanned a range from 2 nm to 50 nm. It is evident that a relatively high relative pressure is needed in order to completely fill all the mesoporous pores as opposed to the isotherm exhibited by activated carbon CWAC 0.5 which only required a relatively low partial pressure of less than 0.1 in order to completely fill up its microporous structure. The reason behind this observation is due to the fact that the mesoporous pores are much larger than microporous pores. Hence, as the relative pressure increases, the mesoporous pores are slowly filled up and when the relative pressures reached unity, the all mesoporous pores are being filled up with nitrogen molecules. From these two nitrogen adsorption isotherms, it can be deduced that only activated carbon CWAC 0.5 can function as an efficient CO₂ adsorbent due to the large percentage of micropores which are present. On the other hand, activated carbon CWAC 0.2 cannot be used as an efficient CO₂ adsorbent due to the large percentage of mesopores and also a small percentage of micropores. In fact, activated carbon CWAC 0.2 is regarded as a non-porous structure.

3.4 Pore Size Distribution of Activated Carbons Treated with Physiochemical Activation

In this section, the pore size distribution of activated carbon are analysed. First and foremost, it is vital to point out that the width of a CO₂ molecule is 0.232 nm [103]. The Horvath-Kawazoe pore size distribution plot showed that the maximum pore size distribution of activated carbon CWAC 0.5 occurred at a pore width of 0.50 nm. On the other hand, the plot also showed that the activated carbon CWAC 0.5 exhibited a micropore distribution which is narrow and spanned a range between 0.30 nm to 0.8 nm. From these results obtained, in accordance to the classification of pore sizes by the International Union of Pure and Applied Chemistry (IUPAC), the pore size distribution of activation carbon CWAC 0.5 are predominantly located in the ultramicropore region. Hence, there exist almost negligible mesopores and macropores present in activated carbon CWAC 0.5.

Besides that, the Density Functional Theory (DFT) on activated carbon CWAC 0.5 are also analysed. It can be inferred that the maximum pore size distribution occurred at two pore sizes, which are at 0.6 nm and 1.4 nm respectively. Firstly, the pore size distribution at 0.6 nm are categorized under ultramicropore region, while the pore size distribution at 1.4 nm are categorized under the supermicropore region. Besides that, there exist a narrow and small pore size distribution which are located at pore width of 2.3 nm. From these observations, it is evident that the activated carbon CWAC 0.5 consists of predominantly microporous structures and a small portion of mesoporous structures. Hence, the results illustrated by the DFT method are in good agreement with the Horvath-Kawazoe method.

In order to maximise the uptake of CO₂ molecules on activated carbons, micropores which exhibit pore widths within the range of less than 0.7 nm are preferred, which translates to a pore size distribution in the ultramicropore region [86]. From a perspective in terms of adsorption of free energy, pore widths of activated carbons have a higher probability of adsorbing adsorbate molecules which are similar in size with its pore width. The main reason behind this phenomenon is due to the fact that there exist a greater number of points which are in contact between the adsorbent and the adsorbate molecules [86]. In a paper published by Adilla, Suzana et al. [2], pore sizes of less than 1.0 nm represents the ideal pore size in order to maximise the uptake of CO₂ molecules which are in total agreement with the pore size distribution of 0.50 nm obtained from this research. However, pore sizes smaller than 0.26 nm is too small and narrow in order to facilitate the adsorption of CO₂ molecules since the width of a CO₂ molecule is 0.232 nm [103]. In addition, based on a published paper by Wei et al. [2], reported that the pore size which are mostly responsible for the CO₂ uptake at ambient temperature and pressure is 0.55 nm which are in excellent agreement with the results obtained in this research which had a maximum pore size distribution centred at 0.50 nm. The pore size distribution centred at 0.50 nm would allow sufficient spaces for the CO₂ molecules to adhere themselves onto the walls of the pores [2]. Lastly, Aime, Luiz et al. [35] also suggest that ultramicropores which are less than 0.7 nm are very essential for a high CO₂ adsorption capacity at ambient temperatures and at atmospheric pressures which are in total agreement with the pore size distribution of 0.50 nm obtained in this research. In fact, they further stated that the total volume of ultramicropores are the main contributor of the CO₂ adsorption capacity at ambient conditions [35]. Based on the pore size distributions obtained, it is reasoned that the physiochemical activation method yielded activated carbons which exhibit pore size distributions in the region of ultramicropore and supermicropore regions particularly at 0.50 nm and at 1.4 nm respectively.

3.5 Effects of Physiochemical Activation on CO₂ Adsorption Performance

In order to compare between the maximum CO₂ adsorption capacities attained at equilibrium conditions for both samples CWAC 0.2 and CWAC 0.5, CO₂ adsorption tests are performed at a temperature of 60°C and at atmospheric pressure of 1 bar. The CO₂ adsorption capacity of activated carbon CWAC 0.5 is higher than the adsorption capacity of activated carbon CWAC 0.2, which corresponds to 0.4637 mmol/g and 0.4401 mmol/g respectively. Besides that, it can clearly be inferred that a relationship exist between the concentration of K₂CO₃ reagent used and the CO₂ adsorption capacity of the resultant activated carbon produced. As the concentration of K₂CO₃ is increased from 20 wt % to 50 wt %, the CO₂ adsorption capacity of the activated carbons also increased correspondingly.

It is evident that the total micropore volumes on the activated carbons played a very essential role in determining the CO₂ adsorption capacity of activated carbons [64]. Besides that, the TGA graph of both activated carbon CWAC 0.2 and CWAC 0.5 demonstrates a sharp and quick rise of CO₂ adsorption when the CO₂ gas is flown through the activated carbon samples at a temperature of 60°C. Based on this observation, it can be reasoned that both the activated carbon samples CWAC 0.2 and CWAC 0.5 have a fast adsorption kinetics towards CO₂ molecules, which makes both

activated carbon CWAC 0.2 and CWAC 0.5 both an efficient activated carbon for the adsorption of CO₂ gas.

Lastly, the CO₂ adsorption isotherm for activated carbon CWAC 0.5 is carried out at a temperature of 0°C and at a pressure of 1 atm. At a relative pressure of P/P_0 of 0.005, the CO₂ adsorption isotherm rises quickly and reaches 50 % of the total CO₂ adsorption capacity of CWAC 0.5. From this observation, it can be concluded that only a small relative pressure is required in order to fill up the pores on the surface of activated carbon CWAC 0.5. Hence, this observation are in good agreement with the DFT model shown in Figure 4.9 which showed that the pore size distribution exhibited by activated carbon CWAC 0.5 are in the region of ultramicropores. These ultramicropores which are < 0.7 nm are easily filled with one or two CO₂ molecule by the pore filling mechanism. Finally, at a relative pressure of 0.03, the CO₂ adsorption isotherm reached its maximum value of 0.4637 mmol/g. On the other hand, it can also be inferred that the rate of CO₂ adsorption rises more slowly as can be seen by the CO₂ adsorption isotherm at relative pressure ranging from 0.005 to 0.03. Based on this observation, it can be concluded that the first layer of CO₂ molecules are filled in the micropores of activated carbon CWAC 0.5 easily without much resistance towards the intermolecular forces between the functional groups and the CO₂ molecules. However, when the relative pressure increases, more CO₂ molecules are pushed into the micropores on the activated carbon surface. Hence, the intermolecular forces between the CO₂ molecules and other CO₂ molecules from adjacent layers would increase correspondingly, and reduces the packing factor of the micropores on the surface of activated carbon CWAC 0.5. Therefore, even though the relative pressure is increased, the rate of CO₂ adsorption increased at a slower rate due to these repulsive intermolecular forces which exist between the functional groups and the CO₂ molecules on adjacent layers.

Conclusions

As a conclusion, the preparation of activated carbons derived from coffee wastes by the physiochemical activation which entails the combination of chemical activation using K₂CO₃ and subsequent physical activation using CO₂ gas showed an increase in CO₂ adsorption capacity. The combination of these two activation methods successfully introduced basic functional groups such as C-N and the reduction of oxygen functional groups such as C=O and C-O groups. These basic functional groups consequently led to an increase in CO₂ adsorption capacity of activated carbons due to an increase in Lewis acid-base interactions between the activated carbons and CO₂ molecules. Besides that, the BET surface area and total micropore volume attained by activated carbons CWAC 0.5 are 189 m²/g and 0.07491 cm³/g respectively. These characteristics which are exhibited by the CWAC 0.5 adsorption isotherm gave a clear indication which suggest that activated carbon CWAC 0.5 is essentially microporous. These results are further supported by the Density Functional Theory (DFT) and the Horvath-Kawazoe pore size distribution plot which showed that a maximum pore size distribution of activated carbon CWAC 0.5 occurred at a pore width of 0.50 nm and exhibited a micropore distribution. The pore size distribution at a pore width of 0.5 nm had been proven to be located at the optimum pore size distribution to attain maximum CO₂ adsorption capacity. In addition, the CO₂ adsorption capacity of activated carbon CWAC 0.5 attained by the CO₂ adsorption isotherm corresponded to 0.4401 mmol/g. Based on all the results obtained, it can be concluded that the physicochemical

activation using 50 wt % K_2CO_3 and CO_2 gas yielded activated carbons which achieved a maximum CO_2 adsorption capacity of 0.4401 mmol/g.

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Investigation of the Coffee-Waste Derived Adsorbent

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Abstract

The emission of carbon dioxide (CO₂) which is the main contributor of global warming phenomena has become a major concern of the society. Due to the rapid development in the industrial sector, the concentration of CO₂ in the atmosphere has increased by 30% over the years. Hence, carbon capture and sequestration (CCS) technology which utilizes coffee waste as the precursor in producing an effective low-cost activated carbon (AC) adsorbent has been proposed in the effort of curbing the devastating consequences cause by CO₂ emission. Studies conducted shown that approximately 50% of the coffee waste composition comprises of carbon. Due to the rich carbon content, coffee waste possess great potential to be utilized as a carbon adsorbent for CCS technology. Thus, in this research study, the CO₂ adsorption performance of coffee waste derived AC produced from physiochemical activation method was evaluated. The effects of different concentration of chemical activating agent used during activation process which alters the chemical structure of the AC produced were analyzed as well. AC was produced by performing carbonization process using dried coffee waste at a temperature of 800 °C prior activation. A two-stage activating process was performed where two different concentrations of 50 wt. % and 20 wt. % of potassium hydroxide (KOH) as the chemical activating agent with an impregnation ratio of 1:1 were studied. The sample was later physically activated at 700 °C under a continuous flow of carbon dioxide gas (CO₂). Characterization of the coffee waste derived AC was analyzed by using Brunauer-Emmett-Teller (BET), Fourier Transform Infrared Spectroscopy (FTIR) and Thermogravimetric analysis (TGA). From the results obtained, it was found that low concentration of chemical treatment leads to carbon with better textural development as well as chemical structure and thus having a higher CO₂ adsorption capacity. The high CO₂ uptake at low concentration were attributed to the presence of micropores (pore diameter < 2nm), narrow micropores size distribution as well as the presence of oxygen functional group. The CO₂ adsorption capacity for sample with low concentration of chemical treatment was found to be 3.3 wt. % while for sample with high concentration of chemical treatment, a CO₂ uptake of 2.3 wt. % was obtained.

Keywords: Adsorption, Coffee Waste, Activated Carbon, Carbon Dioxide, Carbonization.

1. Introduction

Over the years, the intense development of modern civilization has led to the rapid depletion of fossil fuels energy resources such as coal. Extensive utilization of fossil fuels has resulted in the secretion of huge amount of greenhouse gases into the atmosphere [1]. Among the greenhouse gases, carbon dioxide (CO₂) is the major greenhouse gases that contributes to the phenomena of global warming as well as global climate change [2-4]. The drastic increase in the atmospheric concentration of CO₂ due to the burning of fossil fuels has become a serious environmental issue [5]. In fact, over 30 billion tons of CO₂ is emitted into the atmosphere in an annually basis [6]. The average atmospheric concentration of CO₂ has exhibited an increase from 280 to 397 parts per million (ppm) since the beginning of industrial revolution which eventually lead to the increase in global average temperature by 0.6 to 1 °C [7, 8]. From a research studies done by the International Panel on Climate Change (IPCC), it is anticipated that the average CO₂ concentration in the atmosphere may upsurge to 570 ppm by the year of 2100 which will cause an increase in global average temperature and mean sea level by 1.9 °C and 3.8 m respectively [9, 10]. Thus, a great deal of efforts has to be devoted in order to limit the emissions of CO₂ into the atmosphere within an adequate level. Carbon capture and sequestration (CCS) technology from point source emissions has emerged as one of the potential solution in stabilizing the concentration of CO₂ in the atmosphere by 85% or more [1, 11]. The CO₂ gas that is being captured not only able to reduce the effect of global warming but also can be utilized in oil recovery where CO₂ gas is injected into the declining oil field in order to increase the amount of crude oil that can be extracted out from oil fields [12].

In general, CCS is a three stages technology which comprises of capturing the CO₂ gases that is being emitted from point source such as coal-fired power stations, followed by transportation of the captured CO₂ and lastly permanent storage of CO₂ in a geological site such as oil and gas fields [13]. Pre-combustion, post-combustion and oxy-fuel combustion are the three main approaches involve in CO₂ capture technology [1, 13]. Although CCS technology is an effective technique in curbing the effect of global warming, unfortunately, the cost in CO₂ capture phase is relatively high, which makes up 50-80% of the overall cost of CCS technology [14, 15]. Thus, it is vital to reduce the overall cost of CCS technology in order to create a more economical viable technology. From the previous research studies conducted, post combustion capture (PCC) of CO₂ possess great potential in reducing the overall cost of CCS technology. Moreover, it is the easiest technique to be implemented compared to pre-combustion and oxy-fuel combustion in CO₂ capturing from current coal-fired power stations [1, 16]. Till date, most of the industrial sector utilizes amine-based processes and wet scrubbing system in capturing the CO₂ gases emitted [11]. The wide usage of chemical absorption technique is mainly due to higher selectivity as well as CO₂ capturing efficiency even at low CO₂ concentration [10]. However, this technique are costly and energy intensive as large amount of water supply is needed during the process [11, 17]. Another main disadvantage of this method is the degradation of amine through

oxidation which eventually lead to the corrosion of process equipment [4, 11]. Hence, the major challenges in current research is to develop a cost-effective as well as environmentally friendly technologies for CO₂ capture.

As an alternative in replacing gas-liquid absorption, gas-solid adsorption has considered to be the greatest potential in becoming a cost effective technology as well as poses least threat to the environment for CO₂ capture [16, 18, 19]. Adsorption process in CO₂ capture exhibit numerous advantages such as reduction in cost, increased the carrying capacity of CO₂, lower regeneration in energy, minimal pressure drop compared to other technologies, rapid reaction rates and the ease of applicability over a wide range of temperatures and pressures [11, 20]. However, the success of this approach is highly dependent on the capability in developing an adsorbent that can be easily regenerated and durable adsorbent with high CO₂ selectivity as well as adsorption capacity [11]. Among the various type of adsorbent available in the market, activated carbon (AC) has been chosen as a promising and cost-effective adsorbent [4, 11, 21]. This is due to its natural characteristics such as large pore volume, high surface area and reactivity, hydrophobicity in nature, high adsorption capacity at atmospheric pressures, wide availability and minimal initial cost which makes it a suitable adsorbent material for post-combustion CO₂ capture [4, 8, 19]. However, the commercial AC available in the market is generally derived from fossil fuels, which thought to be less environmental friendly. Besides that, the impending inadequacy and surging prices of fossil fuels has necessitated the search for alternative resources in producing advanced carbonaceous material such as AC [22].

Searching for a low cost AC has started a few decades ago as an alternative to replace coal-based AC. In view of that, biomass derived from agricultural and food waste is considered as one of the most promising and preferable selection for AC precursors [23, 24]. The main challenges lies in depolymerizing the complex lignocellulosic matrix in order to yield carbon with desirable properties that is suitable to be used in CCS technology [24]. The selection of biomass resources as an alternative to fossil fuels is mainly due to its renewable properties, abundance in supply and most importantly it would not contribute to the overall degradation of the environment; which can be summarized in a word, sustainable [24]. Over the years, much attempts have been made in developing AC from numerous range of biomass such as rice husk, rubber-wood sawdust, oil palm shell and tea waste [23, 25, 26]. However, the use of coffee waste as a biomass precursor in producing AC has yet to gain the attention of the society. Hence, in this research study, coffee waste has been selected as the precursor in the production of AC.

Coffee waste is mainly derived from coffee ground. After the brewing process of coffee ground, the leftover residue produced is known as coffee waste. In the year 2000, according to the statistical data conducted by “Food and Agricultural Organization (FAO) of the United Nation”, the world coffee consumption was found

to be approximately 6800 metric tons [27]. Due to the massive production and consumption of coffee in the market, the amount of coffee waste generated annually has results in disposal issue to the environment. Thus, alternative and a more sustainable method in utilizing coffee waste as a value added product in the production of AC should be taken into consideration in replacing the conventional coal-based AC as well as solving disposal issue. The selection of coffee waste as a precursor in the production of AC not only depend on the basis of its abundance in supply but also its rich in crude fiber content (lignin, cellulose and hemicellulose) and low level of extractives and ash [28]. Studies have shown that approximately 50% of the coffee waste composition comprises of carbon [29]. The rich carbon content in coffee waste makes it a suitable precursor in producing AC with desirable properties that can be used in CCS technology.

In this research study, combination of two different methods which are physical and chemical activation, also known as physiochemical activation method are used in producing AC from coffee waste. During the production of AC from coffee waste, the concentration of the chemical activating agent used will be manipulated while keeping the carbonization temperature and chemical impregnation ratio constant at 800 °C and ratio 1:1 respectively. The effect of different concentration (50 wt. % and 20 wt. %) of potassium hydroxide (KOH) as the chemical activating agent will be studied. Past research indicates that higher concentration of chemical activating agent will produced AC with lower yield as well as different microscopic structure [30]. Hence, AC that is generated from coffee waste will undergo a series of characterization analysis in order to determine its textural properties. Currently, limited studies have been conducted in utilizing coffee waste to produce AC with high adsorption capacity. Thus, another objective of this research work is to study the adsorption performance of coffee waste derived AC in developing a low cost adsorbent with high CO₂ adsorption capacity that is suitable to be used in CCS technology. Past research shown that the formation of micropores structure and high surface area is the main key element in maximizing the CO₂ adsorption efficiency [31]. Hence, the adsorption capacity of the AC produced in this study will be analyzed by using the Thermogravimetric (TGA) analyzer while the microporosity can be determined from the nitrogen adsorption isotherms using BET (Brunauer, Emmett and Teller) analysis.

2. Research Methodology

The main objective of this research is to develop a low cost effective AC by utilizing coffee waste as the raw biomass precursor which has the capability of adsorbing CO₂ gas for the application of carbon capture. This research work will be divided into two main sections which are the production of AC by using physiochemical activation method and characterization of the AC produced. Two different concentration of the chemical activating agent used during the chemical activation process will be studied, which are 50 wt. % and 20 wt. %. Fig 1 illustrates a simple flow chart of the overall methodology for this research work.

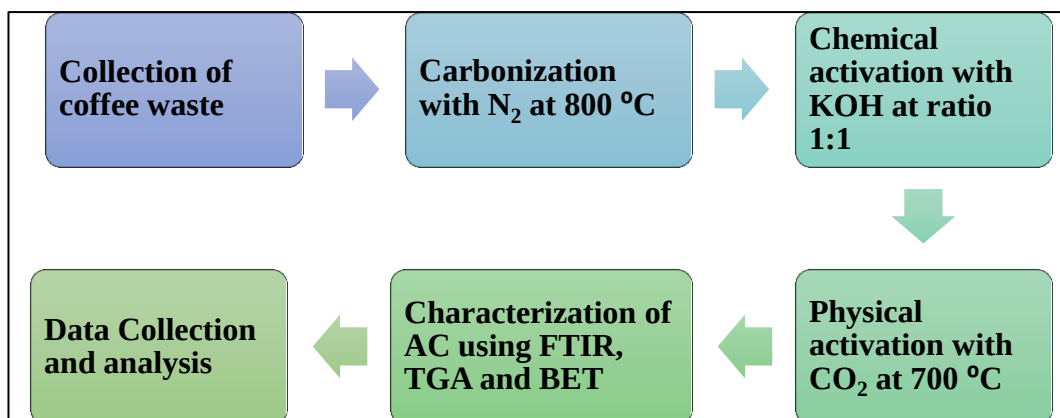


Figure 1. Methodology Flow Chart

2.1 Materials

The precursor, coffee waste was kindly sponsored by Starbucks in Taylor's University Lakeside Campus which was later transformed into AC by physiochemical activation. Prior collection, the precursor is stored in a cool, dry place. In the preparation of AC from coffee waste, potassium hydroxide (KOH) which was purchased from R & M Chemicals has a purity of 99 % was used as the chemical agent during the activation process. The final end product obtained was stored inside a desiccator containing silica gel in order to prevent the formation of water vapor in the sample.

2.2 Pre-treatment of Coffee Waste

The coffee waste was first washed with distilled water in order to remove the impurities present on the surface before undergoes further treatment. Later, the coffee waste was dried inside an oven to remove the moisture content so that the growth of fungal which will eventually affect the efficiency of the AC produced can be avoided. The drying process was held for a duration of 24 hours at a temperature of 110 °C [24, 32, 33]. After drying, the dried coffee waste was stored in a cool, dry place.

2.3 Carbonization Process

Carbolite furnace (Model: HST 12/400) was used to perform the carbonization and activation process for the production of AC from coffee waste. Approximately 30 g of coffee waste samples were placed in a ceramic boat for the preparation of carbonization process. The sample was positioned in the center of the constant temperature zone of the ceramic tubing in the horizontal tube furnace. The ceramic tubing containing the samples in the ceramic boat was flowed with continuous N₂ gas with a constant flow rate of 1 L/min for a duration of 1 hour in order to eliminate the oxygen content inside the tubing. After 1 hour, the sample was heated to a temperature of 800 °C at a heating rate of 20 °C/min under a constant flow of N₂ gas for 1 hour

upon reaching the desired temperature. The sample was allowed to cool to 100 °C after the completion of heating process before it was discard. A small amount of carbonized char was stored for characterization analysis.

2.4 Physiochemical Activation Process

The carbonized char produced via carbonization was impregnated with 50 wt. % of KOH with an impregnation ratio of 1:1, where 100 gram of KOH was diluted with 100 ml of distilled water. 30 ml of KOH solution was later extracted from the mixture and was then impregnated with the carbonized char in order to obtain an impregnation ratio of 1:1. The impregnated sample was stirred at 300 rpm with a magnetic stirrer for a duration of 1 hour for complete impregnation. Once the chemical activation has completed, the sample was filtered with filter paper and washed repeatedly with distilled water until a constant pH of 7 was obtained. The filtered char was later dried in the oven at 110 °C for 24 hours [24, 32, 33]. Similar procedure was repeated for a chemical concentration of 20 wt. % where 25 gram of KOH was diluted with 100 ml of distilled water.

The sample prepared via chemical activation was placed back into the horizontal tubular furnace to be heated up to a desired temperature of 700°C under a constant flow of carbon dioxide gas with a flow rate of 1 L/min for 1 hour. The heating rate was set to 20 °C/min during the physical activation process. The sample was allowed to cool to a temperature approximately 100 °C before it was being discarded from the furnace. After removing the sample from the furnace, the AC sample was stored in a sealed sample flask in a cool, dry environment and were assigned with sample codes as shown in Table 1.

Table 1

Samples Code for Raw and Activated Carbons

Sample	Sample ID
Raw coffee waste	RCW
Carbonized char (without chemical treatment)	CCW
Chemical Activation with 20 wt. % KOH solution	KH2
Chemical Activation with 50 wt. % KOH solution	KH5

2.5 Characterization and Analysis of AC

2.5.1 Proximate Analysis

Proximate analysis was performed using TGA analyzer (Model: Settaram TGA92) which is located in Nottingham University, Malaysia. The moisture level, ash content, fixed carbon and volatile matter content in the raw biomass precursor was determined. In an inert condition, approximately 15 mg of raw coffee waste sample was heated to a temperature of 110 °C with a heating rate of 10 °C/min and a flow rate of 50 ml/min. The sample is heated isothermally for 20 minutes for complete dehydration. Later, the temperature was ramped up to 950 °C and was held isothermally for 30 minutes to eliminate the volatile matters from the sample. N₂ gas was then replaced with air and was held constant at 950 °C for another 20 minutes to promote combustion process, leaving only the ash. The sample was allowed to cool to a temperature of 100 °C before it is being discard.

2.5.2 Thermogravimetric Analysis for CO₂ Adsorption

CO₂ adsorption of coffee waste derived AC was analyzed by using Thermogravimetric (TGA) analyzer (Model: Settaram TGA92) which is located in Nottingham University, Malaysia. Under a constant flow of N₂ gas, approximately 15 mg of sample was placed in a crucible and was heated up to a desired temperature of 60 °C with a flow rate of 50 ml/min. The heating rate was set at 10 °C/min. The sample was heated isothermally at 60 °C for 30 minutes. After 30 minutes, the N₂ gas was replaced with a continuous flow of CO₂ gas under the same temperature and flow rate for another 90 minutes. After completion of the adsorption phase, desorption phase was carried out where CO₂ gas was replaced back with N₂ gas and was allowed to flow for another 30 minutes under the same operating conditions.

2.5.3 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR analysis was performed in order to study the active carbon surface functional groups of the prepared samples. The equipment used for the FTIR analysis was Perkin Elmer Spectrum 100 FTIR Spectrometer equipped with a software named, Spectrum. The discs were prepared by first mixing a small amount of sample at a ratio of 1:99 with KBr powder in an agate mortar. The resulting mixture was placed into a hydraulic press for pelletizing with a force of 10 tons at vacuumed pressure for approximately 30 seconds. The sample was then placed onto a disc holder and it was measured using the FTIR Spectrophotometer. The FTIR spectra were recorded between a wavelength of 4000 to 650 cm⁻¹.

2.5.4 Brunauer-Emmett-Teller (BET) Analysis

The total surface area of the AC produced were determined by N₂ adsorption isotherm at 77 K by using Micromeritics ASAP 2020 Analyzer. The samples were degassed for a duration of 6 hours under vacuum condition at 130 °C prior analyzing process. A relative pressure (P/P₀) range of 0-1.0 for the adsorption data was used in determining the total surface area by utilizing the standard BET method [34]. The textural properties such as specific surface area, micropore volume and pore size distribution were calculated from the N₂ adsorption isotherms by using Brunauer-Emmett-Teller (BET), Dubinin-Radushkevich (DR) and Density Functional Theory (DFT) models, respectively [35].

2.5.5 Burn-off Percentage and Yield of AC

The weight lost during the production of AC was calculated as the burn-off percentage. In this study, two different concentration of KOH chemical agent were studied which are 50 wt. % and 20 wt. %. Thus, for each concentration, the burn-off percentage and the carbon yield were calculated by using Eq. (1) and Eq. (2) [36, 37].

$$\text{Burn off (\%)} = \frac{\text{initial biomass waste} - \text{final AC weight}}{\text{initial biomass waste}} \quad (1)$$

$$\text{Yield of AC (\%)} = \frac{\text{weight of AC produced}}{\text{weight of biomass (coffee waste)}} \times 100\% \quad (2)$$

3. Results and Discussion

3.1 Proximate Analysis

Fig 2 illustrates the thermal degradation behavior of the RCW sample. The thermal degradation of RCW sample can be generally categorized into three main regions which are, (i) the dehydration of water vapor, (ii) decomposition of hemicellulose and cellulose and (iii) the decomposition of lignin and char [38]. From Fig 2, a minor weight loss of 3.6% can be observed at the temperature of around 150 °C which is attributed to the removal of water vapor physisorbed within the micropores structures [35]. The low evaporation of water vapor is mainly due to the adsorption of low water content from the surrounding environment by the hydrophobic surface of RCW. Even after the initial drying process at 110 °C for a duration of 24 hours, a small amount of water molecules are still present on the surface of the biomass. However, only 3.6% of moisture content was observed from the TGA profile. The subsequent degradation event happened at a temperature of approximately 200-560 °C where thermal depolymerization of hemicellulose and cellulose and partial lignin decomposition occurred. The decomposition of the lignin structure continued to have a gradual weight loss at the temperature beyond 560 °C. In the temperature range of 280-480 °C, hemicellulose and cellulose experiencing a rapid decomposition which cause the drastic decrease in the TGA profile. This is due to the decomposition of aromatic compounds in the lignin structure as well as the regular decomposition of secondary organic residues [35]. While the wide range of lignin degradation which occurred at a temperature of 560-960 °C is resulted from the decomposition of benzene ring. Benzene ring has a chemical structure that is harder to decomposed, hence, it has a slower decomposition rate as compared to hemicellulose and cellulose [35, 39]. This trend was verified in the past studies conducted by other researches as well [40-43]. In addition to that, the decomposition of hemicellulose and cellulose as well as partial lignin decomposition represents the amount of volatile matter containing in the RCW sample. From the TGA profile, a volatile content of 83.59% was obtained. From Fig 2, a fixed carbon content of 7% was obtained at 950 °C. Temperature beyond 950 °C will initiates the total decomposition of lignin structure which results in ash formation. Hence, in this research work, the carbonization process was carried out at 800 °C as literature studies conducted indicates that the optimum carbonization temperatures happened at the temperature range of 500-900 °C [44].

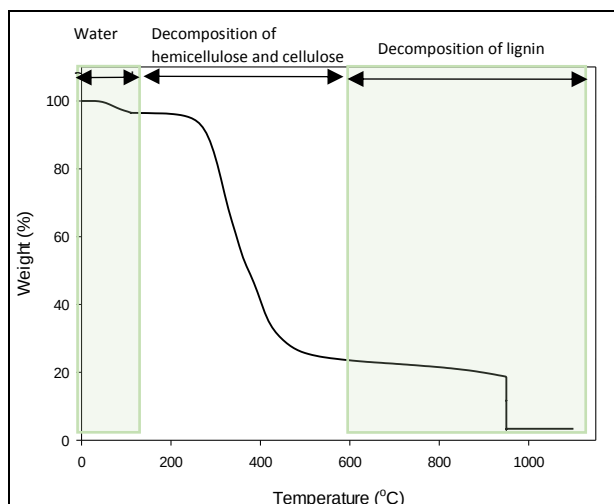


Figure 2. Thermal decomposition of RCW sample

3.2 CO₂ Adsorption Performance

The CO₂ adsorption profile for both KH2 and KH5 samples were illustrated as shown in Fig 3. Based on Fig 3, a rapid increase in CO₂ adsorption capacity can be observed during the initial 60 minutes, and subsequently remains constant until the saturation point is achieved. The drastic increase in adsorption rate is initiated by the interaction between the adsorbent surface areas with the CO₂ molecules. While the beyond 60 minutes, a reduction in active sites occurred and hence slower adsorption rate is observed. Rashidi et al. [45] and Li et al. [46] reported that the rapid adsorption during the initial stage is most likely due to the external surface of the adsorbent and subsequently followed by the slower diffusion process that happens internally. The flue gas temperature in post-combustion process is ranging at a temperature of 40-60 °C [45, 47, 48]. Hence, the CO₂ adsorption analysis performed in this study was conducted at a temperature of 60 °C. Fig 3 illustrates the CO₂ adsorption capacity for both KH2 and KH5 samples. From Fig 3, KH2 obviously demonstrates a higher CO₂ uptake which is of 3.3 wt. % (0.78 mmol/g) as compared to KH5 which only have a CO₂ uptake of 2.3 wt. % (0.53 mmol/g). A similar trend in CO₂ uptake has also been reported by Namane et al [49] which also utilizes coffee biomass to produce AC. Researcher concluded that this may be due to the effect of micropores widening and the formation of mesopores resulted from the chemical effects happening inside the pores [35, 50, 51]. It is reported that AC with high micropores structure will promote better adsorption capacity [35].

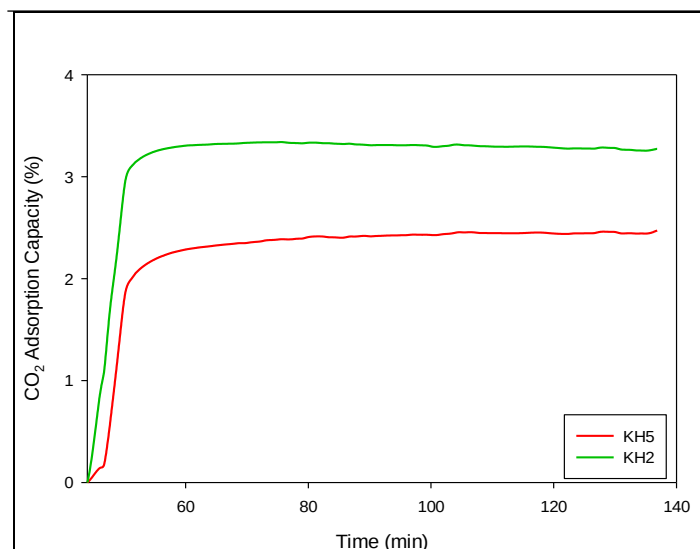


Figure 3. CO₂ Adsorption Capacity Curve

3.3 FTIR Analysis

Adsorption capacity in AC is highly dependent upon its porosity as well as chemical reactivity of functional groups at the surface. This reactivity initiate a discrepancy between forces at the surface, and thus leading to molecular adsorption by the Van der Waals forces. Knowledge on surface functional group would benefit in determining the adsorption capability of the AC produced. Past research studies conducted indicates that the presence of oxygen containing functional group such as carboxylic, lactone, phenol, carbonyl and ether are important in the adsorption capabilities of the AC produced [11, 32, 49]. The presence of the oxygen functional group will initiate the bonding between the adsorbent and adsorbate [24]. Fig 4 illustrate the infrared spectra of four samples (RCW, CCW, KH2 and KH5). The more intense bands of the samples are as shown in Table 2. The FTIR spectra as illustrate in Fig 4 clearly shows the change in spectrum of the four samples. There are a few significant peaks that can be observed for RCW sample, mainly at 3400, 2925, 2854, 1745, 1649, 1390, 1378, 1163 and 1059 cm^{-1} which are assigned to O–H stretching vibration, C–H alkane group, C=O groups (usually presence in the carbonyl and lactones structures), N=O bending vibration and C–O stretching vibration of esters, respectively. The spectrum also revealed two other peaks at the adsorption band of 840 and 758 cm^{-1} which is directly attributed to the bending vibration of C–Cl alkyl hallides groups (usually situated at the edge of the aromatic ring) [34].

The introduction of heat and chemical treatment to the raw biomass sample resulted in the variation in spectrum. A broad band of 3192 to 3236 cm^{-1} can be observed for CCW and KH2 samples which can be characterized to the stretching vibration of hydroxyl groups. The presence of the hydroxyl stretching compound demonstrates that all the samples except for KH5 sample shows strong hydrogen bond linkage. From Fig 4, RCW, CCW and KH2 spectra exhibit obvious peak frequency while KH5 sample portrays a smooth curve that no obvious peaks can be seen. This is due to the elimination of oxygen functional groups or the damage done to the chemical structure of the sample due to the high chemical treatment. The results obtained

conform to the past studies done by other researchers where at higher activation conditions, the spectrum obtained demonstrates a very weak peak intensities [52-54]. The presence of oxygen functional group is vital in contributing to the formation of high microporosity structure in AC. Oxygen containing functional group that is being removed will results in a change of linkage between aliphatic and aromatic bond. In other words, destruction in crosslink and the change in arrangement of the carbon layer will occur which will caused a collapse in the porosity structure within the AC [54-56].

By comparing CCW with KH2 sample, KH2 sample which have undergo complete activation process show a slightly stronger hydrogen bond linkage. This indicates that the sample has undergoes a higher dehydration properties compares to CCW [36]. Although C-H stretching vibration in aromatics exist in all the samples, however, their transmittance intensities is rather weak with a broad wavelength. This is mainly due to the presence of water molecules in the samples [57, 58]. As AC has high absorption capabilities, the sample tends to absorb water vapor from the environment which lead to the high moisture level within the samples. KH2 and CCW samples demonstrates a spectrum that are almost similar. However, when comparing the spectrum for all four samples, most of the peaks have deviated from their initial frequency level or in some conditions, certain functional groups weakens and even disappear at certain concentration level of KOH solution. For instance, the stretching vibration of esters group in RCW sample has disappeared after undergo treatment process. On top of that, the alkyl halides group which is initially absence in the raw biomass sample has formed at the adsorption band of 840 and 758 cm^{-1} after undergoing carbonization and activation process. A similar trend was observed in some of the previous research work done by other researches where some peaks were shifted or even disappeared when comparing with the spectrum of the raw biomass [24, 36]. It is concluded that this phenomena may be due to the destruction done to the lignin structure of some of the functional groups after it has undergo thermal and chemical treatment [24].

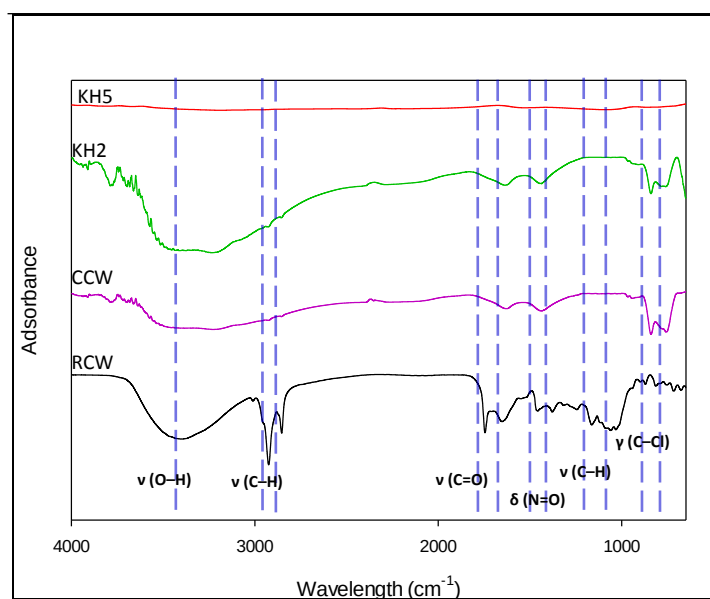


Figure 4. FTIR spectra for raw and activated carbon

Table 2

Infrared bands for raw and activated carbons

Wavelength (cm ⁻¹)	Type of Vibration	Functional Group Name
3400	ν (O – H)	Phenols & Alcohols
2925, 2854	ν (C – H)	Alkanes
1745, 1649	ν (C = O)	Carbonyl Compounds
1390, 1378	δ (N = O)	Nitro Group
1163, 1059	ν (C – O)	Esters
840, 758	γ (C – Cl)	Alkyl Halides

^a ν : stretching vibration

^b δ : bending vibration (in-plane)

^c γ : bending vibration (out-of-plane)

3.4 Textural Properties of AC

The adsorption performance of the AC are govern by several factors such as the active surface areas, pore sizes as well as the type of pores formed [35, 59]. Particularly, the formation of micropores structure will able to yield AC with better CO₂ adsorption performance [34, 35, 37]. Fig 5 shows the adsorption isotherm of both KH2 and KH5 samples which are analyzed through physical adsorption of N₂ at 77 K. A sharp knee was observed at $P/P_0 < 0.1$ for both KH2 and KH5 samples which indicates that the samples exhibited type 1 isotherm where the products are composed predominantly of well-developed micropores [34, 35, 60]. However, from Fig 5, KH2 shows higher N₂ uptake compared to KH5. This indicates that KH2 demonstrate a stronger interactions in the initial uptake for monolayer coverage, followed by micropores filling than KH5. From the N₂ adsorption curve, it is observed that a plateau is not achieved towards the tail of the curve in both samples at $P/P_0 > 0.6$. There is an increase in N₂ uptake at higher partial pressure region which shows an indication that there is a certain amount of mesopores structures presence in both samples [34, 35, 60]. This results conforms to Table 3 where a mesopore volume of 0.0034 cm³/g and 0.003 cm³/g were obtained for both samples respectively. Reffas et al. [37] and Sun et al. [60] have also reported similar trend in adsorption curve where at higher partial pressure region, there is an increase in N₂ uptake which shows the presence of mesoporous structure.

Fig 6 and Fig 7 show the pore size distribution (PSD) for both KH2 and KH5 samples respectively. The PSD profile for both samples were computed by utilizing the density functional theory (DFT) model. For both KH2 and KH5 samples, a major peak can be seen at pore width of 0.2 nm and 1.2 nm respectively which is distributed within the microporous range (pore width < 2 nm). However, the PSD profile for KH5 has a slight variation in trend as compared to KH2. KH5 sample has several low peaks mainly at pore width of 2.5 nm, 5.8 nm and 7.6 nm. All these peaks are distributed across the wide range mesopores structures (2 nm < pore width < 50 nm). The high amount of formation of mesopores structure in KH5 (30%) samples may probably due

to the collapse of pore walls or the aggressive chemical reaction between the activating agent and the adsorbent which results in higher vaporization of organic matter when it is chemically activated at higher chemical concentration thus leading to the widening of the pores [61]. Past researcher had also reported similar results where wider pore structure is obtained when the sample is treated at higher thermal and chemical condition [62, 63].

Table 3 show the detail summary of the textural properties for both KH2 and KH5 samples. From Table 3, a total surface area of 36 m²/g and 16 m²/g were obtained for both KH2 and KH5 samples respectively. It is obvious that KH2 sample yield a higher porosity. It is worth to highlight on the results where sample activated at higher chemical concentration will produce AC that has limited number of micropores as well as low BET surface area with a slightly increased in average pore diameter (D_{avg}). Almost 80% and 70% of the pore being developed fall in the category of narrow microporosity domain for both KH2 and KH5 samples respectively. The percentage ratio attained is in compliance to the micropore volume for both samples whereby KH2 and KH5 having a total micropore volume of 0.0144 cm³/g and 0.007 cm³/g respectively. However, the percentage of mesopore obtained in this work can be consider low as compared to the result obtained by past researcher that is also using coffee waste as the precursor for AC production where a mesopore percentage of approximately 53% was reported by Boonamnuyvitaya et al. [64]. The BET surface area as well as the micropore volume obtained in this research work are generally much lower compare to the past research work done by other researchers. Most of the researchers which also used coffee biomass as the precursor for AC production reported a BET surface area within the range of 500–1500 m²/g [37, 62, 65]. Hence, it is anticipated that there are some limitations during the production of AC as based on the past research done that utilizes coffee biomass, a minimum BET surface area of 500 m²/g could be achieved.

During the carbonization process in the initial stage of AC production, nitrogen gas was used as an inert gas to eliminate the oxygen content in the horizontal tubular furnace in order to prevent the large ash formation during the heating process. The flow rate used during the carbonization process was 1000 cm³/min. Studies conducted shows that when the gas is being flowed at a low flow rate of approximately 50 cm³/min, the volatile matter being released may not be fully eliminated during the thermal reaction, which results in the re-deposition of volatile matter back to the surface of the sample [66]. Hence, this would lead to the blockage of pore as well as obstructing the development of more pores structure within the sample. Conversely, when the flow rate is too high which is higher than 300 cm³/min, the surface temperature of the sample would decrease and results to the incomplete removal of volatile matter. Thus, the development of pore structure would be restricted due to the high gas flow rate. This would eventually lead to the low BET surface area of the product formed [66]. Hence, it is suggested to reduce the flow rate to 100 cm³/min [35].

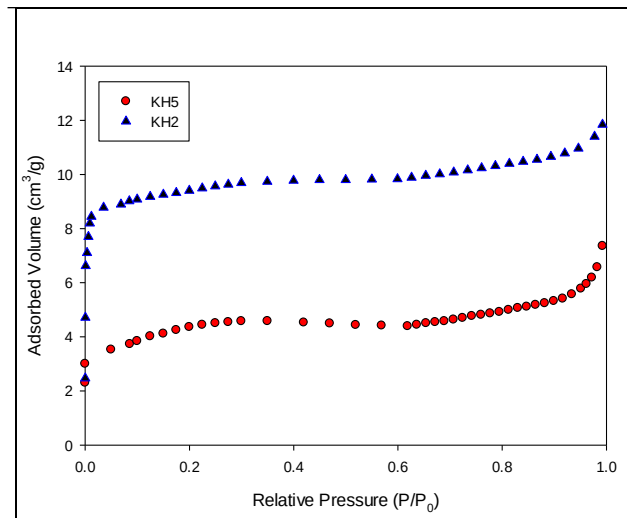


Figure 5 Adsorption isotherm of N_2 at 77K

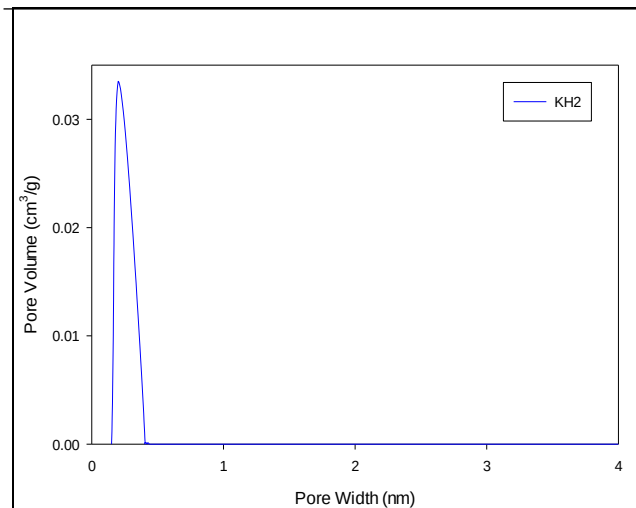


Figure 6 DFT pore size distribution for KH2

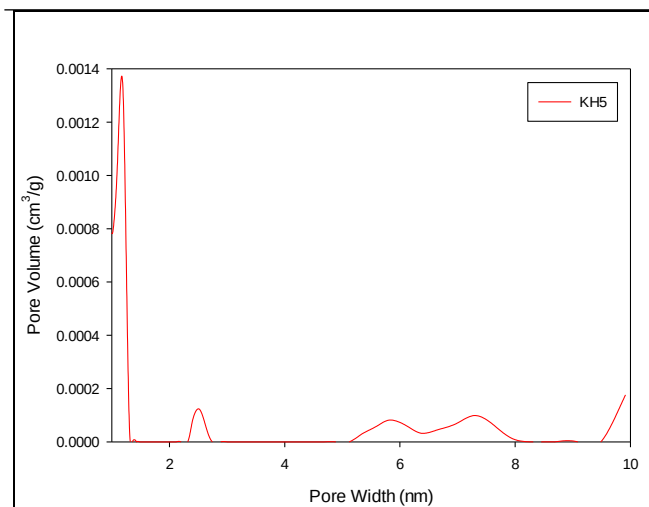


Figure 7 DFT pore size distribution for KH5

Table 3

Textural properties for KH2 and KH5 obtained from N2 adsorption isotherm

Carbon Parameters	KH2	KH5
Total Surface Area, S_{BET} (m ² /g)	36	16
Total Pore Volume, V_{total} (cm ³ /g)	0.0178	0.0100
Micropores Volume, V_{micro} (cm ³ /g)	0.0144	0.0070
Mesopores Volume, V_{meso} (cm ³ /g)	0.0034	0.0030
Micropores Ratio ^a , V_{micro} (%)	80.9	70
Mesopores Ratio ^b , V_{meso} (%)	19.1	30
Average Pore Diameter, D_{avg} (nm)	1.98	2.57

^a The ratio of micropores volume to the total pore volume.

^b The ratio of mesopores volume to the total pore volume.

3.2 Burn-off and Carbon Yield

From the data tabulated in Table 4, it clearly shows that an increase in the concentration of the KOH during the impregnation results in an increase in the burn-off percentage and hence, the yield of the AC produced reduces. The burn-off percentage that was calculated for KH5 was 78.38 % with a carbon yield of 21.62 % while a yield of 23.73 % with a burn-off percentage of 76.27 % was obtained for KH2 sample. The reduced in carbon yield for AC in KH5 sample is due to the chemical reaction happened during the activation process whereby KOH reacted with carbonized char as well as the volatile compound and diffused rapidly out of the surface of the particles during chemical activation [36]. Hence, with a higher concentration of impregnation, the gasification reaction happening on the surface of the carbon atoms became predominant which leads to an increase in burn-off percentage and a lower carbon yield. This conforms to the results obtained by past researcher where a lower carbon yield was obtained for higher concentration of chemical used during impregnation [33, 36]. It is also reported that a lower yield obtained with a higher chemical impregnation concentration is due to the enhancement in burn-off of carbon by the excess of chemical widening micropore into mesopore. From the previous research conducted, it is shown that a higher total porous volume was obtained with higher burn-off value. Hence, it is said that a higher carbon recovery was obtained at a lower impregnation concentration.

Table 4

Burn-off percentage and carbon yield obtained for different concentration of KOH

Parameter	KH5	KH2
Burn- off (%)	78.38	76.27
Yield (%)	21.62	23.73

4. Conclusions

In this research work, a low cost effective as well as sustainable AC can be developed from raw coffee waste for the application of CCS technology. Based on the overall results analysis, it was found that KH2 sample yield better textural properties,

surface chemistry as well as higher CO₂ adsorption capacity. This would give a preliminary indication that KH2 would have a better performance for CO₂ adsorption application. In addition to that, the burn off value obtained for KH 2 was 76.27% with a carbon yield of 23.73%. AC with lower burn off value will favour the formation of micropores structure as compared to higher burn off value. Hence, it can be concluded that sample with lower chemical treatment will produce a more suitable AC for CO₂ adsorption application. However, in the near future, it is suggested that to reduce the flow rate of gas during the carbonization process as well as to study several other factors that might affect the performance of AC produced. This would definitely be beneficial in determining the process condition that able to maximize the performance of AC produced.

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Effect of Alkaline Pre-treatment Conditions of Mesocarp Fiber on its Derived Biochar's Properties for DCFC Application

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Abstract

The production of palm oil has generated enormous amount of biomasses. For 1 kg of palm oil extracted, 4 kg of the dry biomass is generated which consists of mesocarp fibre, empty fruit bunch, palm kernel shell, palm trunk and oil palm frond. Among all, mesocarp fibre with the highest lignin content of 22.7% is believed to be the most promising candidate used to be converted into biochar through pyrolysis process with highest carbon content, that could be suited as carbon fuel in direct carbon fuel cell (DCFC). Nonetheless, past studies have shown that the biochar's properties are greatly influenced by the pre- or post-treatment conditions on the biomass. Alkaline treatment showed the advantage of improving the biochar porosity that is highly desired in DCFC for increase in electrochemical reaction's active sites. Hence, this study focused on the effect of alkaline pre-treatment conditions on mesocarp fibre prior to the pyrolysis process towards the physicochemical properties of the pyrolysed biochar. In this study, the mesocarp fibre was pre-treated with potassium hydroxide (KOH) with different concentration of 0.5M, 1.0M and 3.0M of KOH with different durations of the alkali activation process (2, 6 and 10 hours). The pre-treated samples were subsequently pyrolysed at 550°C for one hour. The samples were studied on the biochar yield, ash content through ASTM method and fixed carbon content through CHNS analysis. From this study, it was revealed that the biochar yield increased with increased in alkaline concentration in pre-treatment processes. However, the ash contents were found lowest in the samples treated with 1 M KOH. Comparing the sample sets with different pre-treatment durations, biochars with 10 hours KOH treatment was found to possess the lowest ash content (8 – 12 %) as compared to 2 and 6 hours KOH treatment. From all samples produced, the biochar with 3M KOH for 10 hours pre-treatment was the best sample among all owing to its lowest ash content (8%) and highest fixed carbon content (72.49%).

Keywords: Mesocarp fibre, Biochar, KOH pre-treatment, DCFC

1. Introduction

In direct carbon fuel cell (DCFC), the solid carbon/biochar is used as the fuel at the anode where the process of conversion of chemical energy into electrical energy takes place through the carbon fuel oxidation. Study has found that the use of DCFC as energy generation device will result in a reduction in greenhouse gases, particulates, NO_x and SO_x pollutant emission by 50% [1], as compared to the products of fossil fuels combustion to generate electricity. Theoretically, the efficiency of DCFC can achieve 100% although in real operating condition, the actual efficiency is approximately 80%. Nevertheless, this efficiency is found to be twice the efficiency of a fossil fuel power plant [1].

Malaysia has been ranked as the second largest palm oil producer in the world. In the palm oil industry, the production of palm oil from oil palm has generated enormous amount of biomass. It was reported that for 1 kg of palm oil extracted, 4 kg of the dry biomass is generated which consist of mesocarp fibre, empty fruit bunch, palm kernel shell, oil palm trunk and oil palm frond [2]. This leads to a huge opportunity in converting biomass into useful energy, such as fuel (biochar) for DCFC application which is known as renewable and carbon neutral [3].

In this study, the biochar is converted from mesocarp fibre by using alkali treatment prior to the pyrolysis process. Mesocarp is one of the major fruit layers of an oil palm that can produce palm oil [4]. All plant's biomasses contain cellulose, hemicellulose and lignin. Lignin is regarded as the strong composite component that can be converted into biochar by pyrolysis process whereas cellulose and hemicellulose will be converted into volatile matter in the process [5]. Previous study has revealed that the mesocarp fibre with 13.2 - 22.7% of lignin content can be converted into biochar due to its strong composite properties [2].

The porosity of biochar was found to increase upon activation through alkaline treatment. In the DCFC application, high porosity of biochar is preferred as it will possess higher reaction sites to allow the chemical reaction with oxygen to occur at an increased rate [6]. When the biochar is oxidised by electrochemical reaction, the carbon in the biochar will break apart from the chemical bonding and react with oxygen to form carbon dioxide and generate electricity which described in Eqs. (1)- (2) and Fig. 1 [7].

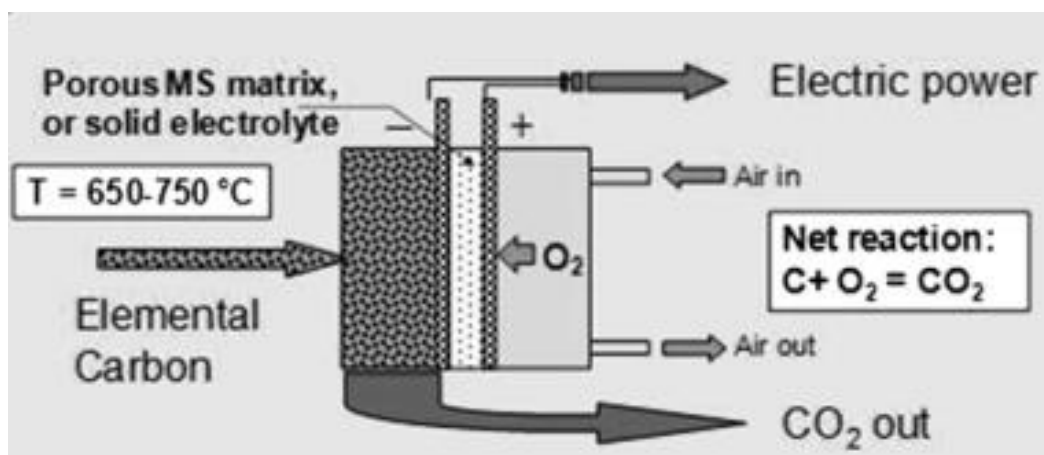
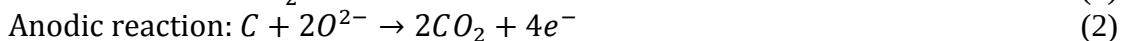


Figure 3: Schematic Diagram of DCFC



Based on the study done by Ahn et al. (2013), the biochar produced from wood with specific surface area of $163\text{m}^2/\text{g}$ and carbon content of 75.9 wt % was able to produce relatively high power density of 40 mWcm^{-2} in DCFC performance test. This high value of power density was attributed to the low percentage of graphitised carbon with higher surface edges and disordered structure that lead to an improvement in the electrochemical reaction [8]. This is due to the fact that carbon atoms that are located at the edges has higher exposure area and thus are more readily to react with oxygen molecules that approach them.

Their study was in good agreement with Xu et al. (2013) who has found that the activated carbon showed more superior performance in DCFC than graphite and German geck carbon. This was attributed to the higher porosity of the activated carbon that lead to the enhancement in rate of oxygen diffusion [9]. Another factor that was contributing to the better performance of activated carbon was the smaller carbon particle size with larger contact area with oxygen gas [9]. Nevertheless, the presence of smaller particle size of activated carbon possessed the drawback of refraining the uniform diffusion process of oxygen through the structure and thus affects the performance of the fuel cell [9]. Ahn et al. (2013) have revealed that the surface area and the carbon content will greatly affect the performance of DCFC [10]. In short, higher power density can be obtained with higher surface area and higher carbon content. These two factors will affect the rate of oxygen diffusion that shows a positive correlation with the efficiency of electrochemical reaction.

Interestingly, chemical pre-treatment of biomass prior to pyrolysis showed significant effect on the performance of the DCFC when the as-produced biochar was used as the carbon fuel. Wang et al. (2013) discovered that the activated carbon produced from alkaline pre-treatment process had shown to possess higher power intensity as compared to that with acid pre-treatment. In alkaline solution, the hydroxide solution with metal such as sodium or potassium hydroxide will increase the surface area of activated carbon because a metal ion will embed into the biochar and enlarge the surface area of biochar and thus enhance the diffusion of oxygen in the electrochemical process [11]. As such, it is worthwhile to investigate on the effect of performing alkali treatment of mesocarp fibre on the biochar's carbon yield, porosity and crystalline structure before the pyrolysis process that will be used as the carbon fuel for DCFC.

2. Methodology

2.1 Biochars Preparation

Mesocarp fibre that was collected from Sri Ulu Langat Sdn Bhd was initially washed with distilled water at room temperature to remove the solid impurity. The raw mseocarp fibre was dried in accordance to ASTM D2867-09 standard strictly, in which the sample was placed in the oven at 105°C for 24 hours under atmospheric pressure for any moisture removal. The dried mesocarp fibre was grounded and sieved to produce particles with size of 2 mm - 0.5 mm. 20 grams of the grounded mesocarp fibre sample was weighed and impregnated into the KOH solutions with different

concentrations of 0.5 mol/L, 1 mol/L and 3 mol/L which shows in table 1. The samples in KOH solutions were subsequently heated and stirred at temperature of 85°C for different duration (2 hours, 6 hours, and 10 hours) under reflux condition. The samples were then collected and washed with distilled water until neutral pH, and finally dried in the oven prior to pyrolysis. A horizontal split tube furnace (Carbolite, UK) was employed to pyrolyse the samples at 550°C with 10°C/min heating rate for 1 hour under nitrogen flow of 1 L/min and was cooled down to room temperature before collection for characterisation. Control set of biochar produced from pyrolysis of mesocarp fibre without alkaline treatment will be used for comparison.

Table 1: Experiment set

Parameters	Concentration of alkali (M)		
Reflux Duration (hour)	0.5	1	3
2	Set A1	Set A2	Set A3
6	Set B1	Set B2	Set B3
10	Set C1	Set C2	Set C3

2.2 Physicochemical Characterisation of Biochars

Carbon yield was calculated using the dry mass basis based on mass of samples before and after the pyrolysis. Proximate analysis of biochar to determine the moisture content and ash content were conducted via ASTM E 190-87 and ASTM E 897-88 techniques respectively. Ultimate analyses on the selected biochars with lowest ash content were performed using Vario MACRO Cube CHNS, Germany. The best sample with the highest carbon content was analysed on its specific surface area and the micro/mesoporosity volumes using Brunauer–Emmett–Teller (BET) analysis (Quantachrome Autosorb 1C). Thermal stability study was performed via thermal gravimetric analysis (TGA) under oxygen condition on Seiko Exstar 6300 to identify optimum operation temperature of the biochar in DCFC. Lastly, X-ray diffraction analysis (XRD) was performed on Bruker Advanced D8 to analyse on the crystalline structure of the biochar. Comparisons were made with the non-alkaline treated biochar as control set for CHNS, BET, TGA and XRD analysis.

3. Result and Discussion

3.1 Visual result

Under the condition of high concentration of KOH and long duration of pre-treatment, the colour intensity of mesocarp tends to be darker as shown in Fig. 2. During the treatment process, oxidation of KOH and mesocarp fibre occurred and impurities were leached out during the washing process [11]. Ray & Sarkar (2001) reported that hemicellulose and semi-cellulose were sensitive to alkali treatment with degradation and the density of the sample also decreased after the pre-treatment process. In the research of Gassan and Bledzi (1999), the fibre was swell and loss of weight after the alkali pre-treatment process. With increase in KOH concentration, more impurities will be removed [12]. Along with some degree of decomposition of hemicellulose and semi-cellulose by alkaline treatment, the unbounded carbon was appeared and thus the samples get darker indicating the appearance of carbon particles [13].

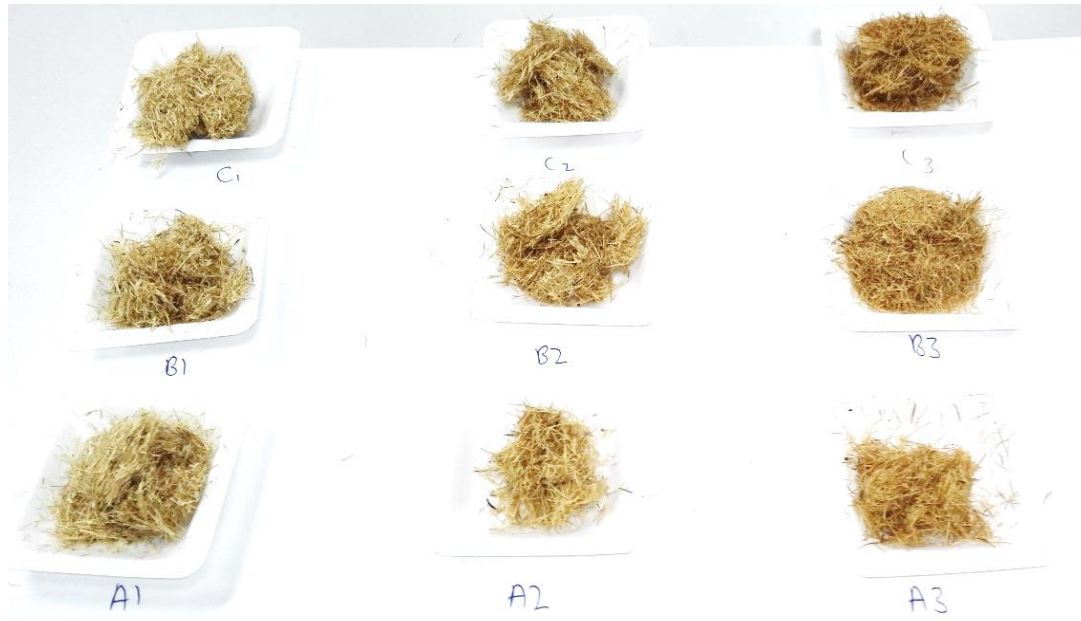


Figure 4: Visual result on the mesocarp after the KOH pre-treatment

3.2 Biochar yield

High carbon yield in biochar is preferred for direct carbon fuel cell (DCFC) application in term of cost feasibility [14]. In general, higher biochar yield would reflect the higher carbon yield in the samples. Table 1 shows the biochar yield prepared from mesocarp fibre under various pre-treatment conditions. Set of biochars with 3M KOH pre-treatment showed the highest biochar yield (31%-33%) compared with that of 0.5 M and 1 M KOH pre-treated samples (26 % - 28 %). This is due to the fact that with increased in KOH concentration, the rate of oxidation reaction of mesocarp fibre increased, and thus, more impurities and volatiles can be removed during the pre-treatment process and left mainly the partially decomposed hemicellulose, cellulose and undecomposed lignin in the mesocarp before the pyrolysis process [13]. Interestingly, the biochar yield from this was slightly above the lignin content in the raw mesocarp fibre (c.a. 22.7%) indicated that compound in the biochar samples was most likely originated from the decomposed lignin layer during the pyrolysis process at 550°C. Further explanation will be given in the latter section. Nonetheless, duration of the pre-treatment did not have significant effect on the yield of the biochar in Table 2.

Table 2: Carbon yield of the biochar with different concentration of KOH and different pre-treatment time

Pre-treatment time (hours)	Concentration (M)	Sample	Carbon yield (%)
2	0.5	A1	26.7
	1	A2	27.7
	3	A3	31.3
6	0.5	B1	26.0
	1	B2	27.7
	3	B3	33.3
10	0.5	C1	26.0
	1	C2	27.0
	3	C3	32.3

3.3 Moisture Content and Ash

In general, biochar is made up of fixed carbon, ashes, volatile matter and moisture content. In DCFC, it is crucial for us to have carbon fuel with high fixed carbon with least ash content in order to improve the fuel cell performance. Hence, moisture content and ash content was determined in this study to further identify the fixed carbon in the samples. Table 3 depicts the moisture contents of biochars and Fig. 3 shows the corresponding ash contents.

Table 3: Moisture content of biochars

Pre-treatment duration (hours)	Concentration (M)	Sample	Moisture Content (%)
2	0.5	A1	7
	1	A2	5
	3	A3	5
6	0.5	B1	6
	1	B2	5
	3	B3	5
10	0.5	C1	6
	1	C2	7
	3	C3	7

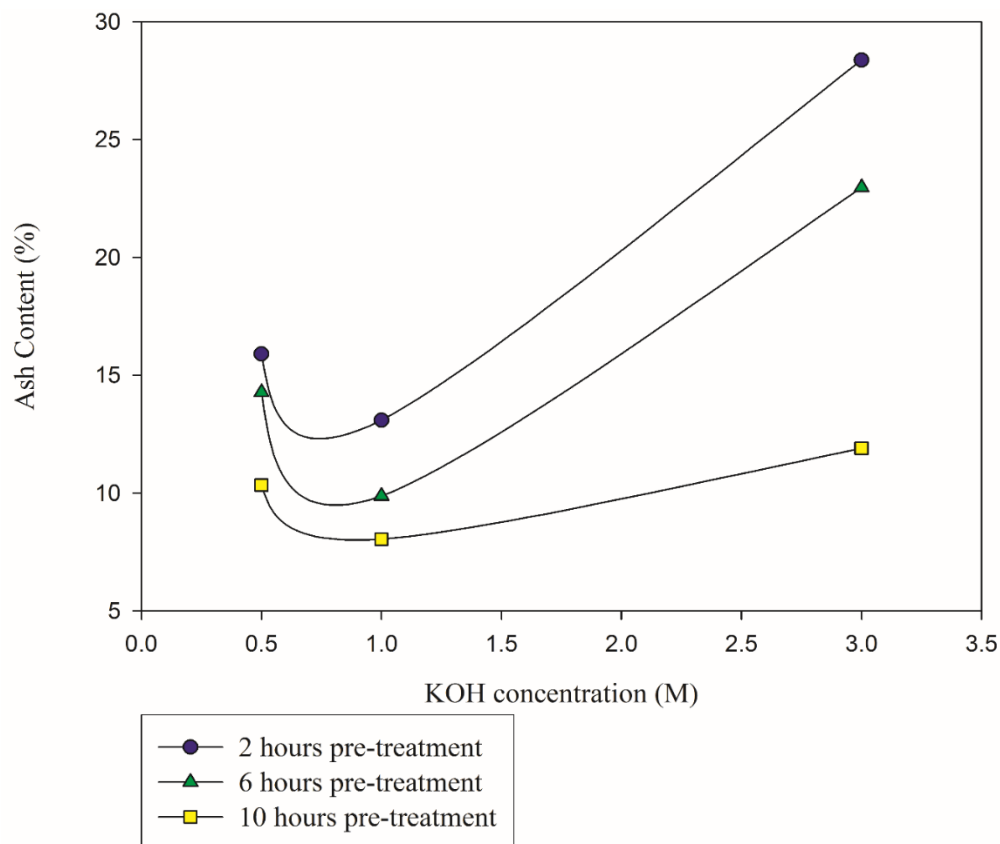


Figure 5: Ash of biochar versus KOH concentration in different pre-treatment duration

Based on Table 3, the moisture contents of the biochars were found in the range of 5% to 7% indicated that the pre-treatment process did not affect the moisture contents of the biochars. Ash is one of the factors that shows adverse effect on the

performance in DCFC. Low ash content of the biochar is preferred to be use in DCFC. Low percentage of ash represented by low amount of organic and inorganic impurities in the biochar is acknowledged as a clean fuel [15]. In DCFC, impurities would hinder the DCFC performance due to the poisoning effect on the electrode [6]. In this study, the ash content of the control sample was found to be 6% whereas the ash content of biochars after the pre-treatment process showed to increase to 8- 28%. According to Muniandy et al. (2014), the potassium carbonate that was produced due to the oxidation process in the alkaline treatment might be decomposed to potassium during the pyrolysis and remained as impurities in the biochar [16]. This could probably explain our result that higher ash content was seen in biochar with alkaline pre-treatment. There could be a possibility that the potassium carbonate was not completely washed off during the neutralisation process prior to pyrolysis. Thus, some potassium mineral might reside in the biochar in the form of ash.

A similar trend on the ash content was seen on the three sets of samples with different pre-treatment durations (Fig. 3). The ash content was shown to reduce from 0.5 M KOH to 1.0 KOH pre-treated sample and increased drastically when concentration further increase to 3.0 M. Comparing the set of samples with different pre-treatment durations, set C with 10 hours pre-treatment duration showed to contain the lowest ash content in this study. This can be easily explained by the higher pre-treatment duration that would increase the surface area that is oxidised by the KOH. With this lowest ash content, set C was selected for ultimate analysis (CHNS) to confirm the fixed carbon content. Among the three samples in set C, the lowest ash content of biochar was found in C2, which is 8%. From the view of the ash content, this sample, among all, would be best suited as carbon fuel for DCFC.

In the study of Oh & Park (2002), the total pore volume of the biochar showed to increase with increase in KOH concentration during the pre-treatment. Also, Ahmadpour & Do (1997) reported that the micropore of macadamia nutshell biochar increased with chemical ratio of 30-80% KOH. However, in their study, the micropore showed to decrease at high KOH ratio (>100%) due to excessive reaction between the KOH and the wall of the nut shell which changed the micropore to mesopore. This help to explain the trend in Fig. 3. The ash content of mesocarp biochar [11] was reduced with pre-treatment process of 0.5-1.0M KOH solution because high impurity was remove and non-porous material in mesocarp could be converted into micropore. However, with huge increase in the KOH concentration (3.0 M), the ash content also increased drastically possibly because of that the micropore were converted into mesopore by breakage of the wall structure of the mesocarp through the oxidation reaction and subsequently more potassium embedded into mesocarp during the pre-treatment process and further oxidise the internal wall of the mesocarp. Hence the ash content and biochar yield showed to increase after pre-treatment process with condition of 3M KOH solution for 10 hours. BET analysis that is yet to perform would verify our result.

3.4 Ultimate analysis (CHNS)

Table 4 shows the result of ultimate analysis for biochar from set C. Carbon content of the biochar is one the main factors to operate in DCFC [17]. Ahn et al. (2013) reported high carbon content of the biochar will generate high power density in DCFC. In this study, sample C2 had the highest amount of carbon content compared with sample C1 and C3. From this analysis, the actual carbon yield can be determined as shown in Table 5. This actual carbon yield from mesocarp fibre showed similar percentage to the lignin content in the raw mesocarp fibre. This result is consistent with study performed by Idris et al. (2010) that based on the thermogravimetric analysis (TGA), the sample weight lost drastically at temperature between 350 - 500°C, indicates the complete removal of hemicellulose and cellulose through devolatilisation process, with carbon derived from lignin remained in the biochar [18]. It is also believed that the alkaline pre-treatment showed some effect on the decomposition of hemicellulose and cellulose layers which discussed on the previous visual result and thus reduce the carbon yield in the biochar. Based on Table 4, sample C3 has the lowest carbon content (63.58%) that is consistent with the highest ash content in set C due to the removal of carbon during the conversion of micropore to mesopore at high KOH concentration. In general, the concentration of KOH solution did not affect the hydrogen content in the biochar which is 3% approximately. The nitrogen content of biochar increased when the KOH concentration increased because more nitrogen was adsorb on the biochar with high porous surface during the pyrolysis process which was under nitrogen gas flow condition. Sulphur is the non-metallic compound which can interrupt the electrochemical reaction in DCFC [19], so low sulphur content is more suitable to applicable to use in DCFC. Nonetheless, the effect of alkaline treatment on the sulphur is yet to be investigated in detail. Although sample C3 has the lowest sulphur content and highest actual carbon yield, it might be less suitable to use in DCFC from the view point of high ash content and high consumption of KOH for the pre-treatment process. Hence, it can be concluded that sample C2 with 1.0 M KOH pre-treatment concentration for 10 hours is the best sample based on the lowest ash content and high carbon yield.

Table 4: Ultimate analysis result of set C

Pre-treatment time	Concentration (M)	Sample	C (%)	H (%)	N (%)	S (%)
10 hours	0.5	C1	69.89	3.329	7.42	3.787
	1	C2	72.49	3.212	9.13	2.183
	3	C3	63.68	3.616	10.04	1.131

Table 5: Actual carbon yield of set C

Sample	Biochar yield (%)	Carbon content (%)	Actual carbon yield (%)
C1	26.0	69.89	18.17
C2	27.0	72.49	19.57
C3	32.3	63.68	20.57

4. Conclusion

This study revealed that the alkaline concentration and pre-treatment duration showed to influence the biochar properties, in which biochar that underwent KOH pre-treatment with concentration of 1.0 M showed to have the lowest ash content as compared to that with concentration of 0.5 M and 3.0 M. Besides, a longer pre-treatment duration was found favourable for the removal of impurities. The present investigation showed that mesocarp fibre biochar produced by combination of chemical pre-treatment (1.0 M KOH, 10 hours) and pyrolysis process (550°C, 1 hour) exhibit the best properties, among all for DCFC application viewing from the aspect of having the lowest ash content and high carbon content. Following these results, comparison on the morphology, porosity and the thermal stability of the selected alkaline treated and untreated biochar will be performed and thus XRD, BET and TGA results will be obtained.

Acknowledgment

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An Investigation on the Effect of rGO Compositied with NCNT and Fe-NCNT on the Oxygen Reduction Reaction via Physical Mixing Method

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Abstract

Oxygen reduction reaction (ORR) plays a major role in fuel cell applications to generates electricity by an electrochemical reaction. To date, platinum has been used as the state-of-art catalyst for the ORR process that contributes to the high component cost in fuel cell. In this research, rGO are composited with Fe-NCNT and NCNT are investigated on the ORR activity. . Studies have shown that the surface edges on the graphene and the iron composited nitrogen-doped carbon nanotubes (Fe-NCNT) due to the effect of chemical functionalisation would favour the oxygen binding process, and thus act as the reaction sites for ORR. In this study, the synthesis of the functionalised nanocatalyst is carried out by using the physical mixing methods. The physical mixing method is done by sonication with presence of pyrrole in this study to produce the desired nanocatalyst. rGO was produced by using simplified Hummer's method. NCNT and Fe-NCNT was obtained from the previously prepared samples using chemical vapour deposition (CVD) technique and electrochemical reduction method. The surface morphologies and microstructures of the synthesised nanocatalysts will be studied using field emission scanning electron microscopy (FESEM). Surface chemical functionality of the nanocatalysts will be investigated using X-ray photoelectron microscopy (XPS). Meanwhile, the ORR performance of nanocatalysts in a half cell will be investigated using cyclic voltammetry (CV) techniques in both alkaline and acidic electrolyte. From FESEM analysis, the surface morphologies of Fe-NCNTs have shown agglomeration on the NCNT and thus hinder the transfer of electrons within the catalyst surface. The XPS result shows that the surface composition on the NCNT/rGO has higher pyridinic-N which claimed to have favored the catalytic activity compared to Fe-NCNT/rGO. Likewise, CV analysis has resulted in a higher onset potential for NCNT/rGO than the Fe-NCNTs/rGO which would in turn exhibits a higher ORR activity.

Keywords: Oxygen reduction reaction, Nanocatalyst, Graphene, Nitrogen-doped carbon nanotubes, Fuel cell.

1. Introduction

Fuel cell utilises a catalyst-facilitated chemical reaction mechanism which generates electricity by an electrochemical reaction in which oxygen and a hydrogen-rich fuel combine to form water [1]. Fuel cell is similar to battery in that it generates electricity from an electrochemical reaction and as a by-product, heat energy is released [2]. However, a battery store limited amount of energy within it and once it is depleted, the battery must be discarded, or recharged by using an external supply of electricity to drive the electrochemical reaction in the reverse direction. On the other hand, a fuel cell uses external supply of energy to go indefinitely, as long as it is supplied with a source of hydrogen and a source of oxygen (usually air). In today's fuel cell, platinum is the most commonly used catalyst in electrodes for fuel cells due to its high catalytic activity [3]. However, using platinum as the catalyst has a drawback due to the cost consuming of its metal components. Thus, commercialising it always been a thought in many minds from practical point of view. In recent studies [4], a group of researchers have developed an inexpensive graphene-based fuel cell catalyst that is claimed to perform better than a commercial platinum equivalent in ORR as well as tolerating both carbon monoxide poisoning, a common issue for fuel cell stacks, and methanol crossover. NCNT has been explored as the metal-free catalysts that also showed to exhibit appreciable ORR activities in fuel cells [4].

In this context, graphene is consider as the most suitable candidate to mix with ORR active nitrogen-doped carbon nanotubes (NCNT) to act as the catalyst to enhance the ORR activity because it can be easily synthesised by using the modified Hummer's method [5] and very cost effective. By utilising the graphene structure which composed of a single layer of graphitic carbon [6], it is shown in previous studies[7] [8] that graphene has properties that can be readily chemically functionalised. The structural morphology of the quaternary-N allows a sp^3 hybridisation of donating 2 electrons to the graphene π system. Besides, functionalised graphene demonstrated as an excellent catalyst for electrochemical reactions, such as oxygen reduction due to their unique electronic properties derived from the conjugation between the nitrogen lone-pair electrons and the graphene π system [9]. On the other hand, through the studies of Wong et al [10], the experimental results through XPS analysis shows that the carbon network facilitated by nitrogen atoms can be assigned to pyridinic-N, quaternary-N, pyridinic-N-oxides and pyrrolic-N that are present on the NCNT after the synthesis process. Pyrrolic-like nitrogen donates two p-electrons to π system and is sp^3 -hybridised while the pyridinic-like nitrogen donates one p-electron and is sp^2 -hybridised. Quaternary nitrogen refers to nitrogen atoms combined into a hexagonal ring by the substitution of carbon atoms which also classified as sp^3 -hybridisation [11]. In the results, NCNT with highest ratio of pyridinic-N/ quaternary-N have shown higher ORR activity in both alkaline and acidic media. In this case, the pyridinic- N edge would most likely be the key on the influence of ORR activity.

When extra electrons introduced into the graphite network through doping, the electron donation process from carbon to oxygen can be facilitated which also leads to the enhanced ORR activity. The enhanced ORR activity can be explained by the modification of electronic structure of carbon by nitrogen which increases the edge plane exposure by creating defects on carbon. This can be done due to the incorporation of nitrogen atom in the matrix of carbon can withdraw electrons from carbon because of the higher electro negativity of nitrogen. From recent research [12],

Fe-NCNT which has shown to have higher catalytic activity in ORR compared to NCNT will be used in this study. Catalytic activity determined from CV analysis shows that Fe-NCNT has a higher value of offset potential, above 0.6 V, compared to NCNT with 0.58 V. Current peak for Fe-NCNTs also shift to more positive which is at 0.4 V compared to 0.3 V for NCNT. Therefore, the objectives of this research are to synthesis functionalised nanocatalysts of Fe-NCNT/rGO and NCNT/rGO using physical mixing method and to investigate the effect of compositing rGO on the surface morphology, surface chemical functional groups and oxygen reduction activity of the nanocatalysts. The reason of selecting physical mixing in this study is due to the fact that, the presence of electron cloud on both the NCNT and rGO is believe to be feasible in the sense that functionalised NCNT provides –OH functional group [13] while rGO provides –COOH carboxylic group [14] which are hypothetically [15] achievable through physical mixing. In this case, a fundamental study on the ORR for Fe-NCNT/rGO and NCNT/rGO using physical mixing method is studied before the method can be fine-tuned to improve the catalytic activity of the sample in order to determine whether they offer improved performance relative to that without rGO composite.

2. Experimental Methodology

2.1 Material

The objectives of this project are to synthesise the graphene/NCNT hybrid from functionalised graphene and Fe-NCNT by physical mixing method. Graphene used in this research was obtained from the Department of Engineering, University Malaya, Malaysia. While the Fe-NCNTs used for this research was taken from previous study of NCNT catalyst by Fuel Cell Institute, University Kebangsaan Malaysia, synthesized via chemical vapour deposition and metal ion reduction methods.

2.2 Synthesis of rGO

The method used for functionalising graphene is known as Simplified Hummer's method. Instead of using the common methods of producing graphene oxide (GO) using chemical oxidation via modified Hummer's method which is quite tedious and involved long experiment time, here; the key point is to reduce the experiment time spent by a researcher working on the experiment during the oxidation process [16]. Therefore, Simplified Hummer's method is able to ensure that researcher is able to achieve the oxidation of graphene in a short period of time from 3–5 hours to less than 5 minutes of work [16]. The whole process was carried out without any temperature control, neither increasing nor decreasing the temperature. The mixture was stirred at room temperature for up to 3 days to achieve a high degree of oxidation. To initiate the proposed Simplified Hummer's method, H₂SO₄ (98%) and H₃PO₄ (85%) were prepared in the ratio of 4:1 where H₂SO₄:H₃PO₄ (320:80 mL). Later on, 1.2g of graphene and 18g of KMnO₄ were added to the mixture slowly and let it stirred for 3 days using Soxhlet equipment. After that, 400ml of deionised water and 35 ml of H₂O₂ were added to stop the oxidation process followed by adding in HCl and deionised water at a ratio of 1:10 where HCl : deionised water (15:150 ml). Washing process were carried out using simple decantation of supernatant via a centrifugation technique with a centrifugation force of 8000rpm for 15 mins (MEGAFUGE 40R)

(mega centrifuge; 50ml falcon tubes). The product was washed repeatedly with deionised water until a pH 7 is achieved. Lastly, the paste was collected and dried at 60°C for 1 day. In common practice, the process requires an ice bath during the initial addition of KMnO_4 and heating during the oxidation stage due to the slight exothermic process, which increases the temperature to around 40°C–50°C. Due to the fact that the method used is relatively simplified, thus, after the addition of H_2O_2 solution to terminate the oxidation process, the temperature will cool down naturally in a short time [16].

2.3 Preparation of Fe-NCNTs/rGO Nanocatalyst

Fe-NCNTs of different composition of ferrum (Fe) were prepared from previous research [12] done by impregnation method using iron (III) nitrate nanohydrate, $\text{FeN}_3\text{O}_9 \cdot 9\text{H}_2\text{O}$ as the precursor. From previous research, 5% Fe-NCNT, 3% Fe-NCNT and 1% NCNT were synthesised. Therefore, those Fe-NCNTs catalyst will be utilised as the parameter for catalyst composition in this research in addition of pure NCNT catalyst. Initially, 10 mg of 5% Fe-NCNT was mixed with rGO with the ratio of 1:1 at normal condition. Then, 100 mg of pyrrole was dissolved into the Fe-NCNT/rGO suspension above at the ratio of 1:10 (Fe-NCNT : pyrrole) while the mixture was diluted using 10mL of water. The resulted mixture was homogenised with the aid of ultrasonication for 2 hours with 40% power output. A second sample of 5% Fe-NCNT mixed with rGO was prepared at the ratio of 1:0 using the same procedures above. The experiment was repeated with the same volume ratio of 3% Fe-NCNT, 1% Fe-NCNT and pure NCNT. The final obtained catalyst was labeled as 5% Fe-NCNT/rGO ratio 1:1, 5% Fe-NCNT/rGO ratio 1:0, 3% Fe-NCNT/rGO ratio 1:1, 3% Fe-NCNT/rGO ratio 1:0, 1% Fe-NCNT ratio 1:1, 1% Fe-NCNT ratio 1:0, NCNT/rGO ratio 1:1 and NCNT/rGO ratio 1:0 based on the volume ratio.

2.4 Physicochemical Characterisation

The surface morphologies of the 5% Fe-NCNT/rGO ratio 1:1 and NCNT/rGO ratio 1:1 samples were characterised by field emission scanning electron microscopy (FESEM) on Hitachi SU8030 microscope operated at 2kV. For FESEM analysis, the samples were loaded evenly on the sample holder before entering the scope chamber. The samples were checked to ensure all samples fit under the gauge and no part of it is touching or taller than the gauge. The nitrogen contents of the surfaces of all samples were determined by X-ray photo electron spectroscopy (XPS) on PHI Quantera II instrument operated at 14kV. The XPS analysis was conducted using a dual-anode X-ray source with Al K-alpha irradiation with energy of 1486.8 eV. A survey scan was performed from 1200 to 16 eV on 5% Fe-NCNT/rGO ratio 1:1 and NCNT/rGO ratio 1:1 samples, followed by a narrow scan specifically on the C 1 s, N 1 s, O 1 s and Fe 2 p regions for 5% Fe-NCNT/rGO ratio 1:1 while C 1 s, N 1 s and O 1 s regions for NCNT/rGO ratio 1:1. The obtained data were analysed using a compatible software with the XPS data.

2.5 Electrochemical characterisation

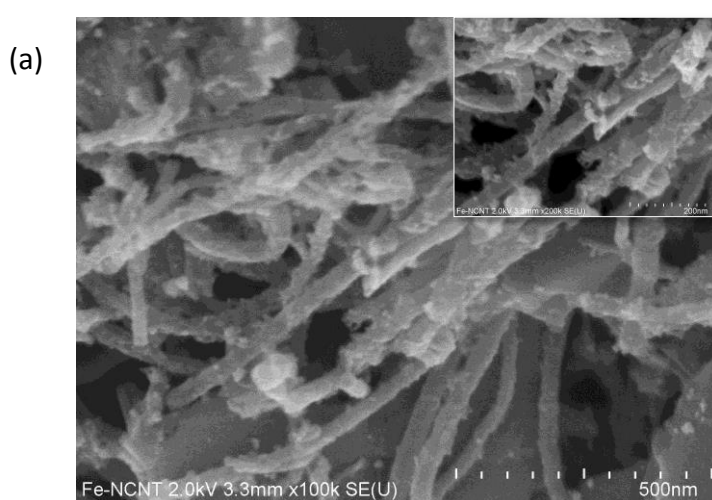
The electro-catalytic activity of the Fe-NCNTs/rGO samples was measured on an Autolab PGSTAT128N potentiostat using the cyclic voltammetry technique in a standard three-electrode cell with 5 mm diameter glassy carbon (GC) served as the

working electrode, platinum wire served as the auxiliary electrode, and Ag/AgCl was used as the reference electrode. The analysis was done in 2 differing condition by utilising electrolyte of either a N₂- or O₂-saturated 0.5 M H₂SO₄ solution and 0.1 M KOH. The catalyst ink that contained of 0.2 mL Fe-NCNTs/rGO mixed with 0.5mL of 10wt% Nafion solution was prepared by ultrasonication for 3 mins at 30% power output using a sonication homogeniser. 15 μ L of the catalyst ink was deposited evenly on the GC electrode surface and was subsequently dried at room temperature careful to prevent contamination on the catalyst ink. The electrode was visually inspected to ensure a uniform film formation and that no catalyst ink was contacting the ring portion of the electrode. Prior to the electrochemical measurements, the as-prepared sample electrode was rinsed with deionised water before being placed into the electrochemical cell. The potential window was set at 1.0 V to -0.4 V in the negative scan mode. Each scan was repeated 3 times to obtain a stable cyclic voltammogram.

3. Results and Discussions

3.1 Physical Characterisation

Field emission scanning electron microscopy (FESEM) was used to perform the physical characterisation of the Fe-NCNTs/rGO samples synthesised in order to study the structural morphology, nitrogen bonding nature and doping contents on the graphene surface. The surface morphologies of the Fe-NCNTs/rGO as shown in Fig.1 clearly observed that the Iron composited carbon nanotube doped on the surface of graphene in an uneven distribution manner. During physical adsorption of Fe-NCNT on the graphene surface, the Iron nanoparticles were not able to bind onto the thin-layer graphene sheet. This resulted in a crooked surface of the nanotube on graphene layers. As observed from Fig. 1(a), the rGO tends to form very dense agglomerates with layered structure around the carbon nanotubes due to the van der Waals interaction between the graphene layers [17]. Agglomeration in such manner has formed a barrier in the active sites, hindering the ORR activity of the nanocomposites.



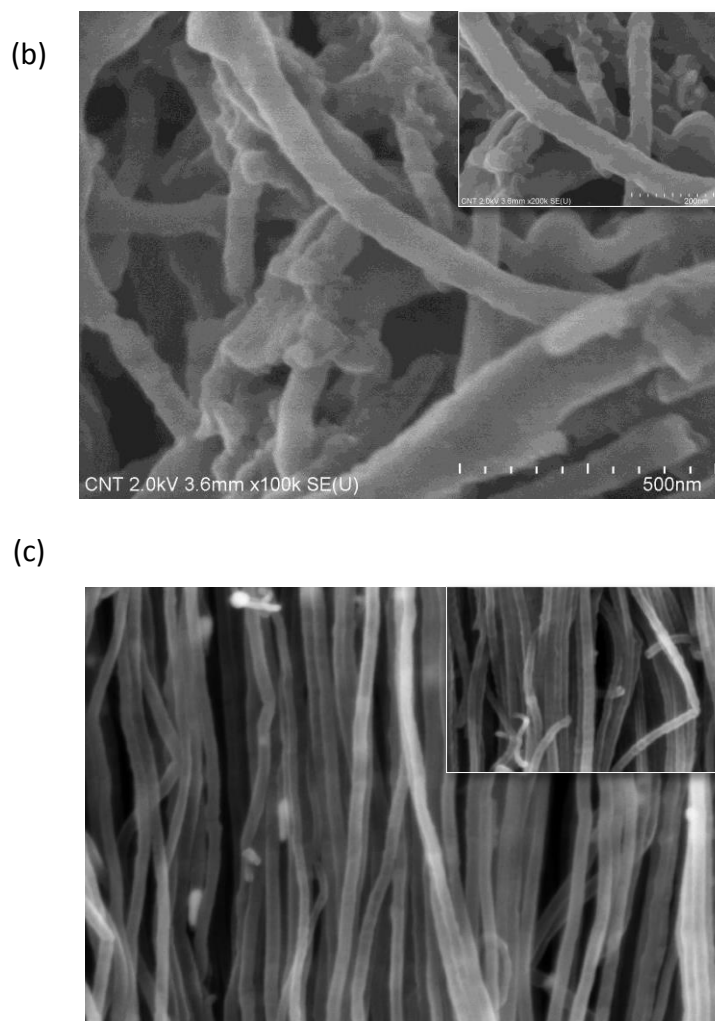


Figure 6. FESEM images of (a) 5% Fe-NCNT/rGO (b) NCNT/rGO and (c) NCNT at magnification of 100,000 times. Insets show the Fe-NCNT/rGO morphology respectively at 200,000 magnification factor.

Similarly, the NCNT/rGO displayed in Fig. 1(b) demonstrated a surface morphology of agglomeration in graphene sheets that forms blockage on the active sites which inhibit the ORR mechanism on the nanocomposite. Agglomeration of graphene sheets presence in the Fe-NCNT/rGO and NCNT/rGO would in turn leads to the ineffective electron transfer within the catalyst surface. Nonetheless, the absence of iron nanoparticles deposited on Fe-NCNT/rGO sample has demonstrated a smoother graphitic structure of the carbon nanotubes on NCNT/rGO sample. As compared to both the Fe-NCNT/rGO and NCNT/rGO surface morphologies, NCNT image shown in Fig. 1(c) has displayed a more corrugated structure which has densely packed carbon nanotubes formed due to the close proximity of the nanoparticles induced a self-ordered arrangement among the formed nanotubes as reported in previous study [18]. The variations in morphologies shown in Fig. 1 has suggested that NCNT composite displayed a higher concentration of surface defects, which would increase the edge-plane exposure on its surface, that in turn enhancing the ORR activity.

3.2 XPS Analysis

To investigate the surface composition and the chemical states of the nitrogen atoms of the synthesised Fe-NCNTs/rGO samples, XPS studies was done by determining the nitrogen content in the samples. From the survey scan on the XPS spectrum as presented in Table 1, the nitrogen content can be seen to have relatively high concentration in both 5% Fe-NCNT/rGO and NCNT/rGO (11.67 at % and 14.31 at% respectively). Although the two samples may seem closely similar in terms of carbon concentration and oxygen concentration, there is the presence of iron particles in the Fe-NCNT/rGO sample which can be observed from the Fig. 2 presented. XPS analysis shows trace amount of iron (0.76 at%) in the Fe-NCNT/rGO sample. Nonetheless, with the presence of iron in the nanocatalyst, the nanotubes surface structural of the samples are observed to be completely different.

Table 6. Atomic concentration of the samples and its N distribution from XPS spectra of the synthesised Fe-NCNT/rGO and NCNT/rGO samples

Samples	C content (at %)	O content (at %)	N content (at %)	Weight distribution of N (%)	
				Pyrrolic N (%)	Pyridinic N (%)
5% Fe-NCNT/rGO	71.55	12.34	11.67	92.5	7.5
NCNT/rGO	63.69	20.14	14.31	30.67	69.33

In order to further study the chemical bonding on the nanocatalyst synthesised, the N 1 s region of both the Fe-NCNT/rGO and NCNT/rGO has to be deconvoluted to study the structural defects in the nitrogen configuration of the nanotubes formed. As demonstrated in Fig. 3, both nanocatalysts possess the nitrogen configuration of pyrrolic-N and pyridinic-N. As stated from previous study [18], the high concentration of surface defects presence in the pyridinic-N configuration at the nanotubes surface favoured the ORR catalytic activity. Therefore, in this research, the distinguishable surface defects of the pyridinic-N will be considered. The nitrogen configuration in N 1 s region of both the samples are shown in Fig.4, the pyridinic-N (binding energy 398 ± 0.2 eV) and pyrrolic-N (binding energy 400 ± 0.2 eV) are exhibited on Fe-NCNT/rGO while pyridinic-N (binding energy 399 ± 0.2 eV) and pyrrolic-N (binding energy 400 ± 0.2 eV) are exhibited on NCNT/rGO.

Comparing both Fe-NCNT/rGO and NCNT/rGO, having relatively similar nitrogen content, the NCNT/rGO showed a higher concentration of tube defects, which consisted of a much higher percentage of pyridinic-N groups. “Pyridinic-N” is implying that the nitrogen atoms bonded to the edge of the graphene planes with two adjacent carbon atoms; these atoms donate one p-electron to the aromatic π system [19] and have been claimed to be responsible for the high degree of defects, that produces a rugged surface. To this, the detail analysis of the N 1 s spectra has shown that the NCNT/rGO makes a more desirable nanocatalyst for ORR mechanism. The ORR activity with respect to the nitrogen groups could be explained by the theory

regarding the edge plane nitrogen groups (pyrrolic or pyridinic) being the active site for ORR due to the lone pair electrons [20]. From this trend, as reported from previous study[18], at higher nitrogen content, the formation of pyridinic nitrogen group are more favourable due to low heat of formation [20] which are demonstrated in this research.

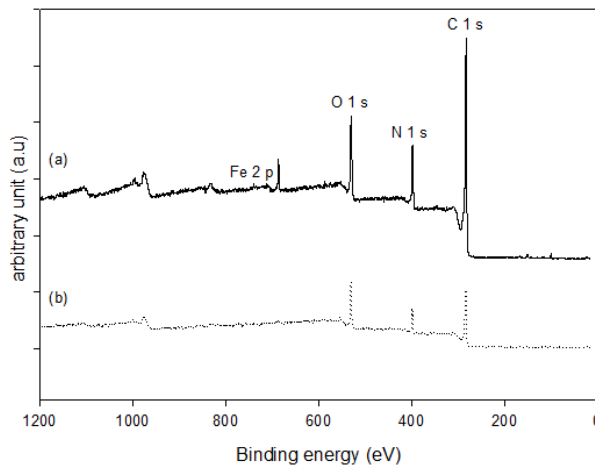


Figure 7. High resolution XPS analysis in survey scans for (a) 5% Fe-NCNT/rGO and (b) NCNT/rGO.

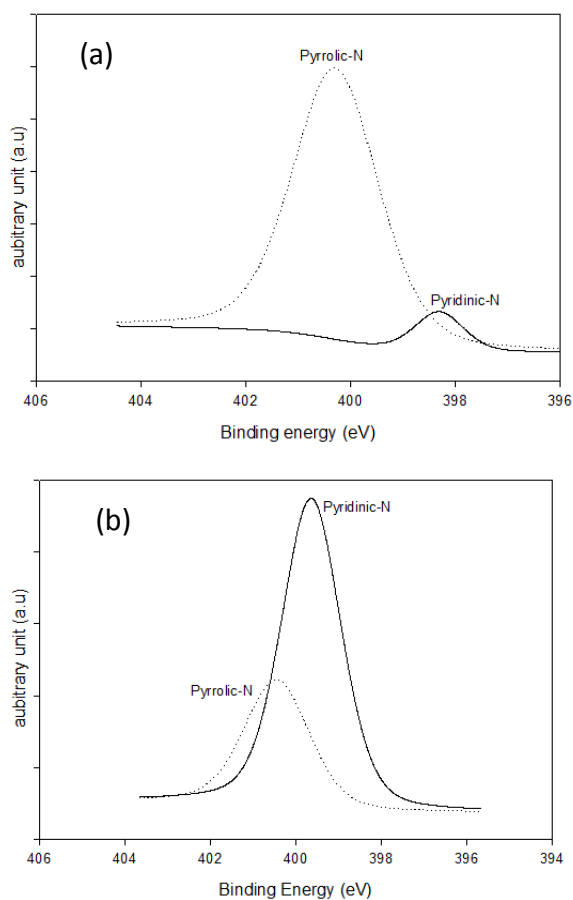


Figure 8. High resolution XPS analysis in N 1 s region for (a) 5% Fe-NCNT/rGO and (b) NCNT/rGO nanocatalyst synthesised

3.3 Electrochemical Analysis

Cyclic voltammetry was used to investigate the ORR catalytic activity of the Fe-NCNTs/rGO and NCNT/rGO synthesised. A qualitative analysis on the oxygen reduction ability of the nanocatalysts which can be determined from the onset potential and reduction peak potential in the voltammograms was done. The CVs test was conducted in two stages in which the samples are exposed in both alkaline media and acidic media to study the catalytic performance. A background scan was performed under the nitrogen-saturated environment as a control set before the voltammogram was recorded in oxygen-saturated environment. At initial, the CV analysis started off with both Fe-NCNTs/rGO and NCNT/rGO nanocatalyst in alkaline media of 0.1 M KOH electrolyte, which the voltammograms recorded is presented in Fig. 4. To elucidate the experimental data, the samples were labelled as such: 5%Fe-NCNT(1:1) for 5% Fe-NCNT/rGO at ratio of 1 to 1 (Fe-NCNT : rGO) ; 5%Fe-NCNT(1:0) for 5% Fe-NCNT/rGO at ratio of 1 to 0 (Fe-NCNT : rGO). Previous study [18] has reported the catalytic activity of NCNTs in acidic media showing a potential window of - 0.4 V to + 1.0 V vs. Ag/AgCl, which will be incorporated into this research. The result has surprisingly exhibited that the 5% Fe-NCNT/rGO shown in Fig. 4(a)(b) has a closely identical catalytic performance as displayed by NCNT/rGO shown in Fig. 4(g)(h) with a peak -0.4 V (vs Ag/AgCl). This in turn, states that the incorporation of metal alloy on the NCNT has not made a significant impact on the catalytic performance on ORR mechanism. At the second phase of the CV analysis, acid media of 0.5 M H₂SO₄ electrolyte was used to investigate the significant difference compared to alkaline media while the samples are conducted in both N₂- and O₂-saturated environment as well. The voltammograms recorded are displayed in Fig. 5. As expected, the Fe-NCNTs/rGO as well as NCNT/rGO nanocatalyst has not shown any significant catalytic performance under acidic media. This occurrence can be related to the sluggish ORR kinetics of oxygen reduction process in acidic aqueous solution particularly on NCNT [21].

The low current density of metal, Fe has reflected on the low onset potential in acid media. On top of that, a variety of non-noble metals are known to be suitable candidate as active catalysts for ORR in alkaline media [22]. The relatively high positive onset potential in alkaline media and the high current density in that of the N₂-saturated condition strongly agree that the NCNT was a very active catalyst for the ORR in alkaline media. Even so, with the agglomeration of graphene sheets on the NCNT as shown in Fig. 1, the effectiveness of electron transfer within the catalyst surface has deteriorated greatly due to the blockage of active sites on the nanocomposite.

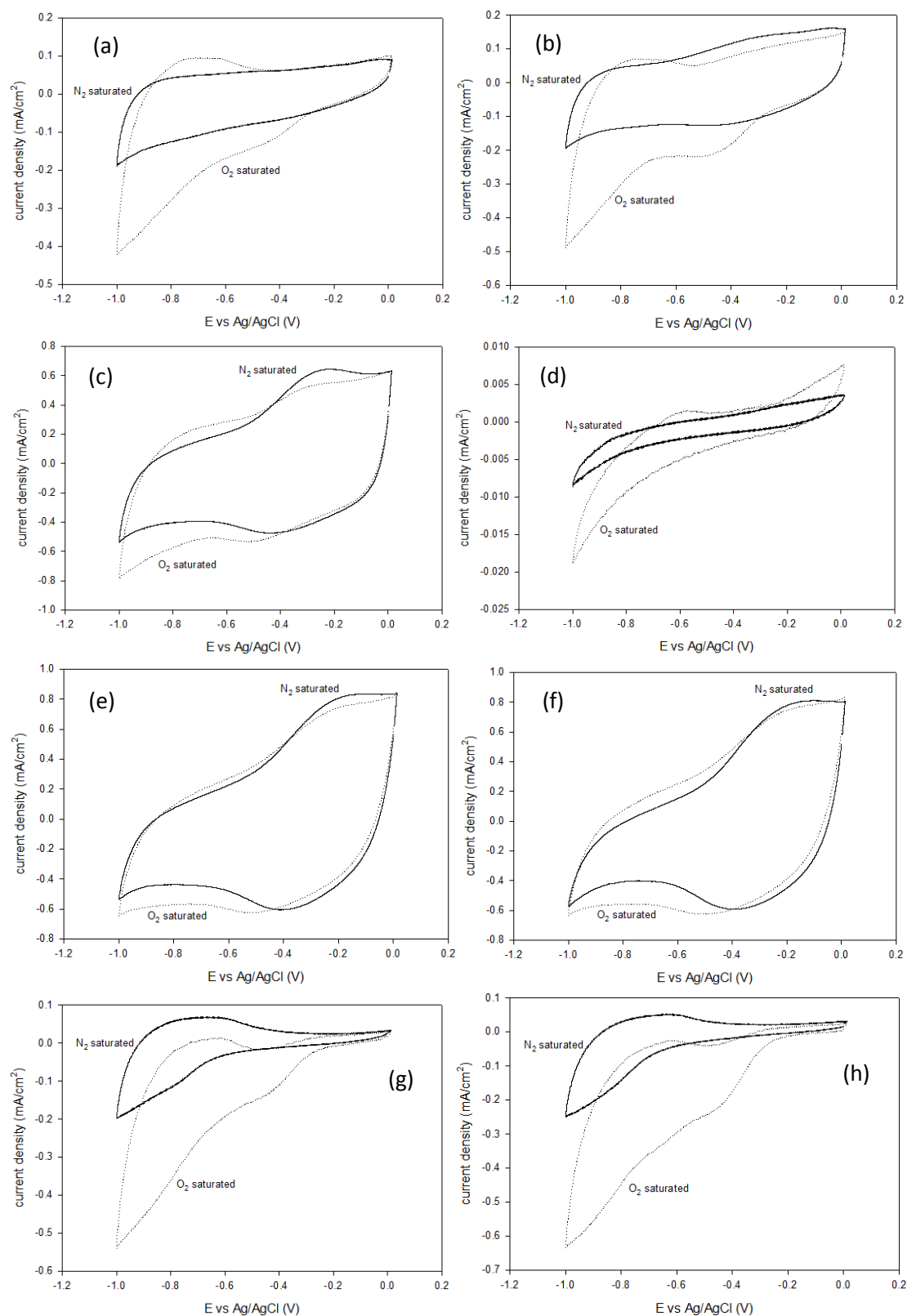


Figure 9. Cyclic voltammogram of (a) 5%Fe-NCNT(1:1) (b) 5%Fe-NCNT(1:0) (c) 3%Fe-NCNT(1:1) (d) 3%Fe-NCNT(1:0) (e) 1%Fe-NCNT(1:1) (f) 1%Fe-NCNT(1:0) (g) NCNT(1:1) (h) NCNT(1:0) GC electrode in N_2 -saturated and O_2 -saturated 0.1 M KOH electrolyte. Potential scan rate at 5 mV/s.

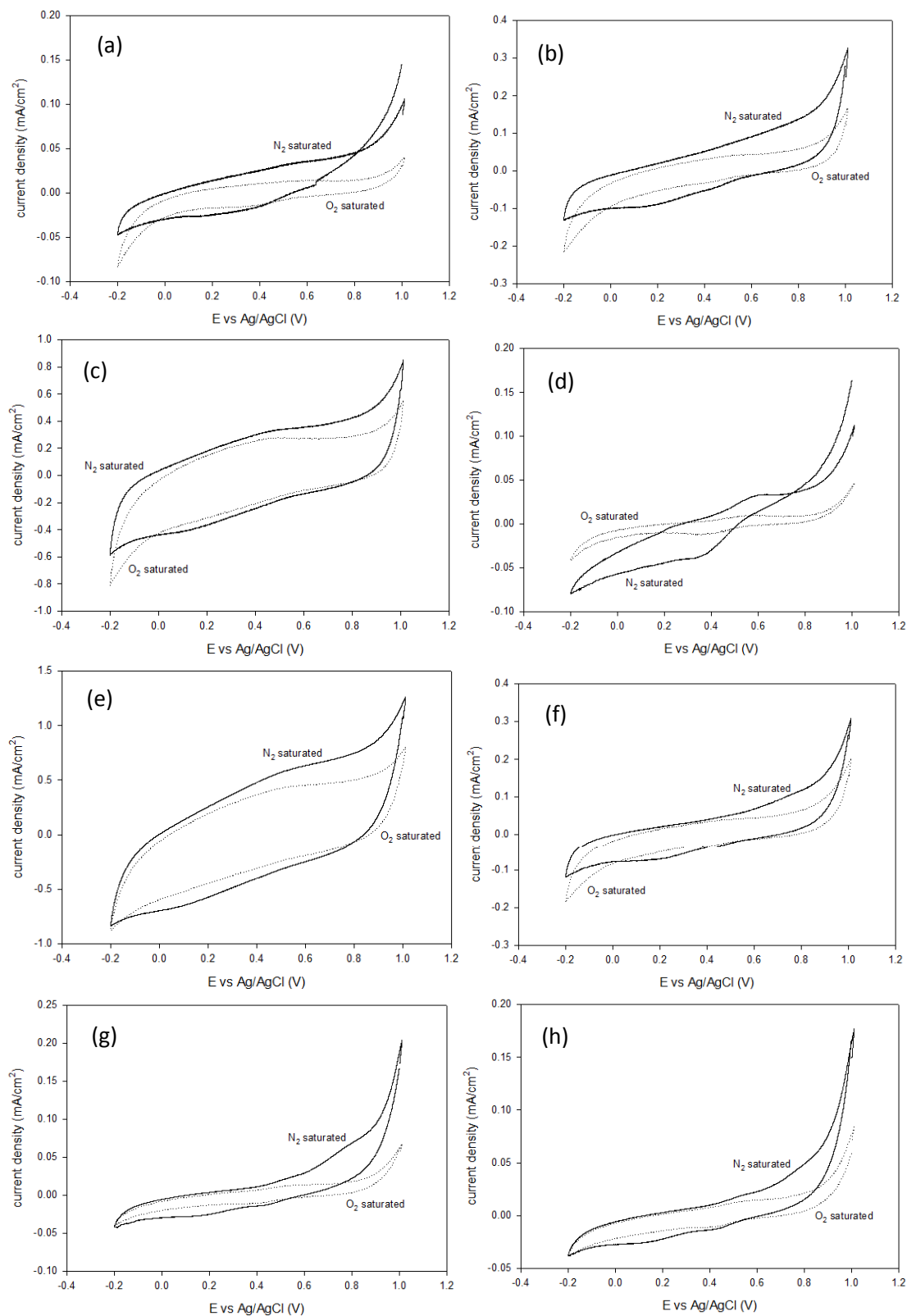


Figure 10. Cyclic voltammogram of (a) 5%Fe-NCNT(1:1) (b) 5%Fe-NCNT(1:0) (c) 3%Fe-NCNT(1:1) (d) 3%Fe-NCNT(1:0) (e) 1%Fe-NCNT(1:1) (f) 1%Fe-NCNT(1:0) (g) NCNT(1:1) (h) NCNT(1:0) GC electrode in N₂-saturated and O₂-saturated 0.5 M H₂SO₄ electrolyte. Potential scan rate at 5 mV/s.

To analyse the CVs result, this study will be focusing on the electrochemical activities in the alkaline media which shows appreciable performance. Referring to the CVs result shown in Fig. 4(a) and (b), the 5% Fe-NCNT/rGO (1:0) demonstrated a significant peak at -0.3 V(vs Ag/AgCl), while 5 % Fe-NCNT/rGO (1:1) exhibit an imperceptible peak at the similar peak as a possible result of agglomeration of graphene on the NCNT as presented in Fig. 1. This agglomeration behavior has severely disrupted the surface structural characteristic of the NCNT which reflected on the low degree of surface defects that is highly crucial to ORR activity by exposing more edge plane nitrogen groups such as pyridinic and pyrrolic nitrogen which could participate in the ORR through the lone pair electrons [21]. Similar behaviors are observed in the NCNT/rGO (1:1) and NCNT/rGO (1:0) presented in Fig. 4(g) and (h) that does not have Fe deposition. Due to the fact that stable dispersion was not able to be established during mixing process, it resulted in graphene sheet agglomerated on the NCNT and thus, inhibited the ORR activity on the nanocomposite. Furthermore, physical mixing was incorporated in this study which possibly leads to the existence of van der Waals forces in the graphene sheets during the dispersion process. For further studies, chemical mixing such as hydrothermal treatment [23] could be an alternative choice in order to break the bonds between the graphene sheets, thus establish a stable reaction between NCNT and graphene.

According to Fig. 4(a) and (g), it can be seen that the NCNT/rGO (1:1) has a higher onset potential of -0.2 V(vs Ag/AgCl) in comparison to that of the 5 % Fe-NCNT/rGO (1:1) at -0.3 V(vs Ag/AgCl). This unforeseen behavior may be due to the lack of efficiency of Fe crystals structure in acting as the active sites for ORR and to further deteriorate it, the number of active sites on NCNT was blocked due to the Fe deposition. In addition, the expected redox peaks were not displayed in the positive potential range of the voltammogram, suggesting that the iron particles did not play a role in ORR in Fe-NCNT/rGO sample.

From this study, it was shown that the 'rGO' component in the Fe-NCNTs/rGO and NCNT/rGO nanocatalyst synthesised via physical mixing does not seem to enhance the catalytic activity towards oxygen reduction comparable to NCNT catalyst. The shortcoming of rGO on the improvement on ORR activity most probably caused by the fact, that physical mixing is not a suitable method for the compositing process.

4. Conclusions

Fe-NCNTs/rGO and NCNT/rGO nanocatalysts were synthesised using physical mixing method by ultrasonication with the presence of pyrrole. Through the physical characterisation, it appears that the graphene sheet forms agglomerates on the NCNT and thus, inhibit the ORR activity on the nanocomposite, through the blockage of the active sites. In conjunction, agglomeration of graphene also results in the ineffective electron transfer within the catalyst surface. In electrochemical wise, the rGO synthesised has not shown significant improvement in ORR activity. The most probable factor leading to this deficiency is due to the compositing process which utilises physical mixing instead of chemical mixing. Likewise, from this study, crystal

structure of Fe might not be effective in acting as active sites for ORR. Surprisingly, NCNT/rGO has shown superior electrochemical properties in comparison to Fe-NCNTs/rGO synthesised. Therefore, as a conclusion, NCNT/rGO is considered a more suitable candidate as per this study for ORR in fuel cell application with proper tailoring of the components' ratio and stable dispersion.

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Review and Design of Electromagnetic Actuated Robot Mechanism for In-pipe Application

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Abstract

Pipeline usage are common in oil and gas industries. Those pipelines are used to transport different types of liquid. Any damages to those pipes can result into wastage of money, therefore, regular inspections are needed in order to maintain those pipelines from being damaged. This paper is about the review and design of the electromagnetic actuated robot mechanism for in-pipe inspection applications. The solenoid actuator is chosen as the best actuator to drive the robot mechanism because it is efficient and cost effective based on a review on all the available actuators which is presented in this paper. In this research, a new design of an in-pipe robot system was investigated and presented. The robot mechanism is modelled using solid works, thus, the controller is designed, analysed and implemented to control the frequency of actuation of the solenoid actuator. The mechanism proposed and designed is adjustable to the changes in the diameter of the pipes. Full mechatronic approach was adopted in the design of the robot mechanism and the implementation of the controller.

Keywords: in-pipe application; in-pipe robot; solenoid actuator; robotics.

1. Introduction

The Pipelines plays a very essential part in everyone's life because it is the main source of transporting important resources such as gas, oil, water and many more. These pipes are usually located in the ground therefore no any distraction to humans but as the pipelines use for a long period it may face issues like corrosion, dent, internal damages, breakages, deformations and many more serious repairs. [1] So to overcome this problem regular maintenance of those pipes are constantly needed. The questions is How can an engineer who is responsible for the pipelines maintenance should know that there is a serious problem is going inside the pipe?, The only way to know is by performing an internal inspection.

Robots are mechanically controlled device which are introduced to make human life easy. Robots are also capable of performing dangerous and tedious task which cannot be done by human beings. Nowadays, robotic fields are emerged as a fast developing field because many industries are using robotics as their base such as automotive industry, oil and gas industries, power generation and many more. The robots are usually design based on its purpose or desired task. Most robot are very complicated because they have a lot of programming , actuators and processes being taken place , in this paper a simple robot actuated by electromagnetic actuator is reviewed and designed for in-pipe application.

There are lot of in-pipe application robots are available. Hyunjun park et al. [2] proposed a robot for in-pipe inspection using tiny ultrasound linear actuator (TULA) which is actually a complex piezoelectric actuator. A robot mechanism using pneumatic actuator is also proposed by Carozza et al. [3] which consist of three mini pneumatic actuators in it to aid its mobility. In addition proposed robots are the three gas-liquid phase change actuator inchworm robot proposed by Kato et al. [4]. Other than that, Lu et al. [5] presented a bristle based inchworm robot mechanism. This robot mechanism consist of main body, pairs of legs, head and bellow seal. The actuator is installed into the main body of the robot mechanism. The translator of the actuator acts as the mobile unit of the robot mechanism which enables it to extend or contract. The front leg is known as the fin that is connected to the main body and the back leg is attached to the movable unit that is also have a bellow seal inside it. This robot mechanism proposed can operate in both liquid and plane surfaces. There are a lot more proposed robot mechanism for in-pipe applications using different types of actuators from various scientist throughout the world.

This research paper is about the review and research of the electromagnetic actuated robot mechanism for in-pipe inspection applications. The objective of this paper is to propose a cost effective and efficient actuator for the in-pipe inspection application robot mechanism, to propose and design a new type of in-pipe inspection robot mechanism and to design , build and analyze a circuit that acts as a controller that control the frequency of actuation of the proposed actuator.

2. RESEARCH METHODOLOGY

This section narrates the methods and approaches of the review, research and design of the electromagnetic actuated micro robot mechanism for in-pipe application from review and research stage to the development stage. The limitation of this project is the designed robot mechanism could not be fabricated due to lack of budget, availability of technology and time constrain. The development stages in this project are clearly explain in the upcoming section.

1. The initial stage of this project is to select the electromagnetic actuator for the robot mechanism. In this stage a lot of journals are reviewed to get the idea of the available actuators and also the type of in-pipe inspection robot mechanism that are available based on its actuator, therefore , the actuator choose should be different from the ones are already available. The actuator should be cost effective, easy to implement, light weight and produces linear motion and force. So various research and review is performed on the available actuators. The review and research is only done on the actuators that works on electromagnetic concept. From there the actuator which satisfy the following requirements; cost effective, high quality of motion, Safety, High quality of tactile interaction, organic form factor, quite operation, robustness to overloading and easy to implement is selected.
2. After choosing the actuator, the controller for the actuator is designed and build. The controller is initially designed using Multisim. The controller is not actually a remote control but it is a circuit that is design and build to control the actuation speed of the actuator so it is called controller. After design and testing it on the Multisim software the real prototype of the controller is built on the bread board and tested with the actuator.
3. The final stage is the design stage. In this stage a lot of existing design of micro robots of both in-pipes and medical micro robots are reviewed to avoid designing a robot mechanism that is already proposed. The concept robot mechanism is designed using SolidWorks software.

The flow chart of the process that being performed throughout this research project is presented in Fig. 1.

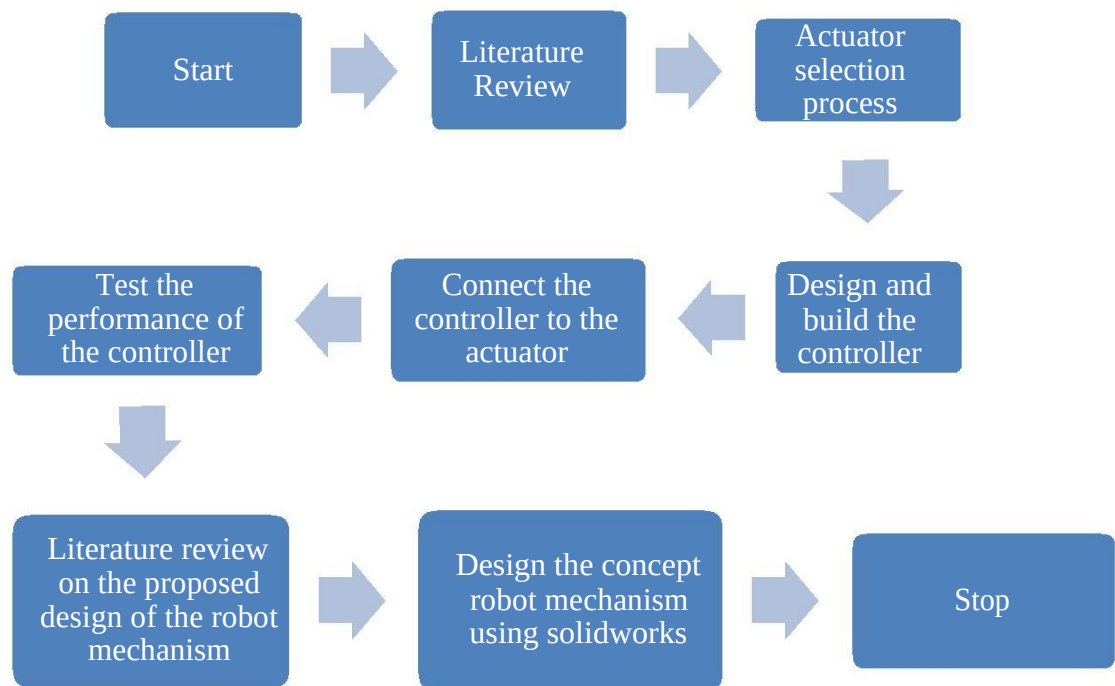


Figure 1. Flowchart of the research methodology

2.1 Actuator Selection

Actuator is the most essential part in a robot that aids its mobility. The main challenge during this project is the actuator selection because there are various types of actuators available in the market. Such as pneumatic actuators, dielectric actuators, three gas phase change actuators, piezoelectric actuators, shape memory alloy actuators, electrotype active polymers, electric motors, solenoid actuator and many more. [6] The actuator use should satisfy certain criteria which is shown in Table 1. The review on all the available actuators are performed and the results are tabulated as the advantages and disadvantages of the actuators. The actuator chosen based from the advantages and disadvantages which states the actuator that should be cost effective and efficient should also fulfill these requirements as shown in Table 1.

Table 1. The Functional requirements and the actuator characteristics

Functional requirement	Actuator Characteristic
High quality of motion	- low friction
	- low damping
	- moderate acceleration
Safety	- low inertia
	- high compliance
	- easy to control
High quality of tactile interaction	- variable in stiffness
	- force controlled
	- moderate power
Organic form factor	- moderate force
	- linear motion
	- small
Quite operation	- no mechanical transmission
	- less moving parts
	- low transmission ratio
	- few mechanical parts
Robustness to overloading	- high compliance
	-less force input
	- low hysteresis
Easy to implement and control	- less time consuming
	-materials are always available and easy to obtain
	- minimize using complicated parts

2.2 Procedure of the Implementation of the Controller for the Selected Actuator

The function of the controller is to control the actuation of the solenoid actuator. The reason for using this controller rather than just connecting the actuator to a constant power source like a 9 volt battery is because to control the frequency of actuation. Furthermore, the controller provides a continual motion at variable speed it can be slow and really fast. The controller is designed using Multisim software. The main component that gives the continual actuation of the actuator is the Timer 555. The Timer 555 consist of 8 legs which are the labeled 1-8, the 1, 6 is the discharge 1 is the ground, 2 is trigger, 3 is the Output, 4 is the reset, 5 is the control voltage charge, 7 is threshold and the 8 is the Vcc. Each pin as its own functions. The pin functions are pin 1 is fixed as the input, pin 2 is fixed as the ground and pin 3 is fixed as the output. The pins are been read from the left to the right. Switch is added to on and off the solenoid actuator as needed. Initially to test if the intelligent controller works, the components are placed in the bread board and after the circuit works. Components needed to prepare the circuit as the controller are:

1. Solder less Bread Board ×1
2. PCB ×1
3. B100K Potentiometer ×1
4. Capacitor R85GP×1
5. TIMER 555×1
6. 3.9K Resistor ×1
7. NPN Power Transistor ×1
8. 2K Resistor ×3
9. Switch ×1
10. LED Flash Light ×1
11. Connecting Wires
12. DC Power Supply×1
13. Crocodile Clips as needed

2.3 Design Parameters

The robot mechanism is designed after performing various reviews on the existing designs to avoid similarities. The robot mechanism designed consist of head, body, and spring/bellow seal in between the head and the body and wheel mechanism. The parts are designed using SolidWorks software. Each components are designed first then the assembly is performed. The dimension of each part of the robot mechanism is presented in the upcoming part for better idea on how to design the robot mechanism as shown in Table 2, 3 and 4.

Table 2. Dimension of the body of the robot mechanism

Design Parameters	Dimension, mm
Total Length	50
Size of the whole body(radius)	35
Size of the square in the middle	30×30
Size of the back circle(radius)	10
Length of the rectangle extrude	42

Table 3. Dimension of the head of the robot mechanism

Design Parameters	Dimension, mm
Total Length	30
Size of the whole body(radius)	35
Size of the square in the front	30×30
Size of the back circle(radius)	25
Size of the small circular extrude to place the wheel mechanism	10×10

Table 4. Dimension of the wheel system of the robot mechanism

Design Parameters	Dimension, mm
Total Length	20
Size of the wheel(radius)	5
Size of the attachment	15×2
Size of the wheel pin	2
Length of the pin	12
Thickness of the wheel	10
Length of the spring	5

2.4 Motion Principle of the Robot Mechanism

The robot mechanism is derived from a concept known as Impact Drive Mechanism (IDM). [7] This concept is about moving an object by impulsive force and the friction theory. How it works? , The robot mechanism consist of four main components which are the body, head, solenoid actuator and the bellows seal/spring in between the head and the body. The initial push may be small and do not result in motion but as the rate of actuation force increases it will result in a motion. This mechanism has limited degreed of freedom because it is designed to travel in a unidirectional motion (Linear Motion Mechanism). The bellows seal can be deploy between the head and the body when the robot is used in liquid environment and spring can be deploy when it working in a dry environment. The wheels are placed such in a circular motion because pipes are not usually straight there are curvy pipes so the wheels at the sides can perform rotational motion. Springs are attached to the legs so that it can be adjusted according to the diameter of the pipe. Self- locking mechanism will be incorporated to the wheel system to prevent the mechanism from

3 Results and Discussion

3.1 Result from the Review of the available Actuators

Most of the available actuators are reviewed during the actuator selection process. The best actuator is selected not only based on the advantages and disadvantages but also chosen based on the functional requirements that the actuator selected should satisfy. The voice coil and solenoid actuators are selected out of the other actuators. Between the voice coil actuators and the solenoid actuators the only difference is the cost of those actuators, the voice coil actuators are slightly more expensive than the solenoid actuator as the aim to implement the most cost effective actuator for the robot mechanism, therefore, the solenoid actuator is chosen as the suitable actuator for the robot mechanism over the voice coil actuator. The specification of the solenoid actuator used is shown in Table 5.

Table 5. Specification of the solenoid actuator used

Specifications	Details
Type	Push and pull type
Force	12N
Stroke	5mm
Dimension	4cm by 2.5cm
Weight	0.3 Kg
Voltage input (Max)	12V
Voltage(Startup)	9V

3.2 Design Overview

In this section the complete design of the robot mechanism is presented. The robot mechanism is purely design considering the dimension and the weight of the solenoid actuator. Explanation of each part of the robot mechanism are presented in this section. In addition, the overall assembly and exploded view of the robot mechanism are presented in this section. The robot mechanism consist of a head, bellow seal in between the head and the body, body to accommodate the solenoid actuator, 4 pairs of wheels, 4 pairs of wheels attachment, 8 wheel pins, 4 pair of springs. The robot mechanism is attached with 4 pairs of wheels because it gives a better motion ability for the robot mechanism to move inside the pipes because not all the pipes are straight they are some corners in the pipe. So having wheels in such arrangement gives the ability for the robot to turn in such corners. The wheels part is attached with spring to act as suspension for the wheel system if there is sudden change in the diameter of the pipes, so the wheels system can compress and adjust its position according to the diameter.

The robot mechanism is a conceptual design which is designed for pipes about diameter of 10cm to 15 cm but there are future plans to design variety sizes of robots for other types of pipes with different diameters. This design is just a conceptual design that

is designed to illustrate the idea of the robot mechanism. The robot mechanism is designed more aerodynamic way because it will have a lesser drag coefficient as the robot is proposed to perform inspection in both dry and liquid environment. Furthermore, Fig. 2 shows the overall assembly of the robot mechanism.

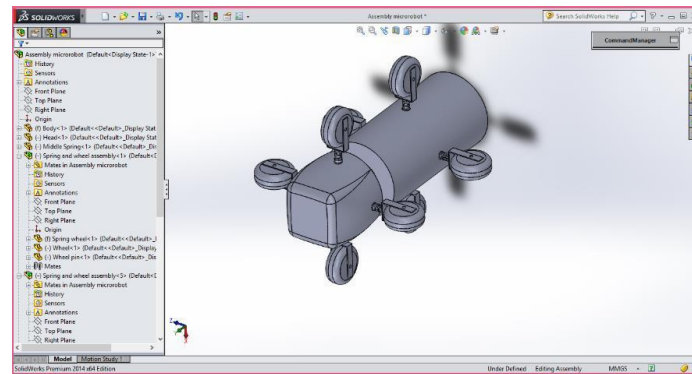


Figure 2. Complete design and assemble of the robot mechanism

3.3 Overview of each parts of the Robot Mechanism

3.3.1 Head

Three types of head are proposed and design initially, first is the square type, circular type and lastly is the hexagonal shape. The Fig. 3 shows the square shaped head, followed by Fig. 4 shows the circular type of head and lastly Fig. 5 shows the hexagonal shaped head. The hexagonal head shape is finalize because according to the drag coefficient principle the drag coefficient is inversely proportional to the area exposed , therefore, the smaller the area exposed , the higher the drag coefficient. The other concept is the drag force is directly proportional to the area exposed, therefore, the smaller the exposed area, the smaller the drag force experienced by the head of the robot mechanism. So when the robot mechanism experience smaller drag force it can move further and faster, for the same actuation force and frequency. Thus, the hexagonal shaped head have more streamlined shape that can easily cuts through the air or any fluid which also reduces the skin friction that is developed between the head of the robot mechanism and the fluid. The head is designed by using the drag equation as the reference. [8] .The drag equation is shown in Eq. 1.

$$c_d = \frac{2F_d}{\rho v^2 A} \quad (1)$$

Where,

F_d Is the drag force

c_d Is the drag coefficient

ρ Is the mass density

A Is the area exposed or reference area

v Is the velocity

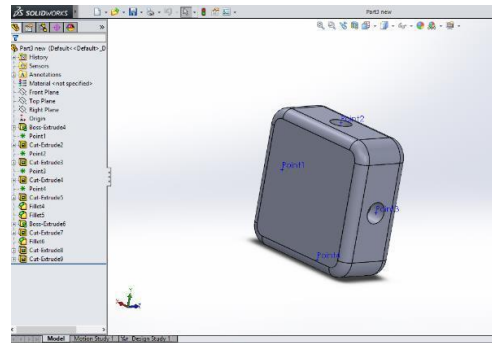


Figure 3. The squared type head design

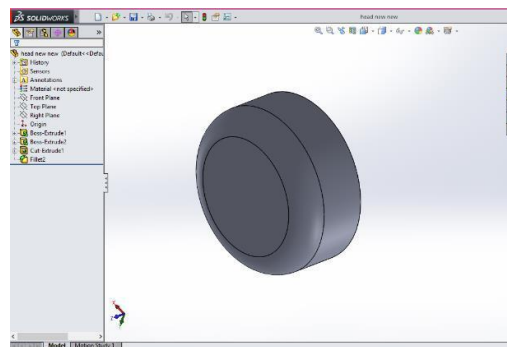


Figure 4. The circular type head design

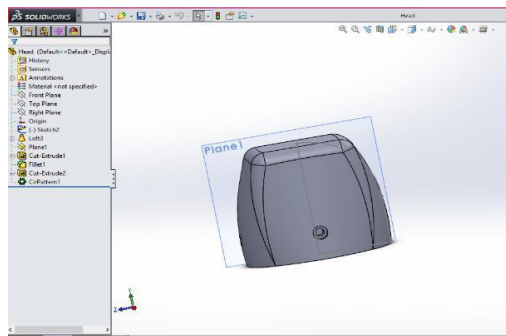


Figure 5. The hexagonal type head design

3.3.2 Body of the robot mechanism

The body of the robot mechanism is designed like a cylindrical shape because the pipes are usually cylindrical so it makes the locomotion of the mechanism easier. The body is designed to accommodate the solenoid actuator but it is not shown in the overall assembly because the design is just the conceptual design. The wheels are attached to the mid part of the body mechanism because to maintain the stability of the robot mechanism. If the wheels are placed too front or back the weight distribution will not be balanced and the mechanism could not move in the pipe. The body is designed wide because to equip the robot mechanism with some mini tools like Bluetooth camera, laser light or

many more mini tools that can aid the in-pipe inspection process. The design of the body is shown in Fig. 6.

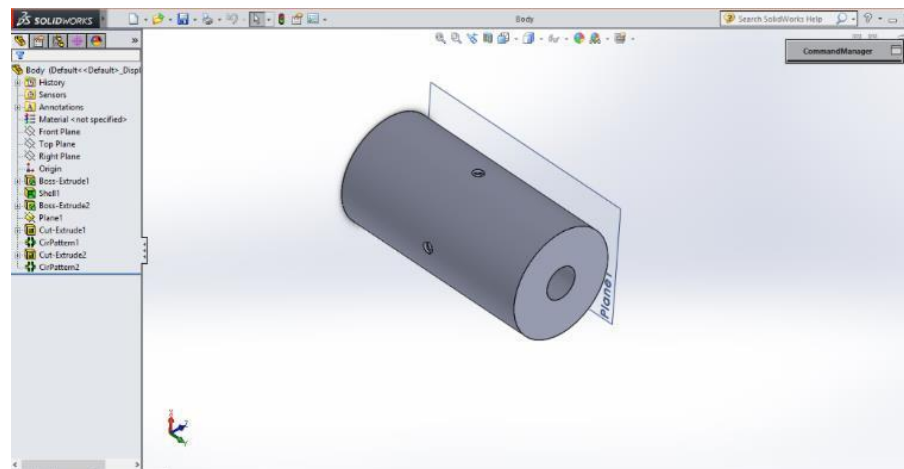


Figure 6. The body of the robot mechanism

Other than that, different type of body is also design as shown in Fig. 7, this body is less complicated because it is designed to accommodate the solenoid actuator by just sliding the actuator into the body , it does not require any complicated screws.

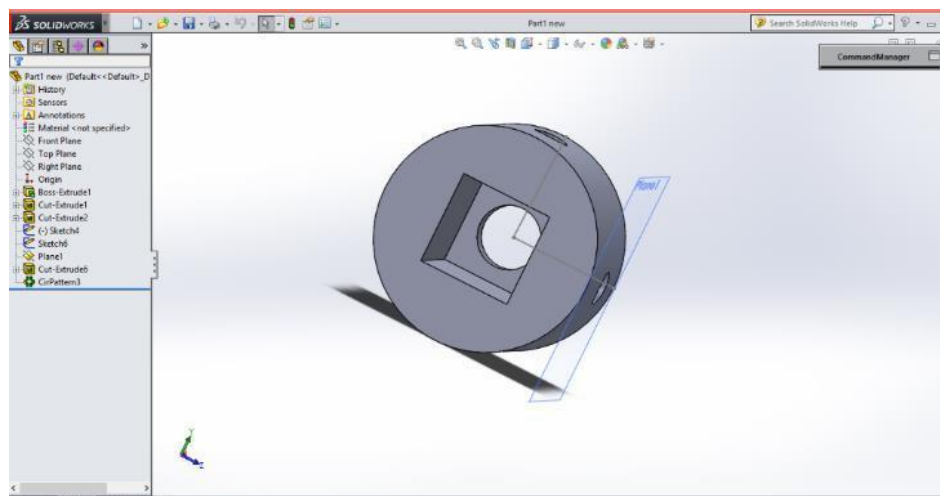


Figure 7. The sliding type body to accommodate the actuator

3.3.3 Wheel Mechanism

The wheels Mechanism consist of wheel, wheel attachment, pin and a spring. The reason for having 4 pairs of wheels perpendicularly is to provide a better traction for the robot mechanism to move and take corners easily. Having such arrangement also provides stability to the mechanism because the wheel system can easily engaged to the walls of the pipe. Fig. 8 shows the whole wheel mechanism. Other than that, Fig. 9 shows each parts in the wheel mechanism.

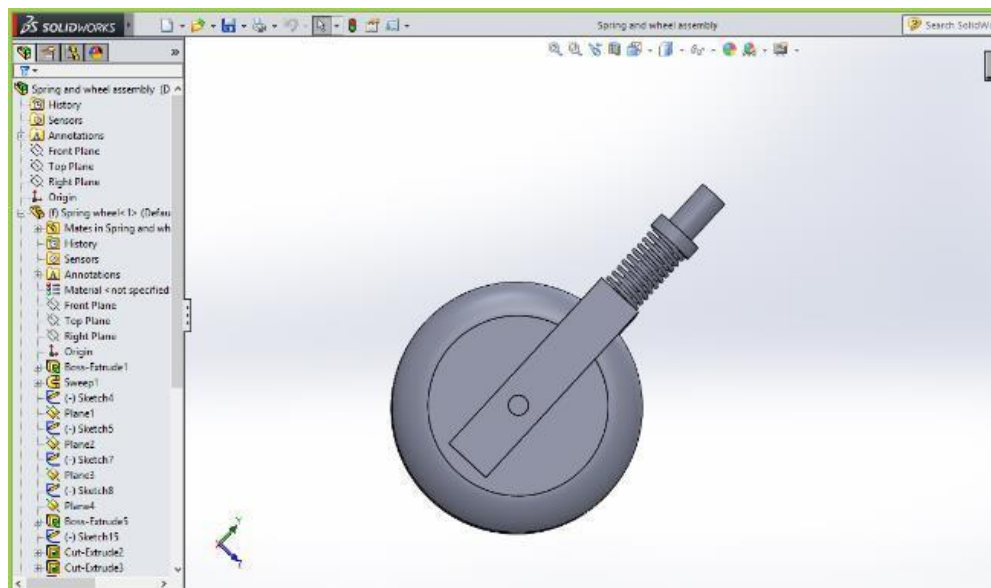
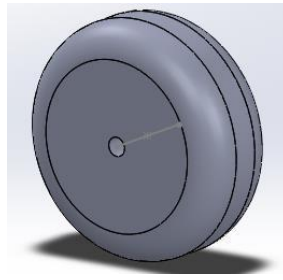
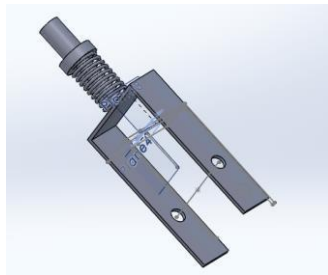


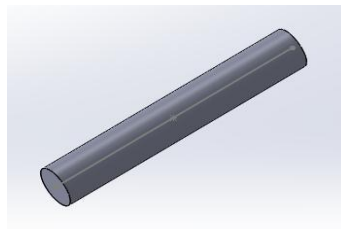
Figure 8. Wheel Mechanism



a) Wheel



b) Wheel Attachment



c) Wheel Pin

Figure 9. The parts in the wheel mechanism

3.3.4 Spring/Bellow Seal

A spring or bellow seal is placed between the head and the body of the robot mechanism. The purpose of the spring or bellow seal is to aid the mobility of the robot mechanism. The concept applied for the locomotion of this robot mechanism is the Impact Drive Motion (IDM). When the stator of the solenoid actuator elongates and hit the head of the robot mechanism would not result in motion but as the constant hit is applied to the surface due to impulsive force and static friction the head will move forward. The bellow seal or spring will contract and expand according to the frequency of the actuation which makes the robot mechanism to move. Bellow seal is chosen because it can work in both dry and liquid environment. If only for dry environment application then spring is more favorable. Fig.10 shows the design of the middle spring.

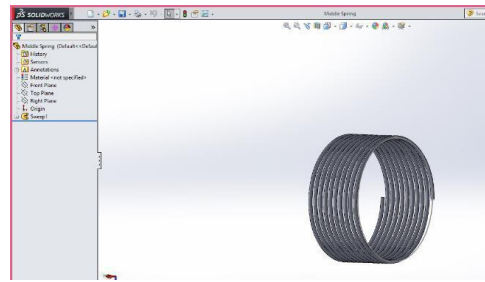


Figure 10. Middle Spring

3.4 Circuit to Control the Solenoid Actuator

3.4.1 Overview of the circuit design and implementation

A circuit is designed and implemented to control the actuation of the solenoid actuator. Initially, when the actuator is finalized with solenoid actuator it was hard to control the actuation speed by just using a direct power supply like battery. To overcome this problem a circuit is designed and implemented to act as the controller to control the speed of actuation. The speed of the actuation is done by controlling the frequency of the actuation, this is achieved by implementing a 555 timer to the circuit which gives an output of continuous pulse waveform of a specific frequency depending on the value of the resistor and the capacitor value. The circuit is designed using the MultiSim software and the outcome is shown in Fig. 11. The results of the implementation of the circuit is shown in Fig.12.

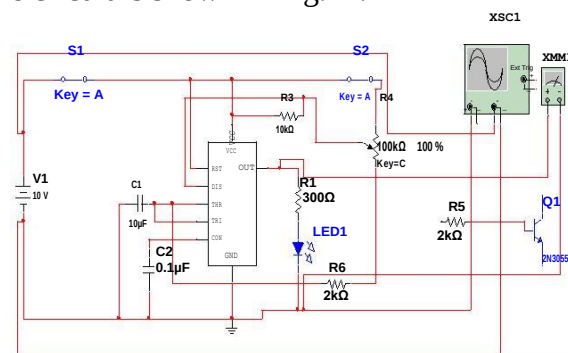


Figure 11. The schematic design of the circuit

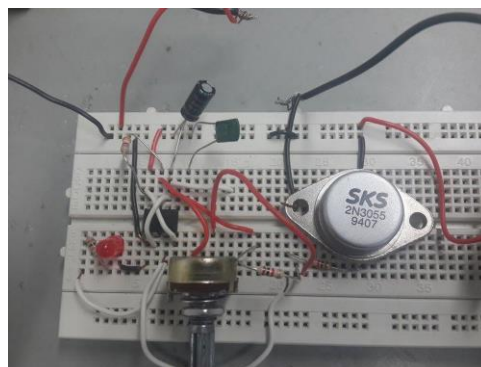


Figure 12. The Implemented Circuit (Controller)

3.4.2 Analysis of the circuit (Controller)

The frequency of actuation of the solenoid actuator is obtained by connecting the controller to the actuator and the whole system to oscilloscope. The results obtained by using different input voltages. The first experiment is to find the initial startup voltage to trigger the actuation of the solenoid actuator. The input voltages and the frequency of the actuation is shown in Table 6. Based on the results obtained, the startup input voltage that triggers the actuation of the stator of the solenoid actuator is about 3.2 V. Based on the results a graph is obtained as shown in Fig. 13.

Table 6. The Frequency obtained

Input Voltage	Frequency	Time, μ s
0.2	0.0	10
1.2	0.0	10
2.0	0.0	10
3.2	0.1	10
4.8	0.1	10
6.2	0.1	10
7.6	0.2	10
8.8	0.2	10
9.4	0.3	10

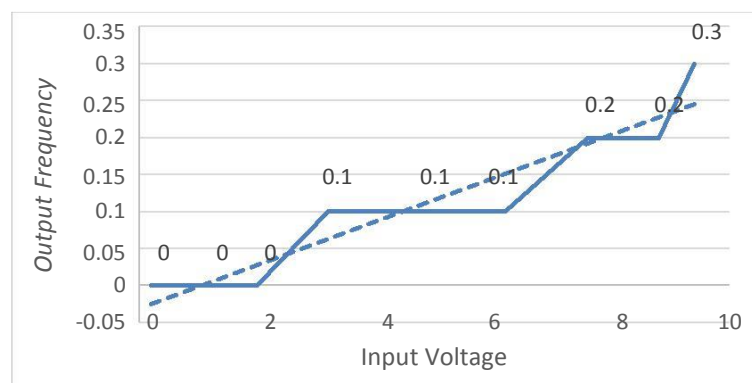


Figure 13. Graph of Input voltage against Output Frequency

4. Conclusion

In this paper, the robot mechanism actuated by the electromagnetic linear actuator (solenoid actuator) is proposed, designed and analyzed. Furthermore, a controller is implemented to aid the mobility of the robot mechanism. The controller is designed, implemented and analyzed which functions to control the solenoid actuator. Through this research the controller is a way to control the rate of actuation of the actuator so it could be easy for the inspection process because through this controller the speed of the robot mechanism can be controlled. The future work to be done is completing the fabrication of the robot mechanism which is still on process. Planning to incorporate other types of actuators such as piezoelectric, pneumatic, shape memory alloy and etc. are the other options to extend this research topic. A review could be considered to find suitable target industries which may need in-pipe applications robots. Using a more advanced

artificial intelligent controllers which is equipped with sensors, cameras and many more can also help the system and micro robot to follow the trajectory tracking purpose too.

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Delivering Holistic Education in an Engineering Curriculum using Personalized Learning, Pedagogy, Technology and Space

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Abstract

'Holistic Education' can be defined in many different ways. In this research, 'Holistic Education' is defined by the Bloom's Taxonomy of Learning Objective: - Cognitive, Affective and Psychomotor. Personalized learning is envisioned to expedite a student's academic success by first knowing the aspirations, interests and learning needs of the student, and providing a customized learning experience for each student. Technology and personalized space plays a crucial and effective role in student learning. *'Can holistic education be delivered in an Engineering curriculum through personalized learning geared to the students' preferred learning style, through collaborative learning pedagogy, technology and space?'* is the research question for this research. To achieve this, a few surveys and an intervention were designed. A learning style survey was conducted using the Index of Learning Styles (ILS) to determine the learning styles of a cohort of engineering students and a module identifying survey to identify a module to intervene. The intervention was conducted in a X-Space where students were placed in groups and are encouraged to use all the technologies available in the X-Space and a post-survey was conducted to determine the significant differences. A visual learning survey was also conducted to test the effectiveness of teaching geared to students' preferred learning style. It was found that most engineering students are, *reflective, sensing, visual and sequential* learners. Thermodynamics and Heat Transfer module was identified to be the most challenging module based on the student survey and the need for this module is supported by the industry survey. Furthermore, the industry survey has also shown the importance of affective and psychomotor learning domains in the industry. Thermodynamics and Heat Transfer was initially selected for the intervention. However due to unforeseen circumstances, it was replaced by Advanced Thermofluid Engineering. The outcome of this invention showed that there was a significant difference in all the constructs except cognitive pedagogy. A significant difference was noted in the visual learning survey, proving that teaching geared to student's learning style is important.

Keywords: Bloom's Taxonomy, Holistic education, Learning Styles, Engineering curriculum, Learning Space

1. Introduction

With the ever-increasing complexity of challenges in the 21st century, it is believed that, cognitive development alone is not sufficient for future engineers. A holistic approach is required to incorporate other learning domains such as affective and psychomotor to strengthen productivity, and excellence of future engineers in an environment that is based on an increasing technology development [1]. In this research, ‘Holistic Education’ is defined by the Bloom’s Taxonomy; Cognitive, Affective, and Psychomotor. The term ‘Holistic Education’ can be defined in many different ways. In a US reaction against the prevailing “mechanistic” worldview of education in the 1980’s, begins the initiatives of holistic education that aim to develop human to achieve their fullest potential [2].

Bloom’s Taxonomy is a well-known taxonomy of learning objective. It separates human development into 3 different domains: - Cognitive, Affective and Psychomotor. According to Bloom et al. [3], the cognitive domain includes objectives that deal with the recall or recognition of knowledge and the development of intellectual abilities and skills. Affective domain on the other hand, includes objectives that describe changes in interest, attitudes, and values, while the psychomotor domain covers the motor-skill areas. Unfortunately, only the cognitive domain is mainly discussed in most researches, as it believed to be the most responsive to studies and forms the basis of the first Bloom’s studies. However, the affective domain is important to complement the cognitive domain [4]. The need to balance both cognitive and affective learning domains has been acknowledged by the American Society of Civil Engineers [2].

Personalized learning can be defined as a student-centered learning approach. Personalized learning is intended to expedite the academic success of each student by first determining the learning needs, interests, and aspirations of the student, and then providing customized learning experience for each student [4]. Majority of public education is delivered in a uniform ‘one size fits all’ approach [5].

A number of studies have previously been conducted on personalized learning. In engineering itself, there were a few studies done regarding this topic. Felder and Brent [6], reviewed some models that have been developed for importance of teaching and learning student differences. The Myers-Briggs Type Indicator, Kolb’s Experiential Learning Model and The Felder-Silverman Model are among the models that have been reviewed and are commonly used in engineering curriculum. According to Felder and Silverman [7], a mismatch between traditional teaching styles and common engineering student’s learning style often occurs. This mismatch usually would cause students to be bored in class, perform poorly in examinations and eventually dropout of the course.

Collaborative classrooms have been shown to have positive impact in “human learning and teaching capability” [8]. Recently, many researches on learning space were conducted. According to Lei [9], there are eight elements that should be considered in designing a classroom;- size, seating arrangement, shape, furniture arrangement, interior lightings, color selections, noise level and technology system arrangement. Graetz and Goliber [10] on the other hand, proposed a different idea. The authors believed that, information technology has a very strong influence in the effectiveness of the classroom.

The aim of engineering education is to provide students with the required learning skills to become a successful engineer [1]. Graduate engineers should have a great understanding of knowledge, a wide variety of skills, and a professional attitude. The acknowledgement of student's learning style preference is vital as most engineering curriculums are usually taught in a 'one-size-fits all' and lecturer-centered approach. Furthermore, an appropriate pedagogy, technology and learning space should be used to support the holistic development of students and to achieve the aim of engineering education.

Hence, through the survey of current literature, '*Can holistic education be delivered in an Engineering curriculum through personalized learning geared to the students' preferred learning style, through collaborative learning pedagogy, technology and space?*' is the research question identified for this project. The objectives of this research is to identify the learning styles of a cohort of engineering graduates, utilizing pedagogy, technology and space to affect the holistic development of a student and understanding the effect of content delivery when adapted to specific student's learning style. This research paper will help educators to understand the importance of addressing their student's learning style and identify possible approach, which could result in a more holistic development of the student.

2. Research Methodology

This project is based on a qualitative and quantitative research whereby surveys and student performances was conducted and evaluated. Fig. 2.1 below shows a flow chart of the overall methodology used for this project.

This research began by conducting two types of survey. After obtaining the results from the survey, an intervention was designed, implemented and evaluated. If the results of the intervention are not satisfied, the intervention will be redesigned, implemented and re-evaluated. However, if the results are satisfied, the research will be presented. The sections below describe the activities of the research in details.

2.1 Survey

Two types of survey were conducted in this research. The first survey was the learning style survey, and the second survey was the module identification survey. Each survey is further elaborated in the sub-sections below.

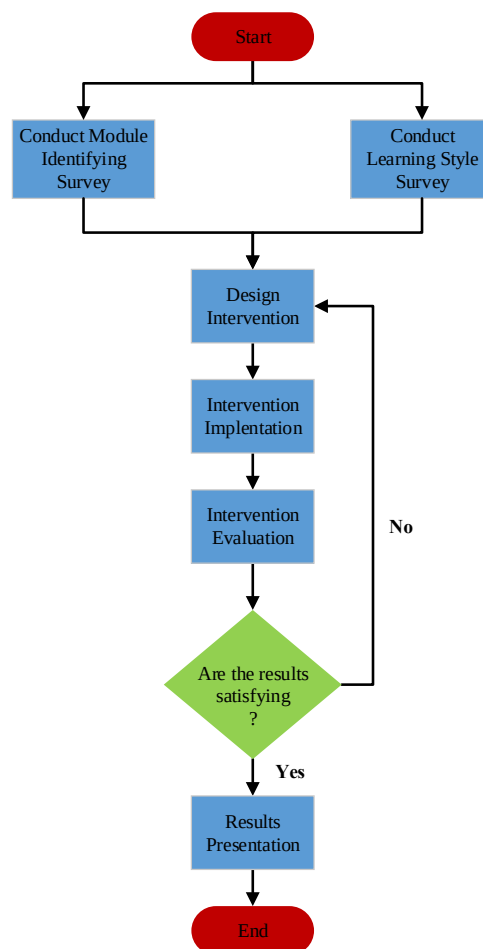


Figure 2.1 Overall Methodology

2.1.1 Learning Style Survey

The Felder-Silverman Index of Learning Style (ILS) model was used to conduct the learning style survey. This learning style model was chosen over other models such as VARK, Kolb's Experiential Learning Model and The Herrmann Brain Dominant Instrument because there have been several studies done in the engineering education field using this model [6]. Moreover, Dr. Richard M. Felder is a Chemical Engineering Professor at North Carolina State University. He has authored more than 200 education-related papers and also received more than 10 awards for his contribution to engineering education [11].

Index of Learning Style questionnaire is a forty-four-item questionnaire with only two-answer options. These questions were designed to assess the four learning style dimensions. These dimensions are, how students process information, learn, remember and understand. By evaluating the answers of these questions, the learning style dimensions can be identified. The four learning styles that the students will be assessed are, active/reflective, sensing/intuitive, visual/verbal and sequential/global. The Index of Learning Style questionnaire is taken from 'Index of Learning Style' page, online [12]. This questionnaire is available for public usage at no cost.

The learning style survey was conducted on Taylor's University Engineering students from Year 1 to Year 4 and also engineering graduates. Besides that, students enrolled in Thermodynamics and Heat Transfer also took part in this survey.

2.1.2 Module Identifying Survey

Two module identifying surveys were conducted; - student's survey and the industry survey. Both surveys were conducted to determine which module needed intervention.

The student's survey form consists of questions regarding the modules offered in Taylor's School of Engineering. This survey was conducted to discover which module does the students find most difficult, and why do they find it difficult? A list of all the modules offered under Mechanical Engineering was attached in the survey form to ease the students in answering the survey. In addition to that, the student's opinion on which module should be improved and how can it be improved was also questioned. This was added to know which module do the students feel need an improvement. This survey form was then given to students of Year 3 onwards and graduate mechanical engineering students, as they would have taken most of the modules offered. A copy of the survey form is attached in the Appendix.

Industrial survey was conducted to understand which module is widely applicable in the industry. The industry survey form was given out to companies that are collaborating with Taylor's University. The main question asked in this survey was, which module is most applicable to their industry/company. A list of modules with the synopses was linked with the survey form for them to understand the modules taught better. Furthermore, a survey on what they expect from fresh graduates and are the fresh graduates meeting the expectation was also addressed. The main purpose of the questions is to know what the industry expects from the graduates, and are the current graduates meeting the expectations. A copy of the survey form is attached in the Appendix.

2.2 Intervention

Based on the results of the survey, Thermodynamics and Heat Transfer was selected to perform the intervention. An interview was conducted with the previous lecturer of this module to find out which learning outcome was the most challenging for the students, based on his experience. After much identification, permission was sought to perform this research on the current module and batch of students from under the guidance of the current lecturer.

2.2.1 Design of Intervention

The intervention was designed to be performed in X-Space. X-Space is a collaboration classroom that is technology-rich designed for flexible formal learning space [13]. X-Space is a classroom that is equipped with round tables and comfortable moveable chairs for better collaborative learning and personal screen for each table for idea sharing and presentations. The facilities and features in X-Space match the research title and objectives. Fig. 2.2 shows the X-Space classroom.



Figure 2.2. X-Space Classroom

An initial intervention was designed for Thermodynamic and Heat Transfer. In this intervention, two tutorial groups were used to compare the results. The control group is the first group where, no changes were made. Tutorial lesson were carried out as usual. The intervened group on the other hand, was performed in X-Space. For the second intervention, one tutorial session was to be performed in X-Space and the results were compared with the regular tutorial sessions. The second intervention was designed for Advance Thermofluid Engineering. The differences between both interventions are that the first intervention used two different tutorial groups from the same week, while the second intervention used the same tutorial group for two different weeks. The reason was because the class size for Advance Thermofluid Engineering was smaller hence it only had one tutorial group.

Visual Learning was the most preferred learning style based on the learning style survey performed. To accommodate the preferred learning style, the module coordinator has been requested to include more visual aid such as pictures, diagrams, animations and videos into the lecture notes.

2.2.2 Intervention Implementation

In X-Space, students were placed in groups. Each group is to complete the tutorial questions together. Students were encouraged to use all the technology and facilities available in X-Space such as the shared screen and group white board. At the end of each tutorial session, a quick quiz was given to the students. For the intervened tutorial group, one copy of the quiz was given to each group, and then 10 minutes to discuss the questions before splitting up to solve it on their own. Students in the control group on the other hand, were not given the opportunity to discuss before the quiz.

Students were grouped differently for both interventions. Students were grouped based of academic results whereby, each group will have a mixture of well performed, average and weak students in the first intervention. However, it was found that the method of grouping was not effective for collaborative learning as students were not willing to work together for discussions. Thus, students were randomly grouped in the second intervention.

The quiz given to the first intervention was aimed to compare the cognitive pedagogy between the intervened group and the control group. For the second intervention, the quiz was given only to the intervened group to test the effectiveness of technology pedagogy for both the cognitive and affective learning domain.

Since visual learning was the strongest preferred learning style, a survey was conducted for two different batches of Advance Themofluid Engineering students regarding the module's lecture slides. The lecturer had enhanced his lecture notes with substantial amount of visual elements compared to the previous time the module was taught. The results were then evaluated using inferential statics in the SPSS Statistic software to determine if there were any significant differences between both batches. This survey was conducted on two different batches because, according to the module coordinator, the lecture slides used for this batch was improved to be more visual compare to the previous batch's lecture slides.

2.2.3 Intervention Evaluation

The results obtained for the first intervention was void, as the procedure was not followed due to unforeseen circumstances. Hence, only results obtained from the second intervention were evaluated.

For this second intervention conducted for Advance Thermofluid Engineering, two sets of post-survey questions were given to the students: - Intervention survey and Tutorial survey. The survey questions are attached in the appendix. The surveys were conducted the following week. The intervention survey was conducted before the tutorial session. At the end of the same tutorial session, the 'tutorial survey' was conducted.

The surveys were divided into six constructs; - cognitive and affective impact on pedagogy, cognitive and affective impact on technology, and cognitive and affective impact on space. Each construct consists of 3 to 4 Likert scaled survey questions that are aligned with the Bloom's taxonomy for cognitive and affective domain. Besides that, at the end of the survey, an optional suggestion/comment question was address for students to give their feedbacks. Table 3.1 below shows the hypothesis.

Table 3.1 Null (H_0) and alternate (H_1) hypothesis for each construct

Constructs	H_0	H_1
Pedagogy Affective (PA)	Student does not attach a value on collaborative learning	Student attaches/places a value on collaborative learning
Space Affective (SA)	Student does not attach a value on the positive effect of specially designed learning space for collaborative learning	Student attaches a value on the positive effect of specially designed learning space for collaborative learning
Technology Affective (TA)	Student does not attach a value on the use of technology on collaborative learning	Student attaches a value on the use of technology on collaborative learning

Pedagogy Cognitive (PC)	Collaborative learning does not improve student's learning (identify, remember, apply, analyze)	Collaborative learning improves student's learning (identify, remember, apply, analyze)
Space Cognitive (SC)	Learning space does not improve student's learning (identify, remember, apply, analyze)	Learning space improves student's learning (identify, remember, apply, analyze)
Technology Cognitive (TC)	Technology does not improve student's learning (identify, remember, apply, analyze)	Technology improves student's learning (identify, remember, apply, analyze)

All the data obtained from the post-survey was tabulated and imported into the SPSS Software for data analysis. Since the sample size was less than 30, a normality test was first conducted to test if the sample results were normally distributed. If the data obtained was normally distributed, a dependent *t*-test was used to test for significant differences. However, if the data obtained was not normally distributed, the paired sample *t* test could not be used. Instead the Wilcoxon signed-rank test was used to test for significant differences. Wilcoxon signed-rank test is a nonparametric equivalent of the dependent *t*-test.

These tests were conducted at 95% confidence interval, or 5% significance level, hence data with *p*-values of less than 0.05 would mean the rejection of the null hypothesis and the acceptance of the alternate hypothesis. 5% significance level means that there is a 5% chance of rejecting the null hypothesis even though it was true. This is called Type 1 error. The 5% significance level is the common standard used for statistical tests.

A sample size of less than 30 was obtained from the visual learning survey. Thus, the same procedure was applied to analyze the results starting from a normality test. If the data obtained was normally distributed, an independent *t*-test was used to test for significant differences. If the data obtained was not normally distributed, Mann-Whitney U test was used to test for significant differences.

3. Results and Discussions

Summarized survey results are presented in this section along with the intervention outcomes.

3.1 Survey Outcomes

The survey outcome for both the learning styles and module identifying survey is presented in the sub-sections below followed by the outcome of the intervention.

3.1.1 Learning Style Survey

A total of 90 participants consisting of, 43 mechanical, 34 chemical and 13 electrical engineering students took part in this survey. Each learning style was compared among the same category/question. For example, active is compared with reflective, and visual is compared with verbal. Table 3.1, 3.2 and 3.3 shows the learning style results for mechanical, chemical and electrical students respectively.

Table 3.1. Learning Style Results for 43 Mechanical Engineering Students

Learning Style	Active	Reflective	Sensing	Intuitive	Visual	Verbal	Sequential	Global
Frequency	21	22	23	20	41	2	23	20
Percentage(%)	48.84	51.16	53.49	46.51	95.35	4.65	53.49	46.51

Table 3.2. Learning Style Results for 34 Chemical Engineering Students

Learning Style	Active	Reflective	Sensing	Intuitive	Visual	Verbal	Sequential	Global
Frequency	15	19	25	9	31	3	21	13
Percentage(%)	44.12	55.88	73.53	26.47	91.18	8.82	61.76	38.24

Table 3.3. Learning Style Results for 13 Electrical Engineering Students

Learning Style	Active	Reflective	Sensing	Intuitive	Visual	Verbal	Sequential	Global
Frequency	5	8	11	2	12	1	6	7
Percentage,(%)	38.46	61.54	84.62	15.38	92.31	7.69	46.15	53.85

Based on the results obtained, it was discovered that visual learning is the most preferred learning style. According to Felder and Solomon [14], a balance between the two styles is desirable because everyone tends to process the information/learning differently in different situations. Nonetheless, one learning style would be much preferred as compared to the other. More than 90% of students in each discipline preferred visual learning style. The next strongest learning preference is the sensing and reflective learning style. This survey has shown that, most students prefer facts to theory and usually prefer to think through what they have learned rather than learning through active participation. Both mechanical and chemical engineering students preferred sequential learning although global learners were stronger in electrical engineering students.

This learning style survey was also conducted on students enrolled in Thermodynamics and Heat Transfer and Advance Thermofluid Engineering. The purpose of conducting this learning style survey on the students enrolled in these modules is to validate the initial learning style finding. Table 3.4 and table 3.5 shows the learning styles of 40 mechanical and 31 chemical engineering students enrolled in Thermodynamics and Heat Transfer while Table 3.6 shows the learning styles of 22 Advance Thermofluid Engineering students.

Table 3.4 Learning Style Results for 40 Mechanical Students

Learning Style	Active	Reflective	Sensing	Intuitive	Visual	Verbal	Sequential	Global
Frequency	16	24	21	19	35	5	17	23
Percentage(%)	40.00	60.00	52.50	47.50	87.50	12.50	42.50	57.50

Table 3.5 Learning Style Results for 31 Chemical Students

Learning Style	Active	Reflective	Sensing	Intuitive	Visual	Verbal	Sequential	Global
Frequency	15	16	21	10	25	6	18	13
Percentage(%)	48.39	51.61	67.74	32.26	80.65	19.35	58.06	41.94

Table 3.6 Learning Style Results for 22 Advance Thermofluid Engineering Students

Learning Style	Active	Reflective	Sensing	Intuitive	Visual	Verbal	Sequential	Global
Frequency	10	12	15	7	21	1	10	12
Percentage(%)	45.45	54.55	68.18	31.82	95.45	4.55	45.45	54.55

Based on the learning styles results obtained from the students in Thermodynamics and Heat Transfer and Advance Thermofluid Engineering, it was established that the strongest learning style is still the visual learning, followed by reflective, sensing and global learning. Table 3.7 below shows the overall learning style result for 183 students and Figure 3.1 shows the total differences between the two learning styles.

Table 3.7 Overall Learning Style Results for 183 Students

Learning Style	Active	Reflective	Sensing	Intuitive	Visual	Verbal	Sequential	Global
Frequency	82	101	116	67	165	18	95	88
Percentage(%)	44.81	55.19	63.39	36.61	90.16	9.84	51.91	48.09

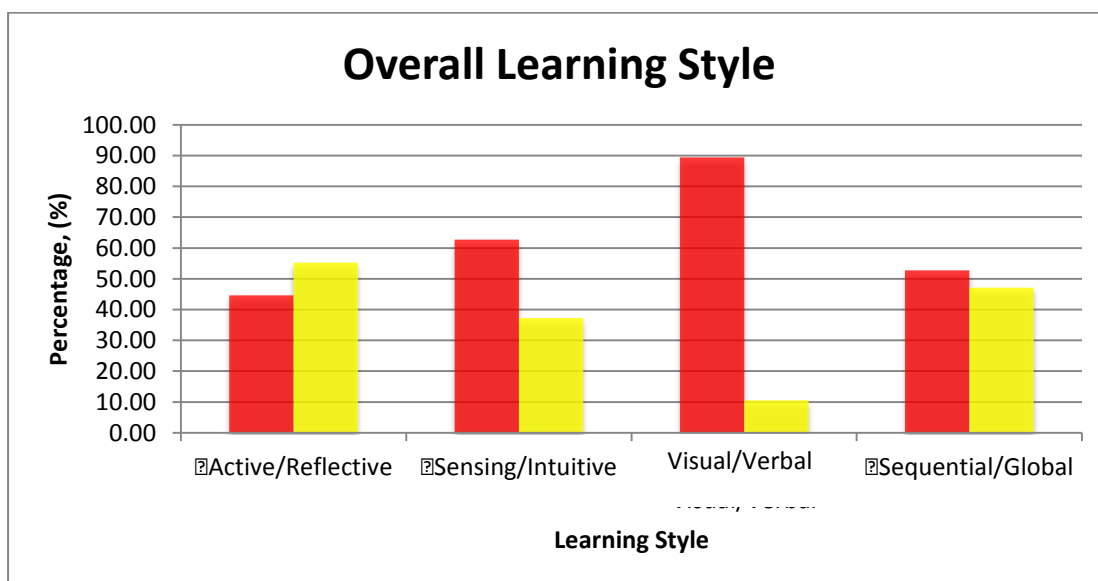


Figure 3.1. The overall percentages of the student's learning style

Different universities have different ways of teaching and learning. Figure 3.1 has shown that, most engineering students in Taylor's University prefers reflective learning over active learning, sensing learning over intuitive learning, visual learning over verbal and sequential learning over global learning. If the teaching styles is not matched to the student's learning style, a mismatch would exist, causing students to lose interest in learning, feel discouraged and perform poorly in examinations [7].

Unfortunately, most lecturers prefer to teach theory rather than facts. Lecturers believe that theory is more important than facts and thus, the lessons are usually “heavily oriented toward intuitors” [6]. Most lectures conducted are usually more verbal than visual. Lecture slides are filled with words and equations rather than images and video. Global students are usually multidisciplinary thinkers with broader vision. The education system in Malaysia has always taught students to solve mathematical problems sequentially. This is one of the reasons sequential learning is slightly more preferable as compared to global learning. Most learning outcomes in Taylor’s School of Engineering is highly cognitive. Thus, there is no surprise that, most students would prefer reflective learning compared to active learning. However, if the same survey is to be conducted in a vocational school in Malaysia, it is believed that there will be more active learners compared to reflective learners.

3.1.2. Module Identifying Survey

A total of 23 mechanical engineering students consisting of Year 3 onwards and graduates participated in this student survey. Table 3.7 below shows the top 5 modules selected by the students in the survey. Based on the responses, Thermodynamics and Heat Transfer has been selected as the most challenging module.

Table 3.7. Top 5 modules selected by the students in the survey

Module	Total number of students
Thermodynamics and Heat Transfer	9
Design of Engineering Component and Systems	8
Automatics Control and Instrumentation	7
Advance Thermofluid Engineering	6
Theory of Machines and Mechanicisms	6

Approximately fifteen surveys were distributed to several companies that were collaborating with Taylor’s University. The main reason the industry survey was conducted was to use it as a confirmation note that the identified module is important for the industry. Among fifteen surveys, ten companies responded to the survey. The responses received were very intriguing.

Based on the ten responses received, one of the companies’ was not from the mechanical engineering field. Thus, that response was void. Out of the nine other companies, three companies have identified Thermodynamics and Heat Transfer as one of the modules that is most applicable to the industry. This module is considered to have one of the highest count besides the other modules such as Managing Project for Success, Final Year Project and the Group Design modules, which were not among the highest count in the student’s survey.

Out of nine questions provided in the survey, one of the question asked is, “What are your expectations for fresh graduates?” 5/9 companies said *good discipline specific knowledge*, 8/9 companies said *good attitude*, 8/9 companies said *good technical hand-on skills*, and etc. These responses have shown that the development of the affective and psychomotor learning domains are as important to the industry as the cognitive learning domain.

As the intervention on Thermodynamics and Heat Transfer was not successful, Advance Thermofluid Engineering was chosen for the second intervention because this module is closely related to Thermodynamics and Heat Transfer.

3.2 Intervention

Two interventions were conducted for this research. The first intervention was conducted on Thermodynamics and Heat Transfer, while the second intervention was conducted on Advance Thermofluid Engineering. The intervention observation is presented in the subsections below.

3.2.1 Thermodynamics and Heat Transfer

A total of 26 students turned up for the intervention class. The students sat together in a pre-set group and each group had a mixture of well performed, average and weak students. Unfortunately, due to unforeseen circumstances arising, the intervention was not conducted the way it was supposed to be conducted. The initial plan for each group to complete the tutorial questions in teams was not performed as the tutorial session was conducted as usual by the module coordinator. Hence, the students were not given an opportunity to use the technologies available in X-Space. At the end of the tutorial session, the quiz question was distributed to the each student instead of just one copy per group. With each student having a copy of the question paper, students did not utilize the allocated 10 minutes for discussion; instead everyone started doing the quiz individually. For the control group on the other hand, only nine students turned up for the tutorial session due to several reasons. As planned, the students in the tutorial group were given the quiz 10 minutes before the end of the session, and they completed the quiz individually without any help.

Based on the quiz results obtained, it was found that the intervened group did not perform as expected. This is attributed to the intervention not properly conducted. Furthermore, the quiz can only be used to gauge the effectiveness of the intervention on the cognitive learning domain. However, the objective of this research goes beyond the cognitive learning domain and other tools are required to measure the holistic outcomes, which include the affective learning domain. This issue was rectified and a new attempt with the intervention was made using Advance Thermofluid Engineering.

3.2.2 Advance Thermofluid Engineering

A total of 23 students turned up for the intervention class. Students were placed into groups at random. The tutorial session started as usual whereby the module coordinator would do a simple recap and discussed a few sample questions with the students before presenting the tutorial question. After discussion, each group was told to work together to solve the tutorial question. Students were given approximately 15-20 minutes to discuss and solve the tutorial question. Throughout the given time, it was observed that most students actively participated in the group discussion. However, there were approximately 1-2 students who chose to attempt the tutorial question on their own.

After solving the tutorial question, a quick quiz was conducted as planned. Each group was given 1 sheet of the quiz questions for discussion and was requested

to utilize the technologies available in X-Space such as the shared screen and internet. Unfortunately, the students were not able to connect their device to the shared screen. Thus, students were not able to use the shared screen as planned. Nonetheless, the students still managed to use the Internet provided in X-Space to discuss the quiz questions. Instead of using the shared screen in X-Space, each group shared 1 technology device (laptop or tablet) among the group to do the research required in the quiz. After the 10 minutes discussion period, each group was split to different tables to solve the quiz questions individually. Based on the observation on this intervention, it was found that group discussion was actively participated, the learning space was conducive and technology was well used. All three factors were effectively applied in the intervention.

3.3 Post-Intervention Survey

A post-intervention survey was conducted to understand the impact of the intervention on students. As this survey was conducted the following week, only 22 students participated. The data obtained was then compared with a control survey in which similar questions related to the regular tutorial class were used.

Since the sample size was less than 30, a normality test was first conducted. Only sample sizes greater than 30 can be assumed to be normally distributed based on the Central Limit Theorem. Table 3.9 below shows the normality test results generated by SPSS. Two normality test results were generated; - Kolmogorov-Smimov and Shapiro-Wilk results. Shapiro-Wilk results are more suitable for small samples sizes [4]. The tests were conducted at 95% confidence interval hence data with a p-values of less than 0.05 would not be considered normally distributed. The paired sample t-test was used if the sample was normally distributed while its nonparametric equivalent, the Wilcoxon Signed Rank Test, was used if it was not normally distributed.

Table 3.9 Normality Test

	Kolmogorov-Smirnov ^a			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
IPA	.160	22	.147	.935	22	.160
CPA	.139	22	.200*	.940	22	.200
IPC	.171	22	.094	.934	22	.151
CPC	.220	22	.007	.877	22	.011
ISC	.162	22	.140	.911	22	.051
CSC	.186	22	.046	.935	22	.159
ISA	.195	22	.029	.925	22	.096
CSA	.112	22	.200*	.973	22	.769
ITA	.170	22	.097	.919	22	.071
CTA	.176	22	.074	.953	22	.362
ITC	.137	22	.200*	.908	22	.043
CTC	.200	22	.022	.940	22	.198

*. This is a lower bound of the true significance.

a. Lilliefors Significance Correction

Based on Table 3.9, CPC and ITC are not normally distributed ($p > 0.05$) while other data are considered normally distributed ($p < 0.05$). Paired t -test was conducted for each construct that is normally distributed and the Wilcoxon Signed Rank Test was used to analyze CPC and ITC sample data that were not normally distributed. Table 3.10, 3.11 and 3.12 below shows the paired sample tests, Wilcoxon Signed-Rank tests and the descriptive statistic results respectively.

Based on Table 3.10, all pairs have shown to have a significant difference ($p < 0.05$) between the intervened tutorial with the regular tutorial for the pedagogy affective (PA), space affective (SA), technology affective (TA), and space cognitive (SC) constructs. The data obtained for pair 2 and 6 is void because CPC and ITC data are not normally distributed. Results from statistical analysis reported in Table 3.11 showed that there is a significant difference ($p = 0.05 < 0.05$) for intervened cognitive technology (ITC) and control cognitive technology (CTC) but no significant difference ($p = 0.761 > 0.05$) between the intervened tutorial (IPC) with the regular tutorial (CPC).

Table 3.10 Paired Sample Test

		t	df	Sig. (2-tailed)
Pair 1	IPA - CPA	2.706	21	.013
Pair 2	IPC - CPC	.053	21	.958
Pair 3	ISC - CSC	2.780	21	.011
Pair 4	ISA - CSA	3.937	21	.001
Pair 5	ITA - CTA	3.806	21	.001
Pair 6	ITC - CTC	3.161	21	.005

Table 3.11 Wilcoxon Signed-rank Test

	IPC - CPC	ITC - CTC
Z	-.304 ^b	-2.826 ^c
Asymp. Sig. (2-tailed)	.761	.005

Table 3.12 Descriptive Statistic for the 6 constructs

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	IPA	3.6818	22	.58849	.12547
	CPA	3.3182	22	.63237	.13482
Pair 2	IPC	3.7727	22	.71092	.15157
	CPC	3.7614	22	.64308	.13711
Pair 3	ISC	3.8636	22	.90214	.19234
	CSC	3.0682	22	.89036	.18983
Pair 4	ISA	3.8864	22	.77046	.16426
	CSA	2.7727	22	.96025	.20473
Pair 5	ITA	4.2432	22	.60146	.12823
	CTA	3.3932	22	.63150	.13464
Pair 6	ITC	4.0764	22	.68940	.14698
	CTC	3.2873	22	.72221	.15398

Collaborative learning in this study was shown to have no significant difference ($p = 0.761 > 0.05$). It is believed that, collaborative learning pedagogy is considered to be quite new to students, as it is not commonly practiced in tutorial sessions. Students prefer a more direct approach whereby the lecturer would discuss the tutorial questions. It would take time for students to adapt to the change of approach. Moreover, among the comments received from the survey, one student mentioned that group discussion is good but self-learning can help him be independent as he is able to analyze something without assistance. In addition to that, there is a very small mean score differences between IPC and CPC. This also showed that, there is not much impact between collaborative pedagogy and the regular pedagogy.

Based on the results obtained from the paired *t*-test, the null hypothesis ‘Student does not attach a value on collaborative learning’ is rejected ($p\text{-value} = 0.013 < 0.05$). Regular tutorials were usually conducted whereby students are supposed to attempt the questions on their own. However, these results have shown that students were more willing to attempt the tutorial questions in a group, than doing it on their own. Students do in fact value collaborative learning, even if they did not consider it more helpful to them in cognitive learning than their regular tutorial.

There is a significant difference ($p\text{-value} = 0.01\text{-}0.05 < 0.05$) shown for both cognitive and affective domain for the technology constructs. This shown that the alternate hypothesis, ‘Student attaches a value on the use of technology on collaborative learning’ and ‘Technology improves student’s learning’ was accepted. ITA and ITC have obtained the highest mean score for this research. This proved that technology plays an important role in student’s learning. Students value the usage and importance of internet during tutorial class to help them learn better. In a regular tutorial session, technology such as the internet is usually not used to aid students in answering the tutorial questions. However, when this was implemented in the intervention tutorial, a positive impact was observed for both cognitive and affective

domain as students were willing and preferred using the internet to aid their tutorial sessions.

In this research, learning space has also shown to have a positive impact on student's cognitive and affective learning domain. The null hypothesis 'Learning space does not improve student's learning' and 'Student does not attach a value on the positive effect of specially designed learning space for collaborative learning' respectively is rejected ($p\text{-value} = 0.001\text{-}0.011 < 0.05$), showing a significant difference between having tutorial session in X-Space and in regular classrooms. A huge difference in mean score between ISA and CSA was obtained from this research. This huge difference clearly shows that, there is a big impact on how student feels about their learning space. Among the 22 surveys received, 3 students agreed and recommended that the X-Space be used more often and no students rejected the use of X-space. Furthermore, one student commented that round table seating gives the illusion of a smaller class. This has shown that, students have attached a value on the positive effect of specially designed learning space for collaborative learning and, it can be concluded that learning space improves student's learning.

According to table 3.12, the mean for ISA and CSA are 3.89 and 2.77 respectively, and 4.24 and 3.39 for ITA and CTA respectively. This showed that, there is a very significant impact on students' affective domain due to space and technology. Student values the importance of learning space and technology on collaborative learning. The impact on pedagogy for both cognitive and affective is not as effective as technology and space. Students will need time to adapt toward a change in pedagogy as they are comfortable with the current pedagogy.

3.4 Visual Learning

Based on the learning style survey, the most preferred learning style was identified as the visual learning. According to the Advance Thermofluid Engineering's module coordinator, the lectures used for this semester was edited to be more visual aided compared to the previous semester. A survey on how the lecture slides helped the student to learn better was conducted.

A total of 20 students from the previous batch and 17 students from the current batch took part in this survey. The outcomes of these results were analyzed using the SPSS Statistic Software. Since the sample size for both batches was below 30, a normality test was conducted. The normality test showed that both sets of data were normally distributed ($p > 0.05$). Thus, an independent *t*-test was conduct. Table 3.13 and 3.14 below shows the descriptive statistic and the *t*-test results generated.

Table 3.13 Descriptive Statistic for Visual Learning Survey

Sem	N	Mean	Std. Deviation	Std. Error Mean
Score Mar14	19	2.9211	.80817	.18541
Mar15	16	3.3750	1.01242	.25311

Table 3.14 T-Test Results

		t-test for Equality of Means			
		Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence ...
					Lower
Score	Equal variances assumed	.150	-.45395	.30766	-1.07990
	Equal variances not assumed	.159	-.45395	.31375	-1.09606

The descriptive statistic in table 3.13 showed that, there is a slight difference in the mean score for both batches. However, the *t*-test has shown no significant differences in survey score of the student's learning between both batches. Upon initial observation it might seem that the more visual lecture slides for this semester did not have a significant impact. However further observation showed a significant improvement in the mean score this semester, 3.37 compared to 2.92 previously, and the presence of an outlier in the data.

The scores obtained for this survey ranged between 2 – 3.75 for the March'14 batch and between 1 - 4.75 for the March'15. For the March '15 cohort, one respondent returned a score of 1, which was inconsistent with the rest of the respondents' scores and hence was treated as an outlier. If the outlier was not considered then the scores for March'15 ranged from 2.25-4.75. The test was repeated by removing the outlier of 1. Table 3.15 shows the mean and standard deviation while Table 3.16 shows the *t*-test results. The standard deviation for March '15 cohort reduced from 1.01242 to 0.81759 when the outlier was removed. This resulting standard deviation with the outlier removed is more similar to the standard deviation of the March' 14 cohort of 0.80817, as shown in Table 3.15.

Tale 3.15 Descriptive statistic without the outlier

Sem	N	Mean	Std. Deviation	Std. Error Mean
Score Mar14	19	2.9211	.80817	.18541
Mar15	15	3.5333	.81759	.21110

Table 3.16 T-Test Result without the outlier

		t-test for Equality of Means			
		Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence ...
					Lower
Score	Equal variances assumed	.037	-.61228	.28057	-1.18378
	Equal variances not assumed	.037	-.61228	.28096	-1.18606

An outlier is a score that is not aligned with the rest of the data. An outlier can cause the standard deviation to increase and thus, causing an inaccurate conclusion from the *t*-test if the outlier cannot be justified. There are many reasons why an outlier

was observed in the data obtained such as, the student reluctantly participated in the survey or did not treat the survey seriously. Furthermore, this could also be a weak student who did not understand the subject and would have given a low score regardless of the type of slides used. This survey results has shown that, visual leaning do help students learn better. Hence, teaching geared to student's learning style is important.

4. Conclusion and Future Work

Based on the research question 'Can holistic education be delivered in an Engineering curriculum through personalized learning geared to the students' preferred learning style, through collaborative learning pedagogy, technology and space?' below are the main findings through this research;-

- Taylor's University Engineering students are mainly, **reflective, sensing, visual and sequential** learners.
- Almost 90% of the students are **visual leaners**.
- The development of the affective and psychomotor learning domains is as important as the cognitive learning domain to the industry.

The initial intervention failed to meet its objective. The full support and commitment of the program and the lecturer is crucial. This was not possible due to unforeseen circumstances that arise. Hence, a second attempt at performing the intervention was made with a different module, Advance Thermofluid Engineering, which was conducted by a different lecturer. Below are the findings from the second intervention:-

- There is **a significant difference** to the effect of technology and space on the students' cognitive and affective domain and the affective pedagogy domain.
- However, there is **no significant difference** to the effect of pedagogy on the students' cognitive domain.
- A significant difference was found in the visual learning survey, proving that teaching geared to student's learning style is important.

Hence pedagogy, technology and learning space do have an effect on students' learning not just cognitively but also affectively. Apart from the cognitive impact of collaborative learning pedagogy, all the other intervention effects were statistically significant. Also, a teaching style delivery more suited to the students' preferred learning style was shown to be helpful.

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Industrial Survey

Hi, my name is Jaclyn Choong. I am a 4th year Mechanical Engineering student in Taylor's School of Engineering. I'm currently doing a research on Engineering Education as my Final Year Project. This research is intended to help produce Engineering Graduates who can contribute effectively to the industry. The identities of companies and respondents will be kept confidential in the research analysis and reports.

Thank you very much for helping to answer this survey.

Have a good day

Warm Regards,
Jaclyn Choong
Mechanical Engineering, Sem 8

Supervisor - Mr Douglas Tong
(douglaskumtien.tong@taylors.edu.my)

* Required

1. Name of company

.....

2. Name of respondent

.....

6. Are the fresh engineering graduates well-versed in the subject(s) you identified above?

Mark only one oval.

- ☐ Very well-versed
☐ Well-versed
☐ Fairly well-versed
☐ Not well-versed

7. What are your expectation for fresh Engineering graduates?

More than 1 answer is possible.

Check all that apply.

- ☐ Good discipline specific knowledge
☐ Good communication skills
☐ Technical hands-on skills
☐ Able to think critically
☐ Able to learn independently
☐ Able to work with others
☐ Good attitude
☐ Ethical
☐ Other:

8. Are the current fresh Engineering graduates able to meet these expectation?

Mark only one oval.

- ☐ Yes, they are able to meet all the expectation
☐ They meet some of the expectation (acceptable)
☐ They meet the expectation but improvement can be done
☐ No, they don't meet the expectation

9. Please explain the reason for your answer above

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Appendix 2 – Student Survey Form

Module Identifying Survey

Hi, my name is Jaclyn Choong. I'm currently doing a research in Engineering Education as my Final Year Project. The objective of this survey is to find out which module offered by Taylor's School of Engineering (Mechanical Department) is the most difficult, in the student's point of view. Your opinion (as seniors) are very important for the future engineering students.

Please do spend a few minutes to read through and provide me your most valued opinion.

Thank you very much for your cooperation.

Have a good day :)

Warm Regards,
Jaclyn Choong
Final Year Mechanical Engineering Student

* Required

Engineering Mathematics 1	Thermodynamics and Heat Transfer
Engineering Mathematics 2	Engineering Statics
Engineering Mathematics 3	Engineering Dynamics
Engineering Mathematics 4	Engineering Fluid Mechanics
Properties and Applications of Materials	Internal Combustion Engines & Emission
Computing Applications for Engineers	Managing Projects for Success
Engineering Design & Communication	Engineering Design & Innovation
Multidisciplinary Engineering Design	Automatic Control & Instrumentation
Mechanical Engineering Group Project 1	Mechanical Engineering Group Project 2
Engineering Solid Mechanics	Theory of Machines and Mechanisms
Mechanical Vibration	Engineering Design & Ergonomics
Advance Thermofluid Engineering	Manufacturing Engineering
Business Skills For Engineers	Industrial Training
Professional Engineers & Society	Electronics & Microprocessors
Final year Engineering Project 1	Final Year Engineering Project 2
Computer Aided Engineering & Geometric Modeling	Numerical Analysis for Engineers with Applications using ANSYS
Data Measurement, Analysis & Experimental Design	Air Conditioning and Refrigeration Engineering
Introduction to Electronics & Electrical Power & Machines	Design of Engineering Components and Systems

1. Throughout your studies in Taylor's School of Engineering, which 3 module did you find MOST DIFFICULT? *

Most difficult first followed by the second and then third

2. Why do you think it was difficult?

3. If ONE module should be improved, which module should it be?

4. How can the module be improved?

Suggestions / Comments

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Appendix 3 – Post Survey Questions

Pedagogy

Intervention Questions

Control Questions

Affective

You were willing to participate in the group discussion	You were willing to participate in regular tutorial classes
You voluntarily contributed your input to your group	You voluntarily contributed your input to the entire tutorial class.
You feel that participation in group discussion is important to help you learn.	You feel that regular tutorial class is as effective as group discussion to help you learn.
After the session in X space, you feel that group discussion is helpful to you and should be continued.	After the session in X space, you feel there is no need for group discussion for tutorial

Intervention Questions

Control Questions

Cognitive

Solving the tutorial questions to together as a group helps you to remember what you learned	The lecturer solving the tutorial questions for you helps you to remember what was taught
Solving the tutorial questions to together as a group helps you to understand the subject matter	The lecturer solving the tutorial questions for you helps you to understand the subject matter
Solving the tutorial questions to together as a group helps you to apply what you learned.	The lecturer solving the tutorial questions for you helps you to apply what you learned
Solving the tutorial questions to together as a group helps you to analyze your tutorial questions	The lecturer solving the tutorial questions for you helps you to analyze your tutorial question

Space

Intervention Questions

Control Questions

Cognitive

If the group white board was used, would it helped you to learn better [yes-no]	
Sitting together around a round table in X-space facilitates your group discussion and therefore help you to learn (e.g. remember,understand,apply,analze)	Sitting in rows in a regular tutorial classroom helps you to learn (e.g. remember,understand,apply,analze)
The ergonomic chair in the X-Space makes you feel comfortable and therefore, help you to learn (e.g. remember,understand,apply,analze)	The regular chairs in the regular classroom makes you feel comfortable and therefore, help you to learn (e.g. remember,understand,apply,analze)

Space

Intervention Questions

Control Questions

Affective

You feel Sitting together on a round table in X-space is important because it facilitates group discussion and increases your willingness to participate.	You feel that the seating arrangement in a regular classroom is suitable for group discussion and participation.
You feel The comfort and maneuverability of the ergonomic chair in the X-Space is helpful for group discussion and active participation.	The chairs in the regular classrooms are useful for group discussion and participation
If the group white board was used, would it help in your group discussion [yes-no]	

Technology

Intervention Questions

Control Questions

Cognitive

The information found on the internet helped you to understand your quiz	You understand the tutorial questions without referring to the internet
You were able to apply the information found on the internet to your quiz	The information found on your lecture notes is sufficient to apply in your tutorial question.
The information from the internet helped you to analyze the quiz question.	You could analyze the tutorial questions by referring to your lecture notes

Intervention Questions

Control Questions

Affective

You were willing to use the internet for group quiz discussion	You were willing to use the internet during tutorial session to do the tutorial questions
You feel the use of the internet helped to facilitate the group discussion during the quiz discussion	You feel that the information learned during tutorial is sufficient and use of internet is not required during tutorial
You feel the use of internet for the quiz discussion is helpful and should be continued	You feel that the current tutorial method is sufficient and there is no need for quiz discussion using the internet.

Optimization Modeling Process of Commercial Computer-Aided-Design (CAD) software

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Abstract

The main objective of this project is to understand the philosophy behind the design methodology approaches and finding the most effective way to implement and integrate it into a Material Handling System (MHS) design process. In 1990, a \$5M worldwide study of the automobile manufacturing industry was published which attempted to shed light on the difference that exists in automotive assembly plants and the variations in productivity of these plants. Referring to Japan, which has the most productive plants in the world, automation of the plant processes only contribute to one-third of the difference in productivity between plants. The least automated Japanese plant, in which 34% of the manufacturing process is automated, is also the world's most efficient plant. It only needs one third the human labor of a comparable European plant. The European plant which is the most automated in the world, which automates 48% of the manufacturing process, needs 70% more effort compared to the Japanese plant. The authors of this study then concluded that no amount of improvements can be made to the productivity of the product design in question is defective. This then clearly shows the relation between the importance of design towards the productivity and efficiency of a manufacturing plant. [1] Relating back to the MHS, the current MHS in consideration is a gravity roller conveyor that is used in the car rim manufacturing industry in Malaysia. Simulation using Solidworks is done to test conveyor structures of different dimensions to get the best possible results in terms of stress, strain and displacement. The optimization of its design is done so that parts reduction can be achieved while also having a lowered cost, time and manpower to manufacture and assemble the MHS.

Keywords: Solidworks, MHS, conveyor, manufacturing, design, optimization

1. Introduction

Design is the first and ultimate step in manufacturing. The design process is essentially a series of steps that are used to create a product. It consists mainly of research, conceptualization, identifying the design requirements, detailed design and production planning. All these are important decisions which affect the final cost of the product. [2]

Many design techniques have been developed throughout the years to help designers in designing products that are easy to manufacture and assemble. The function of these techniques is to reduce the time taken for production, reduce inventory, shorter the time to market and eventually produce a better quality product. [2]

Of the many design tools that are present on the market today, Computer-Aided Design (CAD) is one of the most popular and successful ways to help engineers in designing products. CAD is the use of computer technology to enhance the design process. [3] This is primarily used to increase the efficiency and productivity of the designer, improve the quality of the design, better structure to design documentation and file sharing, as well as creating a database for manufacturing processes. CAD environments consist of more than just shapes and sizes. This technology is used to provide information on materials, dimensions, tolerances, strengths, aerodynamics, and contours depending on the application intended. Current CAD softwares include 3D solid and surface modeling. Solid modeling is essentially the designing of products or objects with a uniform and standard shape or dimensions whereas surface modeling is the practice of designing products with irregular surfaces such as automobiles and sculptures. CAD allows the viewing of designed products from any desired angle, looking in the outer surface and also from inside looking out.

Sketches are always the first step in the design process. [4] These drawings are then produced using CAD drawing programs such as Solidworks which will generate a detailed drawing of parts and assembly to be passed on to the manufacturing and assembly department. The manufacturing and assembly department functions to optimize the processes required to produce the components according to the designs given. Normally, in this stage, manufacturing and tooling problems are encountered and this is where design revisions are requested to fit into the manufacturing limits. The more changes that occur in the redesigning of the components, the more expensive they become. This shows that it is very important to take manufacturing and productions limits into account during the designing phase. Although this makes the designing phase longer and consumes more time, it actually saves time in the long run and compensates for any problems that might occur during the manufacturing phase of the product. This is where the implementation of the Design for Manufacturing and Assembly (DFMA) benefits the manufacturing process by reducing product cost as well as shortening the time taken to market the product.

DFMA provides a structured approach to analyzing a product design. The application of DFMA on a product results in a simplified design which benefits in terms of parts reduction, manufacturing time and the overall cost of the production. DFMA also promotes the communication between the design and manufacturing departments and shows the importance of dialogue and understanding between all parties who play a part in determining the final cost of the product. [5]

The product that is being optimized in this project is an improved version of a material handling system, specifically a gravity roller conveyor. A gravity roller conveyor is essentially a mechanical conveyor belt albeit with the absence of a driving motor. As the name suggests, gravity is used to transport objects on rollers by

the means of a declining angle in the conveyor structure, allowing the transported objects to slide down the conveyor. This kind of conveyor is then much more cost effective as well as easier to manufacture and assemble compared to that of a conventional motor-driven roller conveyor. [6]

1.1 Objective

4. Design and model a Material Handling System (MHS) for the car rim manufacturing industry.
5. Compare and contrast different designs of the gravity roller conveyor to find out the best design possible.
6. Improved design should be cost efficient as well as easy to assemble and manufacture

2. Methodology

2.1. Parameters

The gravity roller in this project is designed to transport car rims in a car rim factory plant in Malaysia. Several parameters must be determined in order for the design and simulation of the conveyor to be precise and accurate. [8]

2.1.1. Roller Spacing

The range of rim size the conveyor is catering for, is determined by surveying the smallest and biggest rim size of the most popular commercial vehicles in Malaysia. The smallest rim size belongs to the Perodua Myvi, with the rim size of 14 inches in diameter, whereas the biggest rim size belongs to the Toyota Hilux, at a rim size of 18 inches in diameter. [7] The roller spacing of the conveyor is then calculated by dividing the largest rim diameter by four, as the standard procedure in the car rim manufacturing industry is to have a minimum of three rollers supporting a single car rim at all times throughout the transporting process.

2.1.2. Roller Capacity

As the range of rim size is from 14 to 18 inches in diameter, alloy rims of these sizes have a range from 12 kg to 20kg. For safety precautions, the maximum rim weight is set at 30 kg as sometimes the biggest rims' weight may vary slightly. Rollers are chosen according to the maximum rim weight and conveyor width.

2.1.3. Conveyor Width

The width of the conveyor is usually specified as the dimension in between the two frames of the conveyor. A clearance of 100 mm is added to the biggest diameter of the range of rim sizes and the sum is the determined width of the conveyor. The total width is then rounded up to a value of 540 mm which is 54 cm.

2.1.4. Conveyor Length

The length of the conveyor is determined by arranging 10 rims side by side and adding the total length of the rims together. The length is rounded up to 4500 mm which is 4.5 m.

2.2. Geometry

2.2.1. Conveyor Frame

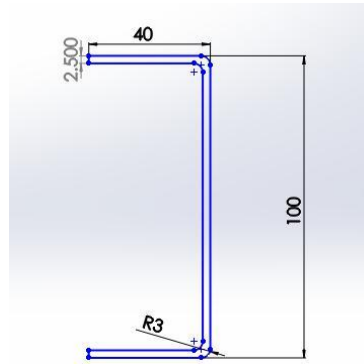


Figure 1. C-channel dimensions

The conveyor frame is made up of a c-channel, made from AISI 1010 steel, hot rolled. The dimensions for this c-channel is 100 mm in height and 40 mm in width, with a bend radius of 3 mm. The thicknesses of the c-channel tested in this project are 3.5 mm, 2.5 mm, 1.5 mm and 1 mm. The above sketch of the c-channel is drawn onto a sketch plane in Solidworks and the command, boss extrude, is used to form a solid conveyor frame with a length of 4.5 m.

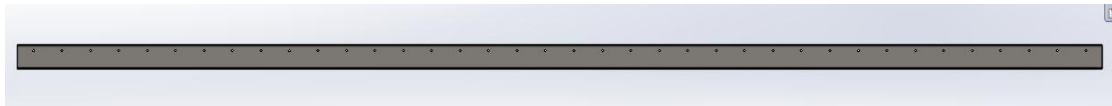


Figure 2. Conveyor frame holes

A hole with the diameter of 8 mm is then drawn on the side of the conveyor frame with a position of 24 mm below the top of the frame and 27 mm to the right of the side of the frame. The command, linear sketch pattern, is then used to create multiples of the holes with an interval of 114 mm. This then creates 40 circles on the frame. The command, extrude cut, is then executed to cut the 40 holes into the conveyor frame. These holes are the spacing to fit in the rollers and make them stay in place.

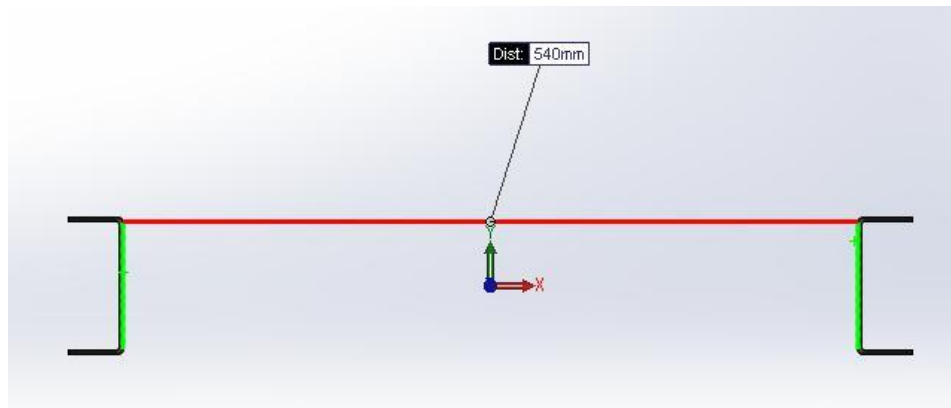


Figure 3. Conveyor frame sketch

The frame is then duplicated on the right side with a distance of 540 mm in between the two frames. This is done by creating a new plane that is 270 mm away from the left frame and using the mirror command to duplicate the frame. This structure completes the conveyor frame.

2.2.2. Conveyor Stand

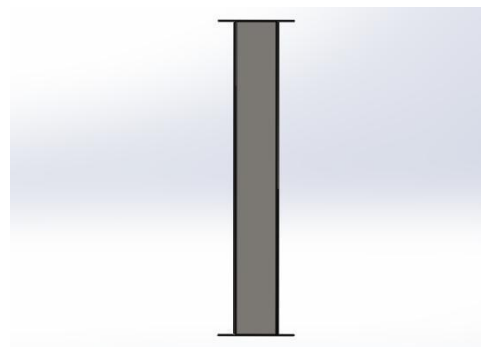


Figure 4. Conveyor stand

The conveyor stand is made up of a c-channel, identical in dimension to that of the conveyor frame, and a flat piece of metal joined on the two ends of the c-channel. The height of the stand is set to be 700 mm. The flat pieces of steel are the attachment points of the conveyor stand to the ground, on the lower end, and to the bottom of the conveyor frame, on the upper end. The arrangement of the c-channel can be seen in Figure 5, using the hidden lines view in Solidworks.



Figure 5. Conveyor frame sketch

The thicknesses of the conveyor stands tested in this project are also identical to that of the conveyor frame, which are 3.5 mm, 2.5 mm, 1.5 mm and 1 mm.

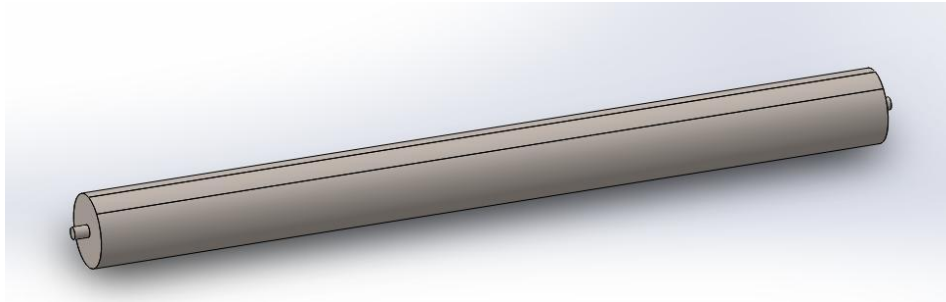


Figure 6. Conveyor roller

The conveyor roller is specifically chosen to be able to support the weight of rims transported.

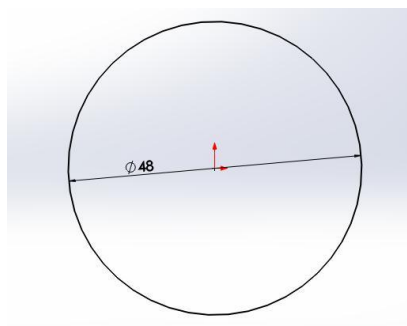


Figure 7. Conveyor roller sketch

The outer diameter of the roller is 48 mm, the dimension of a circle sketch drawn onto a sketch plane. The sketch is then made into a solid roller of 530 mm length, using the boss extrude command.

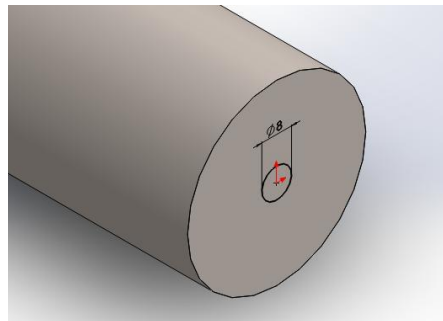


Figure 8. Roller additional sketch

The attachment points for the rollers onto the conveyor frame are two small cylinders on either end of the roller. This is made by sketching a circle of 8 mm diameter on the end face of the roller, positioning it right in the middle of the face. It is then extruded to form a solid 10 mm cylinder. This step is repeated for the opposite end of the roller so that there are two small cylinders of length 10 mm in total in the roller structure.

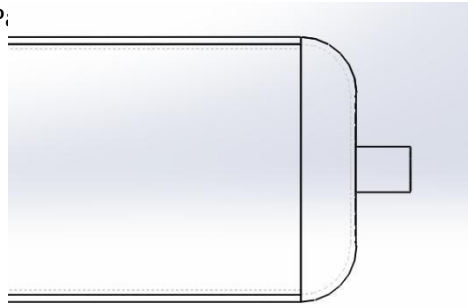


Figure 9. Conveyor roller shell

The roller is then made hollow with a thickness of 0.9 mm using the shell feature in Solidworks. This is done to recreate the strength of a realistic gravity roller that has the ability to support loads of up to 30 kg.

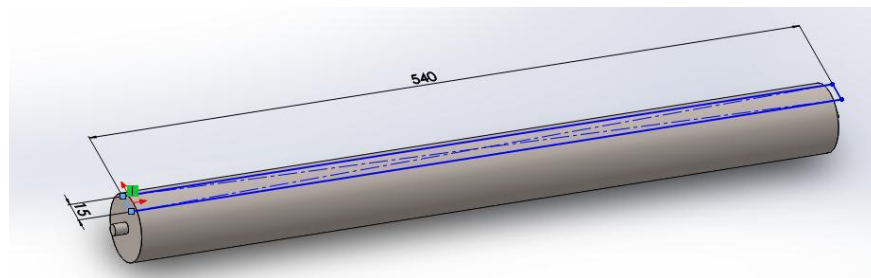


Figure 10. Split line sketch

A split line is drawn onto the top most face of the roller. The split line function is used to separate a singular face into multiple faces. This is particularly needed in the roller structure as during simulation, when a force is being applied, the top most face of the roller, separated from the singular circular face using the split line feature, can be selected as where the force is being applied on. This is to simulate a more realistic scenario of a conveyor, where the transported rims only apply force on the top of the conveyor rollers.

2.2.4. Horizontal stand support

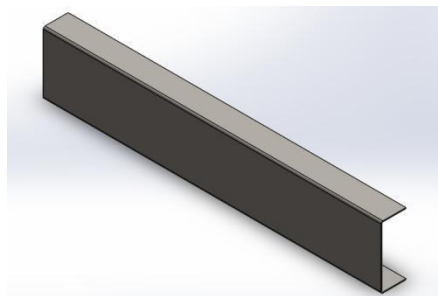


Figure 11. Conveyor horizontal support

The horizontal stand support is essentially the exact same c-channel as the conveyor frame. However, it is at a length of 540 mm to fit in between the conveyor stands to provide lateral support.

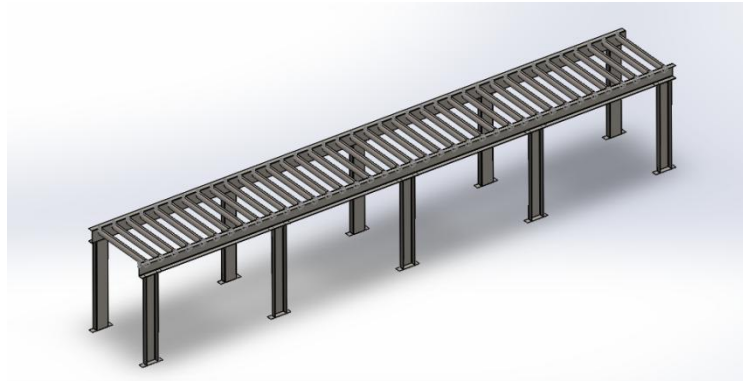


Figure 12. Conveyor assembly

To complete the full structure of the gravity roller conveyor, all three types of conveyor components are assembled together in Solidworks in an assembly file. First, the conveyor frame is inserted into the assembly.

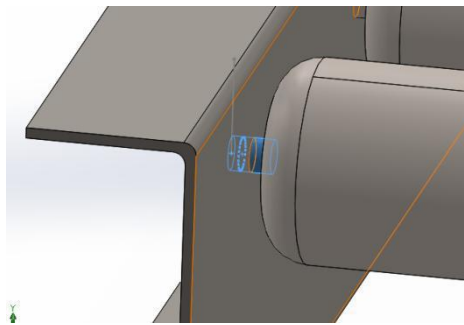


Figure 13. Assembly mate 1

The rollers are then mated to each hole in the conveyor frame using the concentric feature, choosing the inner surface of the conveyor frame hole and the outer surface of the small cylinder of the roller. This is to make the roller in line with the hole in the conveyor frame so that the cylinder can fit through the hole properly.

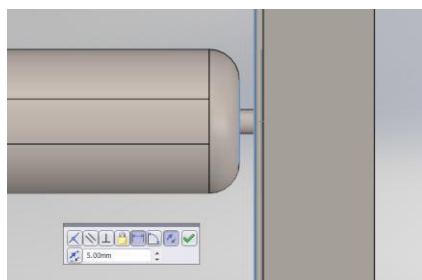


Figure 14. Assembly mate 2

The end surface of the roller is then mated to the inner surface of the frame by using a distance mate, specifying the distance at 5 mm, so that the distance of both ends of the roller to the inner surface of the frame will be identical, thus creating a symmetrical structure.

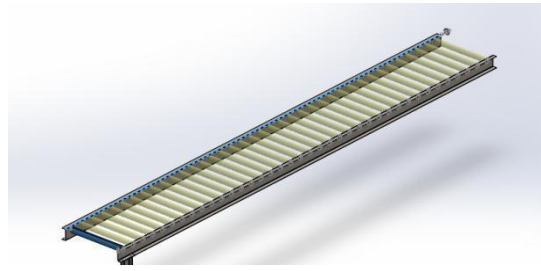


Figure 15. Assembly mate 3

The roller is then multiplied by using the linear pattern components function. Choosing the roller as the component to be patterned and the direction that the pattern takes place, at an interval of 114 mm, 40 rollers are patterned to fit into the 40 holes present in the conveyor frame.

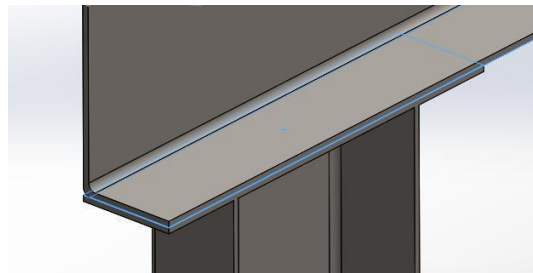


Figure 16. Assembly mate 4

The stand is then added into the assembly. It is first mated by selecting the top most surface of the stand and the bottom most surface of the frame.

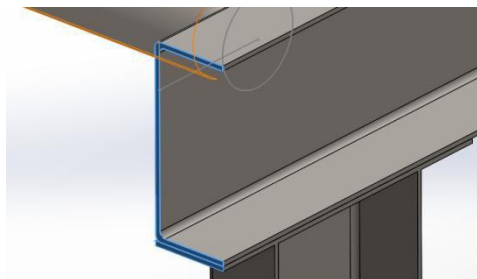


Figure 17. Assembly mate 5

The two left most surfaces of the stand and the frame are mated together. This is done so to make sure that the stand is in a proper position.

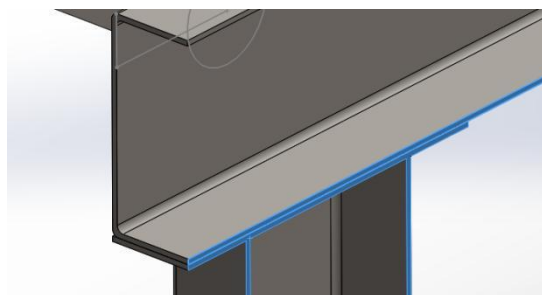


Figure 18. Assembly mate 6

The other two surfaces of the stand and the frame are mated together. This is done to lock the stand in place and to make sure it is a fixed component.

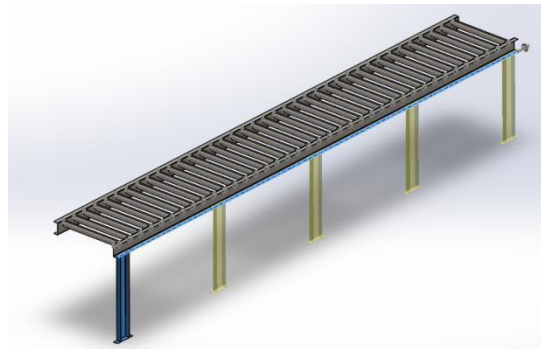


Figure 19. Conveyor stands linear pattern

The stand is then multiplied by using the same method as the multiplication of the rollers. This time however, the interval is set at 1082.5 mm, to have 5 stands to support one half of the conveyor frame.

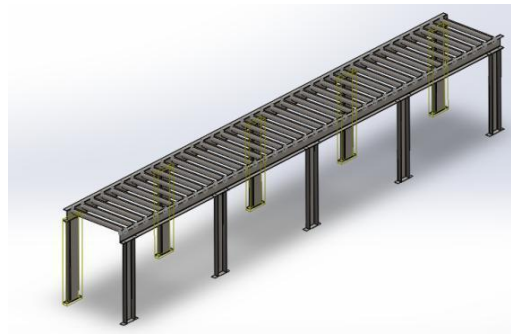


Figure 20. Conveyor full assembly

The stands are then mirrored across the other half of the frame to form 5 complete sets of conveyor stands. This is done by creating a plane in the middle of the two halves of the frame and by using the mirror components feature, selecting the 5 stands to be mirrored onto the opposite half of the frame. In this project, the conveyor is also tested with the assembly of the conveyor frame and 4 sets of stands as well as with the addition of horizontal stand supports.

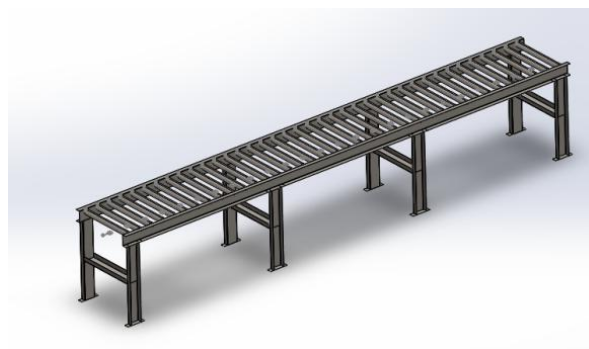


Figure 21. Conveyor full assembly with horizontal support

The horizontal stand support is attached in between one set of stands and is set at 350 mm above the ground. It is then linearly patterned so that every set of stands has a horizontal stand support.

2.3. Simulation

A static study in Solidworks simulation is created to test the stress, strain and displacement that take place in the conveyor structure when a force is loaded onto it.

2.3.1. Materials

The conveyor frames, stands, and horizontal supports are all set to AISI 1010 steel, hot rolled, as the material of choice. This is because it is the most common type of metal available and is cost effective. The rollers are set to stainless steel.

2.3.2. Fixtures

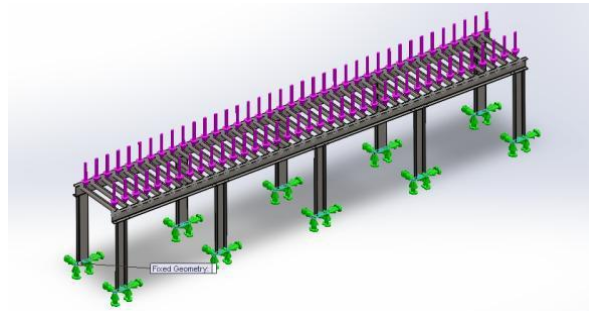


Figure 22. Fixed geometry

The bottom most surfaces of all the conveyor stands are set as fixed geometry. This is done to simulate an actual scenario where the conveyor will be attached to the ground via the bottom of the stands.

2.3.3. External Loads

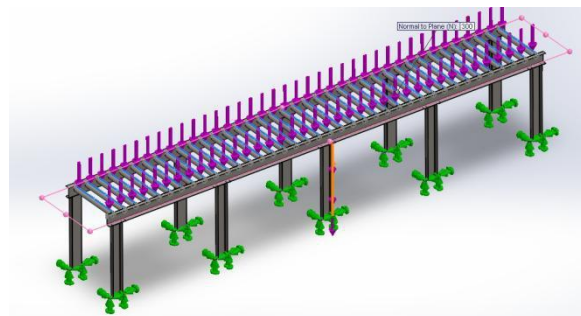


Figure 23. Force applied

The top most surface of the rollers that were created using the split line feature are selected to be applied with a load of 300 N for each roller. The force is applied downwards, simulating the load that is supported by the conveyor when rims are loaded onto the rollers. The value of 300 N is chosen because the theoretical weight that a single roller should be able to support is 30 kg, based on the length and size of the rollers chosen.

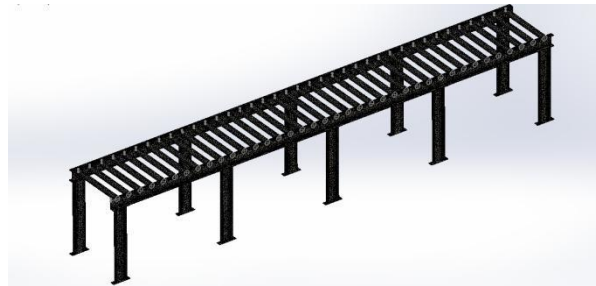


Figure 24. Conveyor structure meshing

Meshing for the conveyor structure is done by setting the mesh to the finest density. This is done as the conveyor structure is very thin and the results obtained should be as accurate as possible. In the mesh perimeters, the type of mesh is changed to curvature based mesh as there are small curves in the structure due to the bends in the c-channels. The simulation is then run to obtain the results in terms of stress, strain and displacement that take place in the conveyor structure.

3. Reported Outcomes

Table 1. Solidworks stress simulation results and analysis

Thickness of C channel (mm)	Number of pairs of stands	Horizontal Support	Force Applied (N)	Max Stress von Mises (N/m ²)	Percentage of stress increment
3.5	5	No	300	35331208	6%
3.5	4	No	300	57910840	74%
3.5	4	Yes	300	44997336	35%
2.5	5	No	300	33232206	0%
2.5	4	No	300	68942544	107%
2.5	4	Yes	300	58663208	77%
1.5	5	No	300	70323608	112%
1.5	4	No	300	97529904	193%
1.5	4	Yes	300	88937976	168%
1	5	No	300	80436800	142%
1	4	No	300	162485984	389%
1	4	Yes	300	229836176	592%

Table 2. Solidworks displacement simulation results and analysis

Thickness of C channel (mm)	Number of pairs of stands	Horizontal Support	Force Applied (N)	Max Displacement URES (mm)	Percentage of displacement increment
3.5	5	No	300	7.66E-02	2%
3.5	4	No	300	1.78E-01	137%
3.5	4	Yes	300	1.83E-01	144%
2.5	5	No	300	7.48E-02	0%
2.5	4	No	300	2.61E-01	248%
2.5	4	Yes	300	2.49E-01	233%
1.5	5	No	300	2.45E-01	228%
1.5	4	No	300	5.05E-01	574%
1.5	4	Yes	300	4.90E-01	555%
1	5	No	300	2.99E-01	299%
1	4	No	300	7.69E-01	927%
1	4	Yes	300	9.87E-01	1219%

Table 3. Solidworks strain simulation results and analysis

Thickness of C channel (mm)	Number of pairs of stands	Horizontal Support	Force Applied (N)	Max Strain ESTRN	Percentage of strain increment
3.5	5	No	300	1.07E-04	0%
3.5	4	No	300	1.77E-04	66%
3.5	4	Yes	300	1.40E-04	31%
2.5	5	No	300	1.10E-04	3%
2.5	4	No	300	2.06E-04	93%
2.5	4	Yes	300	1.81E-04	69%
1.5	5	No	300	2.00E-04	87%
1.5	4	No	300	2.64E-04	147%
1.5	4	Yes	300	2.42E-04	127%
1	5	No	300	2.59E-04	143%
1	4	No	300	4.92E-04	360%
1	4	Yes	300	5.56E-04	421%

The first four columns of the tables consist of the manipulated and fixed variables. The green columns are the reported results obtained from the simulation done in Solidworks. In the green columns, the results in red of each column are the lowest values obtained of each conveyor thickness tested. The blue columns are the analysis of the results obtained from the simulation. This is done by using percentage of increment over the lowest value obtained in the stress, strain and displacement results. The yellow highlighted boxes are the three least increments in the stress, strain and displacement results.

4. Conclusions

According to this analysis, the conveyor with the c-channel thickness of 2.5 mm, 5 pairs of stands and no horizontal support is has the best average overall results. It has the lowest stress and displacement values as well as very minimal 3 percent increment over the lowest value in the strain results. It is then considered that this option is the best overall design. The composition of the structure of the conveyor was designed to be cost effective as the c-channel of the same dimensions is used for the frame as well as the stands. This is so that no extra processes have to be undertaken and the manufacturing as well as assembly of the conveyor will be as minimal as possible.

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Analytical and Experimental Analysis on Design Parameters of Double-Pipe Heat Exchanger – Developing Empirical Models

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Abstract

Double pipe heat exchangers are units used to transfer heat from a higher temperature fluid to lower temperature fluid as the higher temperature fluid possess more energy. Due to its functional complexity, the double pipe heat exchanger usage in the industry such as food and dairy industry contributes to high cost and high time wastage. Hence, this paper presents the development of empirical models to analyse the important design parameters affecting the performance of the heat exchanger such as the overall heat transfer coefficient (OHTC), amount of heat exchanged (HEX) and the flow rate of the hot and cold fluids fluid FR_H and FR_C respectively. These empirical models provides a quick, simple and yet accurate and reliable means for the heat exchanger designers to identify the design parameters that are more influential on the performance of the double-pipe heat exchangers during the preliminary design stages. In this paper, 4 models were created and from these 4 models, Model 1 and Model 4 were selected for the OHTC and HEX variable as it shows the highest percentage of accuracy from the multiple regression analysis. Model 1 shows accuracy of up to 92.2% whereas Model 4 shows accuracy of up to 89.3% based on the statistical analysis obtained. The empirical formulae obtained for Model 1 is $OHTC_{parallel} = 274 (FR_H) - 183(FR_C) + 204$, whereas the empirical formulae for Model 4 is $HEX_{counter} = 300 (FR_H) + 350(FR_C) + 161$. However Model 2 and 3 are slightly least accurate compared to Model 1 and 4 with an accuracy of 91.9% and 86.9% respectively. The empirical formulae for these two models was obtained as $OHTC_{counter} = 329 (FR_H) - 228(FR_C) + 270$ and $HEX_{parallel} = 264 (FR_H) + 305(FR_C) + 250$. Therefore to make the empirical models more reliable and reduce the overall error of the system, more parameters can be investigated and included into the empirical models

Keywords: Double pipe heat exchanger, Water, Experimental, Analytical, Empirical models.

1. INTRODUCTION

Heat exchanger is a device built to transfer heat from one region to another, even though there is a wall barrier that separates the two different regions so that they fluids in the region will not be able to mix. Heat exchangers are widely used in space heating, refrigeration, air conditioning, power plants, chemical plants, petrochemical plants, and other applications

In co-current flow arrangement of heat exchanger, both hot and cold fluid enters the heat exchanger in the same direction, whereas for counter-current flow arrangement heat exchanger, the hot and cold fluids enter the heat exchanger in an opposite direction.

The first law of thermodynamics or the conservation of energy states that, energy can neither be created nor destroyed during a process; it can only changes its forms. In another word the net change of the total energy in a system during a process is equals to the difference between the total energy entering and the total energy leaving the system [1].

Typically heat exchanger involves two flowing fluids that are separated by a solid wall. Hence, the heat transfer that will take place throughout the fluids flow in the heat exchanger will be conduction and convection Conduction is the heat transfer due to its molecular interaction whereas convection is heat transfer due to the fluids that were carried to another region of space in a system.

In addition, there are many parameters that will affect the efficiency and heat transfer efficiency of the heat exchanger. Some examples of these parameters are the flow rate and the power emitted and absorbed by the fluid, as these are the parameters that would give significant impact on the effectiveness of the double pipe heat exchanger.

Hence, the main objective of this research is specifically driven by the need to develop reliable empirical formulae which may replace the tedious and complicated process when designing the heat exchanger. These formulae do not need to use the tables and other theoretical means. Therefore, the main purpose of this paper is to provide a quick, simple and yet accurate and reliable means for the heat exchanger designers to identify the design parameters that are more influential on the performance of the double-pipe heat exchangers during the preliminary design stages. This will also reflect in saving money and time when performing tedious calculations, experiments and tests.

2. Methodology

2.1 Double Pipe Heat Exchanger

Figure 1 show the experimental set up used in this research.

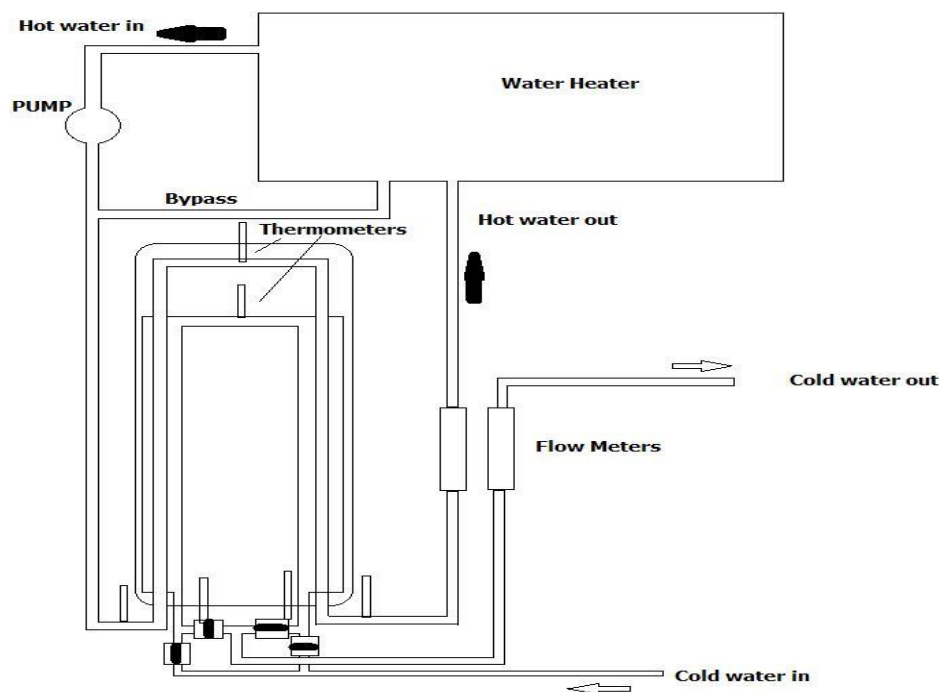


Figure 1. H900 Concentric Double Pipe Heat Exchanger

The experiments for this research were conducted using the H900 Concentric Tube Heat Exchanger unit by P.A Hilton Ltd as shown in Fig. 1. In this paper, the double pipe heat exchanger was used to conduct the experiments to obtain the temperature of the hot fluid and cold fluid upon flowing through the concentric tube of the double pipe heat exchanger. The working fluid of this research is water, as the H900 Concentric Tube Heat Exchanger unit that is provided for this research only allows the usage of water as its working fluid. In addition, the H900 Concentric Tube Heat Exchanger unit consists of six thermometers, one cold water and hot water flow rate meter and several valves to change the flow of the double pipe heat exchanger unit from co current flow to counter current flow and vice versa [2]. Besides that, in this system the cold water and hot water was supplied from the nearest water pipe source at the laboratory. The temperature of the water from the pipe will be around room temperature, approximately 30 °C depending on the time at which the experiment was conducted and the hot water input will be pre-heated by the water heater to around 65 °C to 66 °C in order to begin the experiment analysis.

2.2 Parameters Selections and Assumptions

In the current work, several parameters have been analysed to study the effect of the overall heat transfer coefficient and the amount of heat exchanged throughout the system. This was conducted by varying the hot water flow rate while fixing a constant flow of cold water flow rate into the system of two different types of flow

arrangements which are, parallel and counter current flow rate The lists of parameters that are considered in this research are;

7. Overall heat transfer coefficient (OHTC)
8. Amount of heat exchanged (HEX)
9. Flow rate of hot and cold fluid (FR_H , FR_C)

This experimental unit was specifically designed to study the effect of manipulating the hot and cold water flow rate on the overall heat transfer coefficient (OHTC) and the amount of heat exchanged (HEX) by the hot and cold fluid throughout the experiments that was taken place by using two main conditions, co-current and counter current flow of the fluid. In a study that was conducted by Chaudhari et al., it was discovered that some of the most common challenges in the industry was to extract maximum amount of heat from a process in order for the heating process to occur efficiently to increase the overall heat transfer coefficient of the industrial process [3]. Hence the current solution of this industrial problem was done by increasing the surface area of the heat transfer area however this approach seems to increase of cost of the industrial manufacturing process [3]. This shows the importance of considering the inclusion of the total heat energy exchanged throughout the operation of a double pipe heat exchanger in the industry. In addition, Chaudhari et al. also stated that traditional design methods such as trial and error approach was used to investigate the design variables that affects the performance of the double pipe heat exchanger. However this approach was said to be very tedious and time consuming. As a result of this, by including the total heat energy exchanged and the overall heat transfer coefficient in the empirical model that was developed, it will be a good approach that will save time and cost of the manufacturer in the preliminary design stages of the development process in a specific industry.

For this research, due to the limitation of the available resources and flexibility of the H900 concentric tube heat exchanger, the OHTC and HEX were chosen as the independent variable whereas the flow rate of the hot (FR_H) and cold fluids (FR_C) are the dependent variables of this research.

Double pipe heat exchanger is said to be a complex system if many variables were considered throughout its operation. Hence in order to isolate the behavior of the two main parameters of this research that is the OHTC and HEX, several assumptions were made;

- 2.4 Atmospheric/Room temperature = $25^{\circ}C$
- 2.5 Kinetic and potential energy are considered negligible
- 2.6 The system runs in a steady state
- 2.7 Pressure drop across the system is negligible

Upon obtaining the overall heat transfer coefficient (OHTC) and total amount of heat exchanged (HEX) by the double pipe heat exchanger during its flow in parallel and counter current flow, comparisons were made by its theoretical values that have been calculated. The main reason is to analyze the difference and its percentage of errors of the experimental values in respect to the analytical values of the two parameters that were mentioned above.

2.3 Overall Heat Transfer Coefficient (OHTC)

The overall heat transfer coefficient of a system is an important parameter to investigate the effectiveness of the heat that is transferred from a hot fluid to a cooler fluid. This mainly occurs in a heat exchanger unit at which the heat is transferred from a hotter fluid to the wall by convection, through the wall by conduction and again from the wall to the cold fluid by convection [4]. However for this research purpose, the conduction phase of the concentric tube is neglected as the heat transfer due to conduction is significantly small. To calculate the overall heat transfer coefficient, there are two phase involved which are; experimental calculations and analytical calculations.

2.3.1 Experimental Calculations

The experimental calculations of this research are mainly based on the formulas given by the H900 Concentric Tube Heat Exchanger handbook. Therefore to calculate the overall heat transfer coefficient, the main formula that was used is as shown in Eq. (1);

$$U = \frac{Q}{A \times T_{LMTD}} \quad (1)$$

U = Overall heat transfer coefficient ($\frac{W}{m^2 \cdot ^\circ C}$)

Q = Power absorbed (W)

A = Heat transmission area (m^2)

T_{LMTD} = Temperature of the Log Mean Temperature Difference ($^\circ C$)

As seen from the equation above, the overall heat transfer coefficient is a function of the power absorbed by the cold fluid from the hot fluid, the affected area at which heat energy is transferred and also the temperature of the Log Mean Temperature Difference (LMTD). For this H900 experimental unit, the area at which heat energy is transferred was given in the handbook with a constant value of $0.067m^2$ [2]. The formulas that were used to calculate the power absorbed is as shown Eq. (2);

$$Q_{absorb} = \dot{m} \rho_c C p_c (tc_{out} - tc_{in}) \quad (2)$$

$\dot{m}$ = mass flow rate of the cold fluid (kg/s)

ρ_c = density of the cold fluid (kg/m^3)

$C p_c$ = specific heat capacity of cold fluid ($J/g \cdot ^\circ C$)

tc_{out} = temperature of cold fluid outlet ($^\circ C$)

tc_{in} = temperature of cold fluid inlet ($^\circ C$)

Upon calculating the overall heat transfer coefficient and power absorbed from Eqs. (1) and (2), the experimental value of the overall heat transfer coefficient of the system with two different types of flow that are concurrent and counter current flow can be calculated.

For this research, the range of flow rates that were manipulated is 1 L/min, 1.5 L/min, 2 L/min, 2.5 L/min, 3 L/min, 3.5 L/min and 4 L/min. Therefore, in order to calculate the theoretical overall heat transfer coefficient, firstly the velocity, V of the flow must be obtained by using the formula in Eq. (3);

$$V = \frac{\dot{m}}{\rho A} \quad (3)$$

Upon calculating the velocity of the flow in (m/s), the next step will be to calculate the Reynold's Number for each case of the flow rates with the given formula in Eq. (4);

$$Re = \frac{DV\rho}{\mu} \quad (4)$$

where μ = dynamic viscosity of the water (Pa.s)

By applying this formula, the Reynold's number for each flow rate was obtained. The Reynold's number varies according to the flow rate of the hot fluid into the system. Therefore it was observed that there are different ranges of Reynold's Number that was affected by the flow, leading from laminar flow all the way to turbulent flow. For the laminar flow, at which with the Reynold's number less than 2300, Mehrabian et al. [5] stated that the Hausen's correlation being used to calculate the Nusselt number as this relation is said to be used for a flow that is developing hydrodynamically at which the Prandtl number, Pr is more than five [1]. Therefore, as the Prandtl number for this research is more than 5, the Hausen's correlation can be used as shown in Eq. (5);

$$Nu = 3.66 + \frac{0.065 \left(\frac{D}{L}\right) Re Pr}{1 + 0.04 \left[\left(\frac{D}{L}\right) Re Pr\right]^{\frac{2}{3}}} \quad (5)$$

The main reason the above correlation was used is because, when the Reynold's number is less than 2300, it is said to undergo laminar flow [6]. According to Cengel et al., this is the correlation that can be used to evaluate the Nusselt number of the flow. For the flow that has the Reynold's number with the approximation of 2800, Cengel et al. stated that different correlation needs to be applied with the usage of hydraulic diameter, D_h [1]. This is because the hydraulic diameter applies when the fluid flows through an annular tube similar to experiment set used in this research. Thus, the correlation used for this case is as shown in Eq. (6);

$$Nu = 7.54 + \frac{0.03 \left(\frac{D_h}{L}\right) Re Pr}{1 + 0.016 \left[\left(\frac{D_h}{L}\right) Re Pr\right]^{\frac{2}{3}}} \quad (6)$$

where; $D_h = D_{outer} - D_{inner}$

Finally for the Reynold's number which are greater than 3000 falls under the turbulent flow thus the best correlation that can be used for this range of Reynold's number is the Gnielinski correlation which provide better accuracy of the Nusselt number value as shown in Eq. (7);

$$Nu = \frac{\left(\frac{f}{8}\right)(Re-1000)Pr}{1+12.7\left(\frac{f}{8}\right)^{0.5}\left(\frac{Pr}{Pr^{\frac{2}{3}}}-1\right)} \quad (7)$$

Besides that, there is a new factor that is included that is the friction factor, f . Friction factor is an important factor to be considered in this paper as it will provide a more accurate correlation to consider frictional factor that occur in a pipe [7]. This friction factor varies according to the Reynold's number and it is given with the formula as shown in Eq. (8) [7];

$$f = (0.790 \ln Re - 1.64)^{-2} \quad (8)$$

By applying the correlations stated in Eq. (8), depending on the value of the Reynold's number obtained, the Nusselt number can be calculated for each case. Upon calculating the Nusselt number, the convective heat transfer coefficient, h can be calculated using the formula in Eq. (9)

$$h_{in} = \frac{Nu \times k}{D_h} \quad (9)$$

The final step of calculating the analytical overall heat transfer coefficient was done by applying the calculated convective heat transfer coefficient, h_{in} and the constant value of h_{out} as the convective heat transfer coefficient of the air surrounding the concentric tube into the Eq. (10) [8];

$$\frac{1}{U} = \frac{D_{outer}}{D_{inner} \times h_{in}} + \frac{1}{h_{out}} \quad (10)$$

In this equation, one small assumption was made that is the resistance due to the conduction of the wall of the tube was neglected as the value shows significantly small value [9]. As a result, resistance due to conduction was cancelled out in this equation to provide a less tedious work on the calculation of the overall heat transfer coefficient as conduction provides small difference in the overall heat transfer coefficient of the system.

2.4 Amount of heat exchanged (HEX)

In this research, another parameter that has been taken into consideration was the amount of heat exchanged between the hot fluid and the cold fluid. It is important to consider the effect of the amount of heat exchanged between the fluids for the performance of the double pipe heat exchanger. Besides that, the amount of heat exchanged between the fluids also widely dependent of the flow rate of the hot and cold fluid because, if a higher flow rate of hot fluid was being flowed across a lower flow rate of a cold fluid, the amounts of heat energy exchanged will be the highest.

2.4.1 Experimental calculation

According to the First Law of Thermodynamics or known as conservation of energy principle, the total energy absorbed in a steady state system is equals to the total energy that is emitted in a system [1]. During the consideration of this parameter, by obeying the First Law of Thermodynamics, the total amount of heat energy absorbed by the cold fluid is equals to the total energy emitted by the hot fluid. Therefore to calculate the experimental amount of heat exchanged as shown in the handbook of the experimental as shown in Eq. (2).

2.4.2 Theoretical calculation

As the H900 concentric tube heat exchanger unit is a closed system. Therefore for a steady flow system with one inlet and one outlet, Cengel et al. stated that the rate of the mass flowing out of the control volume must be equal to the mass flowing into the system [1]. Hence, the theoretical amount of heat exchanged in the system was calculated based on the Principle of Conservation of Energy as shown below;

$$\dot{Q} = \dot{m}C_p (t_{out} - t_{in}) \quad (11)$$

2.5 Multiple Regression Analysis

In this research, the data was manipulated and analysed using premium statistical software called IBM SPSS Statistics 21 [10]. This software is well established statistical analysis method as it provides the user a wide range of options of conducting statistical analysis, at which for this research purpose is the multiple regression analysis.

As previously mentioned the dependent variable used in the development of empirical model is the overall heat transfer coefficient (OHTC) and the amount of heat exchanged (HEX) whereas the independent variable is the flow rate of hot and cold fluid (FR_H , FR_C) for both concurrent and counter current flow. The outcome of the study was to develop an empirical model in the form of a linear equation as shown in Eqs. (12) and (13). Additionally, Patil et al. stated that to form empirical model coefficients such as A, B and C will be added into the equation to obtain a more accurate empirical model [11]. Therefore, Eqs. (12) and (13) show the sample of equation of the empirical model with the dependent variables of OHTC & HEX;

$$OHTC = A_1 (FR_H) + B_1 (FR_C) + C_1 \quad (12)$$

$$HEX = A_2 (FR_H) + B_2 (FR_C) + C_2 \quad (13)$$

3. Results and Discussions

In order to evaluate the OHTC and HEX of the double pipe heat exchanger, the experimental data was analysed with respect to the mass flow rate of the hot and cold fluid. Conversely, the OHTC and HEX values were also compared with the theoretical values as mentioned at the research methodology section to investigate the percentage of errors of the experimental values. As a result, the complete theoretical

values, experimental data and the optimized formula was produced based on multiple regression analysis.

3.1.Overall Heat Transfer Coefficient (OHTC)

The overall heat transfer coefficient is an important factor in investigating the effectiveness at which heat is transferred from a hot fluid to a cooler fluid. The OHTC for each run of the experiment was calculated using the procedure listed in the research methodology section. The OHTC was analysed from two different arrangements of flows; concurrent and counter current flow. The comparison of the experimental OHTC is shown in the Fig. 2.

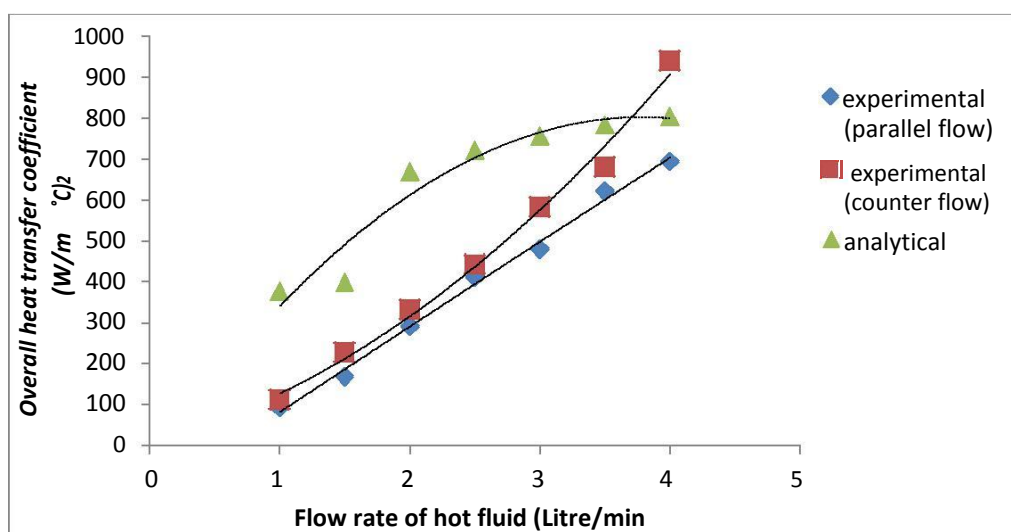


Figure 2. Effect of overall heat transfer coefficient on the flow rate of hot fluid with comparison from the analytical values

Fig. 2 shows the trend of the effect of OHTC on the flow rate of hot fluid for two types of flow arrangements when the cold water flow rate was set to 3L/min. From Fig. 2, it was observed that the OHTC of the counter flow shows higher gradient than the OHTC of the concurrent flow. In a counter flow, as the flow rate of hot fluid increases, the tendency of the hot fluid to transmit heat to the cooler fluid tends to be more efficient than the concurrent flow. However, the analytical value of OHTC shows a greater reading than both the experimental results because during experimentation there will be heat loss to the surrounding due to natural convection occurring across the concentric tube. However when the flow rate of hot fluid was set to 4L/min, the experimental reading of counter flow shows higher reading than the analytical value of OHTC. The reason of this may due to the overheating of the water heater in the double heat exchanger. This is because, when the hot fluid flow rate was set to 4L/min, it is the last run of the experiment, therefore by this time the water heater could have heated the water for almost two hours. As a result, it may cause the slight increase of the experimental OHTC.

The experimental OHTC of both the flow arrangements is shown in Figs. 3 and 4.

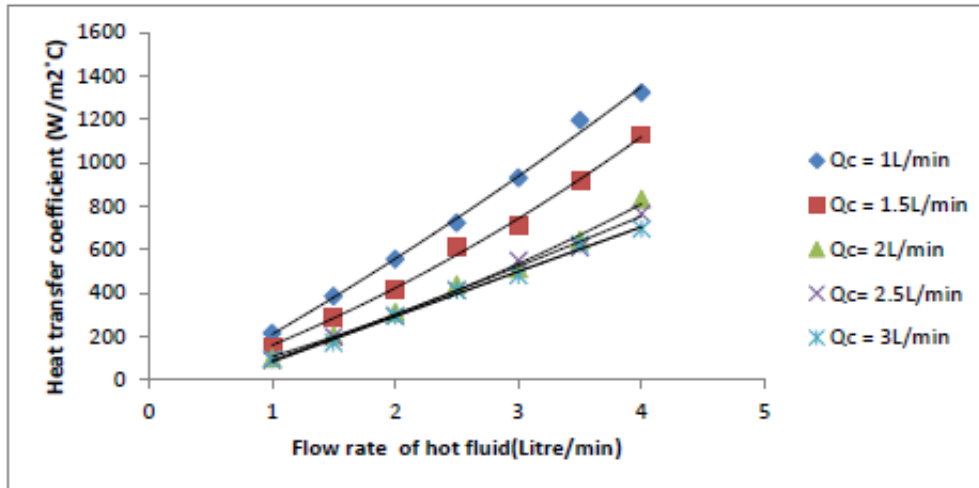


Figure 3. OHTC effect on flow rate for co-current flow

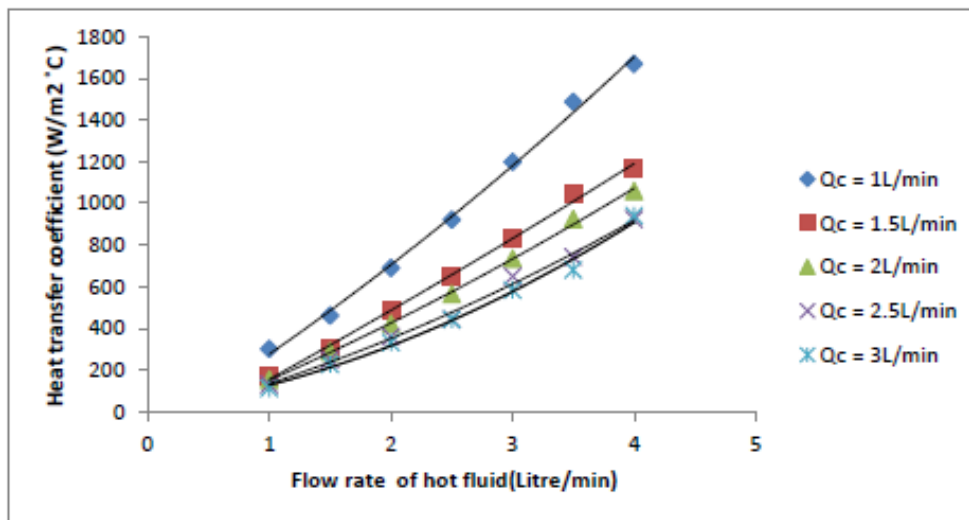


Figure 4. OHTC effect on flow rate for counter current flow

From Figs. 3 and 4, it is observed that the OHTC of the system increases as the flow rate of the hot fluid increases, however whenever the cold fluid flow rate increases, it was also observed that the OHTC decreases. Thus, with higher flow rate and temperature difference of the fluids, there will be higher heat transfer rate between the hot and cold fluid, thus affecting the overall heat transfer coefficient of the system drastically. In addition, Desgrosseilliers et al. also perform several simulations on the effect of the performance of double pipe heat exchanger and identified that counter flow has higher heat transfer coefficient compared to co-current flow [12].

3.2.Amount of heat exchanged (HEX)

In addition, the other parameter that is essential to investigate the performance of the double pipe heat exchanger is the amount of heat exchanged between the fluids. Therefore, Fig. 5 shows the data tabulated of the comparison of the theoretical heat exchanged and the experimental heat exchanged for both types of flows;

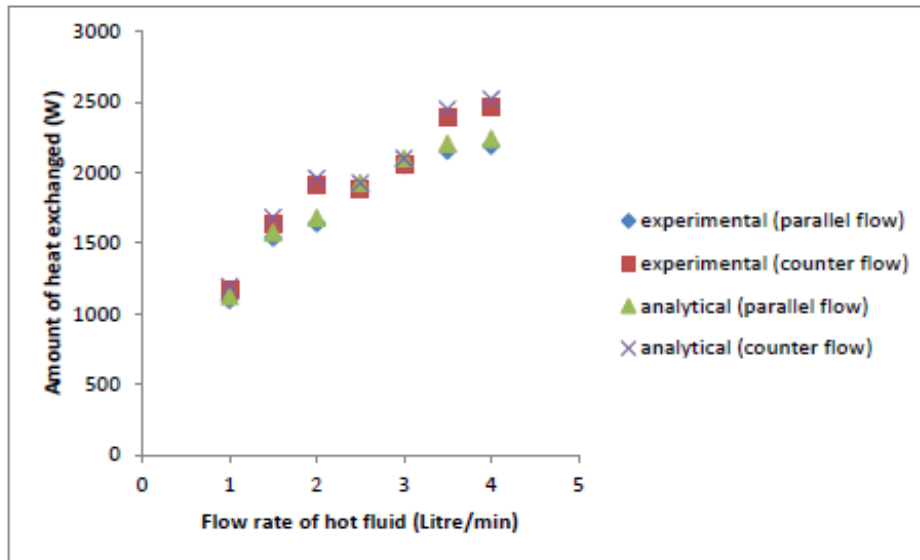


Figure 5. Effect of amount of heat exchanged on the flow rate of hot fluid with comparison from the analytical values

As observed in Fig.5, it shows that the analytical amount of heat exchanged for counter flow possess the highest reading. In theoretical point of view, there is no loss of heat from the fluid to the surrounding as it was assumed to be operating in a steady state. In addition, it was also observed that the amount of heat exchanged for counter flow is higher than concurrent flow of fluid, as in counter current flow, the flow of the hot and cold fluid will flow in opposite direction thus creating a better exposure of heat energy to the surface of the wall of the tube. Thus, the counter current flow shows a larger amount of heat transferred compared to co-current flow of fluid as shown in Figs. 6 and 7 of the experimental results obtained.

From Figs. 6 and 7, the amount of heat exchanged for both flows shows slight difference. The counter current flow shows a slightly higher reading of HEX than concurrent flow, because by manipulating the type of flow arrangement, it only causes small impact on the amount of heat exchanged. Additionally to that, Onarheim et al. also conducted a research regarding the performance of double pipe heat exchanger in counter and co-current flow of fluid and proved the theory at which counter current flow provides a much efficient heat transfer rate compared to co-current flow [13].

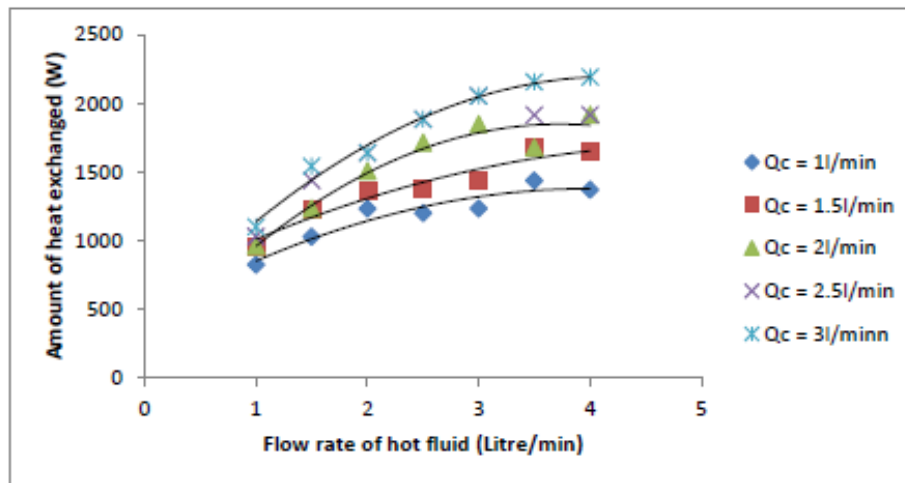


Figure 6. HEX effect on flow rate for co-current flow

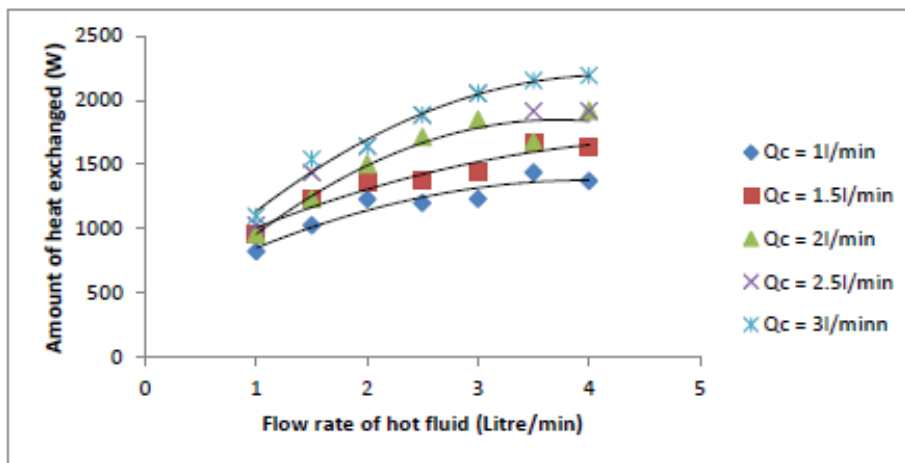


Figure 7. HEX effect on flow rate for counter current flow

3.3 Multiple Regression Analysis

Based on the experimental results, it was conclusive that an increase in both the FR_H and FR_C had positive correlation to its dependent variable that is the OHTC and HEX. The expected outcome of this study was the development of empirical model in the form of linear equation that could be able to predict the OHTC and HEX based on its FR_H and FR_C .

According to the statistical analysis done on the IBM SPSS 21 Statistical software, the results of the regression analysis is shown using four models in the table 1 and 2.

Table 1. Unstandardized and Standardized Beta Coefficients

Models	Dependent variable set	Independent variables	Unstandardized coefficient B	Standardized coefficient β
1	OHTC _{parallel}	Constant	203.6	0.00
		.	273.8	0.87
		.	-182.7	-0.41
2	OHTC _{counter}	Constant	270.2	0.00
		.	329.4	0.86
		.	-227.7	-0.42
3	HEX _{parallel}	Constant	250.3	0.00
		.	264.7	0.72
		.	305.1	0.59
4	HEX _{counter}	Constant	161.4	0.00
		.	299.9	0.73
		.	350.0	0.60

Table 2. Model Summary of the analysis

Models	R	R Square	Adjusted R Square
1	.960	.922	.917
2	.959	.919	.914
3	.932	.869	.860
4	.945	.893	.886

These tables shows the set of unstandardized and standardized coefficients based on the beta levels were produced. The major difference between these two sets of coefficients was that the standardized coefficients for each of the variable were converted to the same scale. As a result, the unstandardized coefficients would be most likely to be chosen as the coefficient to be used in the empirical formula provided that the independent variable that is the flow rate of the hot and cold fluid is known. Based on table 5, it shows the behavior of R-square and adjusted R-square for all the models, the most appropriate model was Model 1 for the dependent variable of OHTC in co-current flow, whereas Model 2 is for the OHC in counter flow of the system, whereas Model 3 and 4 show the dependent variable of the amount of heat exchanged in the system in co-current and counter flow. From table 2, the R squared value indicates the Hence, by replacing the coefficients A, B and C in Eq. (12) and Eq. (13),

the empirical model for each dependent variables OHTC and HEX with different types of flow arrangement would be presented as shown Eqs. (14), (15), (16) and (17).

$$OHTC_{parallel} = 274 (FR_H) - 183(FR_C) + 204 \quad (14)$$

$$OHTC_{counter} = 329 (FR_H) - 228(FR_C) + 270 \quad (15)$$

$$HEX_{parallel} = 264 (FR_H) + 305(FR_C) + 250 \quad (16)$$

$$HEX_{counter} = 300 (FR_H) + 350(FR_C) + 161 \quad (17)$$

As a result , Eq. (14) to Eq. (17) shows the empirical formulae to predict the dependent variable of OHTC and HEX based on the two different types of flow arrangements and also two independent variables that are the flow rate of hot and cold fluid,(FR_H , FR_C)

4. CONCLUSION

In conclusion, it was observed that both the dependent variable, OHTC and HEX had a significant impact on the performance of the double pipe heat exchanger. Therefore by using statistical analysis, four models of equations were identified. From the model summary, the accuracy of Model 1 and Model 4 shows the highest reading with 92.2% for Model 1 representing OHTC and 89.3% for Model 4 that representing the HEX variable, whereas Model 2 and 3 shows the least level of accuracy with accuracy of 91.9% and 86.9% respectively. Hence, the two empirical model with the

best level of accuracy that was identified using the statistical analysis are *OHTC*

$= 274 (FR_H) - 183(FR_C) + 204$ and $HEX_{counter} = 300 (FR_H) + 350(FR_C) + 161$. Whereas for the slightly least accurate empirical model that was developed in this paper are

$OHTC_{counter} = 329 (FR_H) - 228(FR_C) + 270$ and $HEX_{parallel} = 264 (FR_H) + 305(FR_C) + 250$. As a result of applying this empirical model, predictions can be made on the

overall heat transfer coefficient and the total amount of heat exchanged in the system correspond to the flow of hot and cold fluid in the system with different flow arrangements.

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Improving Energy Efficiency of a Wind Turbine

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Abstract

Wind power is getting popular since 1996 because of the growing demand of energy consumption. In recent years, researchers around the world search for different ways to increase the power efficiency of wind turbine. One of those methods are done by amending the turbine blade design. In this research, the concept of the dimple on the golf ball that delay the separation flow and thus reduced drag has been implemented into the wind turbine blade to study the effect on the efficiency of wind turbine. S833 airfoil was the chosen airfoil to conduct this experiment. ANSYS Fluent simulator was the solely tool used to conduct this study through 2D and 3D design, while XFOIL simulator was used to verify the methodology. From the ANSYS CFD given results, the dimpled airfoil increased the coefficient of lift up to 8.5% at Angle of Attack (AoA) 16° and delayed the airfoil stall from 14° to 16° AoA. This research contributed to increase the power efficiency of the wind turbine by improving the aerodynamic properties of the wind turbine blade (rotor blade) so that wind turbine are feasible to be implemented in Malaysia in the near future.

Keywords: Wind turbine, Dimple, Separation flow, Drag, Efficiency.

1. Introduction

The increasing demand of energy shows the trends of harnessing the wind power become globalized. The statistical data provided by Global Wind Energy Council (GWEC) has shown that PR china, Germany, United Kingdom, India and other countries in the list have installed wind turbine with overall capacity of 35,289 MW in 2013. The trend of installing the wind power is climbing since 1996 until 2013 according to GWEC report. The increasing installed capacity of the wind turbine not only shows the demand of wind energy globally, but also shows the increase of efficiency of the wind turbine design and its reliability throughout the years. [1].

As the demand for energy increasing, many researchers started to examine the available wind speed in Malaysia by using common measure parameter which is Weibull distribution. One of the researcher, Masseran [2] had used Weibull distribution to predict the wind speed in Malaysia comprise a Peninsular part and Sabah and Sarawak and has found that the southeast, northwest, northeast of Peninsular, and the southern region of Sabah was possible to harvest wind energy as they have possessed higher theoretical mean power compare to the other places. Meanwhile, most of the researchers in malaysia relied on the wind speed reading provided by the Meteorological service stations in Malaysia which had standardized the measuring height of 10 m above the sea level [2]–[5]. The mean wind speed provided by 10 wind stations shows about 4 – 5.5 m/s at the beginning and the end of the year while mean wind speed are relatively low at the midde of the year which is 2.6 m/s [6]. As a result of low wind speed in Malaysia, small scale wind turbine are much more feasible to be implemented in Malaysia.

In this study of research, an additional dimple on the airfoil upper surface were chosen to study the indirect effect on the energy efficiency of a horizontal wind turbine. Dimples on the golf ball surface are well known to be able to reduce drag and allow golf ball to travel further in the air. This is due to the reduction or delay of separation flow behind the golf ball. Separation flow occurs when the boundary layers of fluid flow against the original flow direction. This phenomenon causes recirculation vortexes inside the boundary layer and decrease the pressure on one side of the object surfaces and hence created drag. According to Bearman and Harvey [7], the drag reduction by the dimples was explained as the dimples generate discrete vortices energizing the boundary layer flow . Similar concept as the golf ball, dimpled surface was applied on the chosen airfoil.

According to Christopher [7], the ratio between the dimple depth to dimple print diameter, δ/D should at around 0.22. This shows good compromise of vortex production and low pressure losses. Dimple print diameter refers to the rim diameter of the dimple on the airfoil surface where the depth is the indented height from the surface. Hence the $\delta/D \approx 0.22$ relation will be used to design the dimple on the airfoil in this study. Moreover, the possition of the dimple of the airfoil was maintained at 1D to 5D from the separation point, where D refers to the diameter of dimple rim. Christopher's studies shown that different position and dimple array will significantly affect the separation point occurs depending on different angle of attack. If dimple placed too front than the separation point actual occurs on the chosen airfoil, separation flow or wake will begin in advance. If dimple placed too rear, the

turbulence mixing produced by the dimples will dampen out before the separation point and give little or no change to the expecting results.

Blade element momentum (BEM) theory was used to study the coefficient of power generated from the designed airfoil. BEM theory approaches two mathematical methods to acquire power output of an operating horizontal wind turbine, which are the conservation of momentum on a rotating blade and blade element theory that solely relied on the lift and drag coefficient of different blade elements. Both methods provided a series of equations which enabled BEM analysis to solve iteratively to acquire the coefficient of power, C_p . For momentum method approach, axial induction factor, a and angular induction factor, a' were defined to yield the equation of the axial and tangential force. In this model, induction factor in wake is twice of those on the rotor plane. The reason where induction factor is introduced is because a portion of wind energy was extracted by the rotor plane and forced the fluid to form annular streamtube behind the rotor plane and hence affected the velocity of wind flow. On the other hand, blade element theory estimated the air flow conditions over the rotor blade by developing a set of equations related with coefficient of lift and drag to acquire another set of axial and tangential force. The following references [8], [9] explained the details study of BEM theory. The coefficient of lift and drag of an airfoil profile was simulated by the ANSYS fluent software and verified with XFOIL airfoil simulator which this software is applicable for low Reynolds number simulation case.

The objective of this research is to decrease the drag by delaying the separation flow formed on the airfoil trailing edges so that increase the power coefficient of the wind turbine.

2. Methodology

2.1 The Efficiency of Power Generated from a Wind Turbine

Power coefficient, C_p is commonly used to distinguish the efficiency of power generated by a wind turbine from the moving air particle (wind). Different design of wind turbine, especially its rotor diameter and airfoil profile would directly affect the power coefficient. Figure 1 shows the basic horizontal wind turbine rotor swept area where wind is captured.

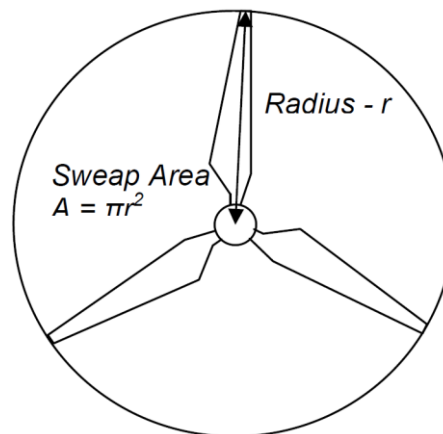


Figure 1. Wind turbine rotor swept area.

The kinetic energy, E of the moving air particle that captured by the wind turbine are converted into mechanical energy to turn the rotor, and was expressed in power (W),

$$E = \frac{1}{2}mv^2 \quad (1)$$

$$\frac{dE}{dt} = \frac{1}{2}\dot{m}v^2 \quad (2)$$

$$\dot{m} = \rho Av \quad (3)$$

By substituting the mass flow rate, $\dot{m}$ equation (3) into (2),

$$P_{wind} = \frac{dE}{dt} = \frac{1}{2}\rho Av^3 \quad (4)$$

where t is the time in second (s), ρ represents the density of the air, A is the swept area of the rotor (m^2), and v represents the velocity of air particles (m/s). However, it doesn't mean that the aforementioned wind power is equal to the actual power extracted by the wind turbine. Albert Betz and Joukowsky were the famous aero-dynamists in 1920 who proved that an ideal wind turbine can only extract as much as 59.3% of power from the wind and this Betz's limit is represented as the coefficient of power, C_p [10]. Hence, the extracted power from a wind turbine is the function of C_p and the wind power.

$$P_{extracted} = P_{wind} \cdot C_p \quad (5)$$

In real world, the power coefficient, C_p of wind turbine is well below the Betz's limit. The C_p variations are caused by the mechanical losses of the wind turbine such as frictional losses from bearing, generator and surface roughness of the blade. In practical, C_p lies between 35 to 40 percent [11].

2.2 Airfoil Selection

NREL (National Renewable Energy Laboratory)'s S833 airfoil is designed for low noise and high performance usage for small scale wind turbine. This specific airfoil usually work as primary airfoil when combine with root and tips airfoil which are S835 and S834. Generally, a primary airfoil grouped with different thickness of airfoil to achieve maximum performance out of the wind turbine. For root section airfoil, it has the maximum thickness to chord ratio to accommodate blade structural considerations whereby tip section requires thinner airfoil to minimize the drag and blade soiling losses. Soiling losses is the accumulated dirt on the airfoil caused the power loss to overall wind turbine performance[12].

However, NREL's S833 was the only airfoil chosen to study the dimple effect due to it played as primary role in turbine blade design as well as the limitation of time and knowledge to design the whole turbine blade structure with consideration of twisted angle and pitch angle as well as the thickness of airfoil from rotor hub to tip of the blade. All those mentioned parameters would definitely affect the power efficiency extracted from the rotor blade.

2.3 Numerical Study of 2D and 3D Airfoil

ANSYS fluent simulation software has been used to carry out 2D and 3D numerical analysis on the effect of dimple to the airfoil. As 2D in ANSYS require less time and computer memory usage to generate the necessary coefficient of lift and drag compare to the 3D, the plain airfoil model was simulated in 2D to graphically identify the separation point of the airfoil S833.

Through the vectors diagram and XY plot of X-wall shear stress, the separation point on the airfoil wall could be determined by observing the gradually decrease of wall shear stress along the x-direction until it reached zero. Wall shear stress falls to zero is due to the adverse pressure gradient of the fluid flow started to retard at the separation point and formed recirculated flow inside the boundary layer. Inside the separation flow gives a negative value of wall shear stress that represented as favorable pressure gradient.

For accuracy purposes, viscous model of transition-SST from ANSYS CFD was used to yield the require results. Transition-SST gave promising results compare to the fully turbulence model k-omega-SST. Transition model take transition flow into account whereby fully turbulence model ignore the transition flow. The transition flow cannot be neglected because of the low Reynolds number of 2.8×10^5 was being used to simulate the results as Malaysia's mean wind speed lies at 4 m/s while the density and viscosity are assumed as constant at 10 m height above sea level.

3D simulation requires more computational power and time than the 2D simulation. However, 3D simulation is necessary to study the dimple effect which involved turbulence in 3- dimension. The reference area in references value setting was set according to the body projected area so that to print an accurate coefficient of lift and drag of the simulated airfoil S833.

2.4 Mesh Dependency study

Different grid sizes and poor or good meshing will experience different level of time consumption to get a converged result. Poor meshing either experiences hard convergence or give a non-accurate results, in contrast good meshing costs less time to converge and give high accurate results. Grid size was set to the smallest so that computer is able to capture the tiniest change of the fluid flow. However, small grid size has the side effect that required large computational time and memory usage. In mesh dependency study, different grid sizing from 16215 to 77118 elements sizes were compared and discussed in discussion section.

The quality of mesh has been judged by its aspect ratio, angle, resolution and smoothness. The aspect ratio refers to the ratio of shortest edge length divided by the largest edge length of a quad or triangle cell. Angle is the internal angle for each element and the default range is 0 to 90 degrees. If the angle is too low (angle= 0 degrees), error will occur before the simulation started. Moreover, the resolution was set to small enough to capture the changes of boundary layers near the wall which at the lowest height of $7.7e-5$ m wall distance. The wall distance estimation was calculated by applying the y^+ formula. At last, the smoothness which are the spacing between the cells were set at 1.2 ratio because the maximum change in grid spacing should be lower than 20 %. Same meshing technique was applied to 3D, but the grid size for 3D mesh has limited by the computer memory compatibility [13].

2.5 XFOIL analysis for verification

XFOIL is the 2D single element program that design by M.Drela of MIT which applied critical-N factor method to predict the amplification of transition flow between the laminar to turbulence flow. The critical-N factor was assumed as 9 because it works well to predict the transition region in many cases. XFOIL coupled viscid-inviscid interaction to simulate the laminar and turbulence flow along the surface of the airfoil. The imported 2D surface of S833 airfoil is panelized into different nodes in order to solve the viscid and inviscid equations linearly. Each airfoil panel has linear vorticity distribution and a constant source strength to create a linear system at each nodes. In order to calculate high accuracy coefficient of lift and drag, grid size of the panel was playing a major roles to determine the accuracy of the results. Hence, the 360 panels were set to simulate the required coefficient of lift and drag of S833 airfoil. The optimized number of panels was proven by the journal that error in transition location at 360 panels have no more than 0.25% of the chord [14].

2.6 Limitation of the research

The limitations of this research are to validate the numerical results from the experimental acquired results from the wind tunnel. Since no real experiment was conducted, both ANSYS and XFOIL simulated results may not be valid. Besides, in order to perform 3D simulation on the dimpled airfoil, heavy computational time and memory usage are required which turn out to be not practical. Meanwhile, only basic knowledge of the meshing technique and solver configuration was being involved in this area of research which limited the field of exploration like testing the fluid flow over the complete rotor blade. Solely primary airfoil of S833 had been covered in this research, but in reality there are root, S835 and tip, S834 airfoil involved to complete a wind turbine blade. Due to large computational time is required to simulate the 3D dimpled airfoil, BEM method was not be able to use until full set of coefficient of lift and drag were generated from the dimpled airfoil. The reason where 2D simulation cannot be applied to simulate dimpled airfoil is because 2D failed to predict the exact movement of vortexes generate in Z-direction inside the dimple that could affect the accuracy of the overall results.

3. Results and discussion

3.1 Verification between ANSYS and XFOIL Results

In order to verify the methodology, ANSYS fluent generated results were compared with the XFOIL generated results. Both software applied different set of equation to calculate the results however the methodology to acquire the solution is about the same which are the finite difference method. Finite differences method is a mesh size dependent solution to calculate the values from the discrete places on a meshed geometry. The numerical solution from both software are thus compared under their finest mesh where the acquired results has the least changes. The acquired results in Figure 2 (a) and (b) used 149,544 element size in ANSYS to compare with 360 panels grid size in XFOIL. In Figure 2 (a), the coefficient of lift generated by ANSYS 2D shows over-estimated results from the beginning of 0° to 6° degree of angle of attack (AoA) compare to the XFOIL generated results whereby same goes to the drag coefficient in Figure 2 (b) shows over-estimated results from 0° degree

onwards. The simulated results from ANSYS 2D experienced stall earlier than the XFOIL simulated results which indicated in Figure 2 (a) at the moment when coefficient of lift started to fall against the increasing of angle of attack. The angle of attack is the angle between the incident flows of fluid relative to the airfoil. However, both of the simulated results require further validation to be done by comparing with experiment data in order to confirm their reliability. From this verification study, ANSYS 2D shows promising result where the variation between both simulation software are lower than 12 % for coefficient of lift, and 20 % for coefficient of drag when airfoil stall is not considered.

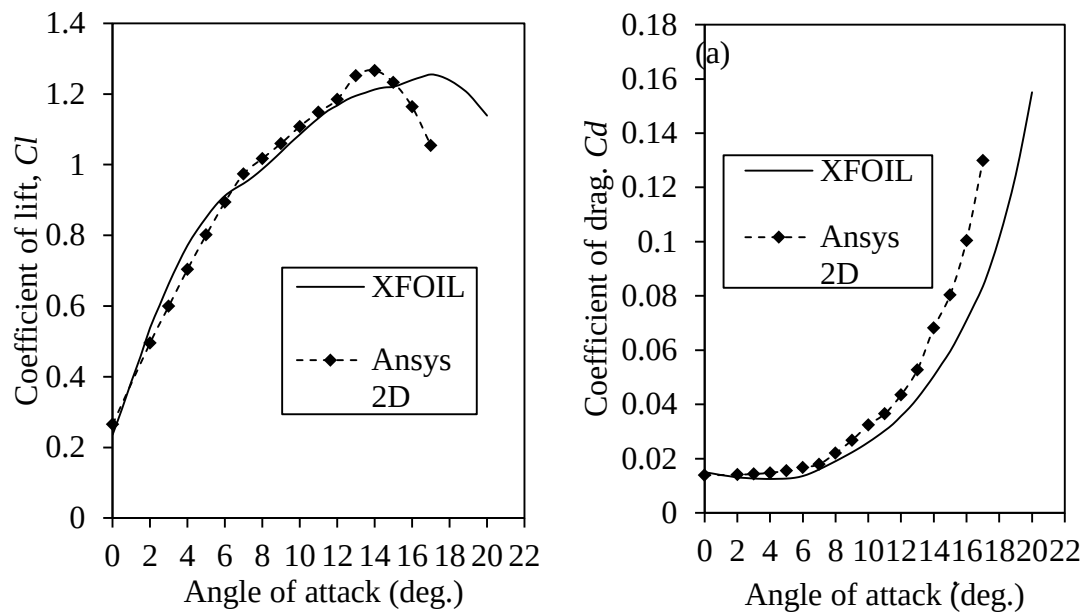


Figure 2. Comparison between ANSYS and XFOIL generated results; (a) coefficient of lift, C_l , and (b) coefficient of drag C_d .

3.2 Effect of meshing on different meshing size

In mesh dependency study, different element sizes were tested to acquire the reading of coefficient of lift and drag from airfoil S833. In order to get good quality mesh, all the affecting parameters were taken into account such as the aspect ratio, angle of the grid, smooth ratio as well as the resolution size that detect the boundary layers near the wall. Aspect ratio was maintained from minimum $10E-1$ to $10E+3$ where close to zero indicates worse quality whereby 1 is the best. Aspect ratio is one of the challenging part to be maintained in high quality because of the necessity of fine mesh near the wall that stretched the quadrilateral cells into rectangular shape instead of square (aspect ratio = 1). The inner angle of the quadrilateral cells are require to maintain in 90 degree to yield an accurate results and minimize the error. While the smooth ratio of 1.2 was set to smoothen the adjacent grid cells with below 20% differences in size. The smoothness between the grid cells is important as the simulated results could provide a rather off values although the simulation process are converged. Moreover, the resolution of grids near the wall were set at $7.6e-5m$ height to detect the small changes of boundary layers above the wall. The value of estimated wall height was estimated by the governed equation of Reynolds number and wall shear stress.

By combining all the required components, different sizes of mesh listed in table 1 were compared with their respective generated coefficient of lift, (C_l) and drag, (C_d). In table 1, steady state and transient state results are simulated for element size 16,443 and 27,138. The reason where the steady state result from 44,418 element size onwards are blanked because of the ANSYS fluent solver detected transient flow from the finer grid size. Hence, transient flow are used to compare the generated results. In table 1, 16,443 element size shows rather different result compare with other element size is because coarse mesh give inaccurate result. From 149,544 element size onwards, the generated results show stable and gave identical results until 209,844 element size of meshing. However, it doesn't mean that the finest mesh gave the most accurate results, because it was impossible for the solver to solve a "dot". Hence, 149,544 element size was used to simulate the following results with respect to different angle of attack because it requires less time and memory usage compare to 209,844 element size and yet provided similar results.

Table 1. Coefficient of lift, C_l and coefficient of drag, C_d that affected by the different elements size at 0° of incidence flow.

Elements size	Steady		Transient	
	C_l	C_d	C_l	C_d
16,443	0.215	0.018	0.208	0.017
27,138	0.250	0.014	0.261	0.013
44,418	-	-	0.267	0.014
149,544	-	-	0.265	0.014
166,904	-	-	0.265	0.014
209,844	-	-	0.265	0.014

3.3 Determination of the separation point

At 0° Angle of Attack (AoA), the separation point on airfoil's upper surface started at about 0.6 m chord length and reattached at about 0.8 m. This phenomenon is commonly seen in every airfoil or flat plate surfaces because of the transition flow. When fluid flow at low Reynolds number, laminar to turbulence flow will always take place. Figure 3 shows the recirculating separation bubble formed after the separation point and reattached at the entry of the turbulence boundary layers. This phenomenon was being identified as the transition of fluid flow from laminar to turbulence.

Besides graphically identify the separation point, it was also predicted by the wall shear stress of the airfoil surface. Wall shear stress, τ_w is the adverse pressure gradient experienced by the wall because of the present of fluid viscosity. The formula used to calculate the wall shear stress (Pa) is governed by the dynamic viscosity, μ of the fluid multiple by the velocity parallel to the wall, $\frac{\partial u}{\partial y}$, where the equation is written as $\tau_w = \mu \left(\frac{\partial u}{\partial y} \right)$. In laminar and turbulence boundary layers, wall shear stress is always greater than zero because of the adverse pressure gradient.

When the fluid travelled far enough along the wall surface, it started to gain the momentum to oppose the fluid flow direction. This gives a favorable pressure gradient of boundary layers that caused the wall shear stress dropped to zero and gave negative values. The negative results will continue until the next turbulence boundary layers formed.

Hence, separation point was determined at the beginning of the negative velocity gradient (favorable pressure gradient). Figure 4 shows sudden drop (crest) of wall shear stress in X direction value of the airfoil's upper and lower surface indicated where the separation bubbles occur as well as the separation point was identified.

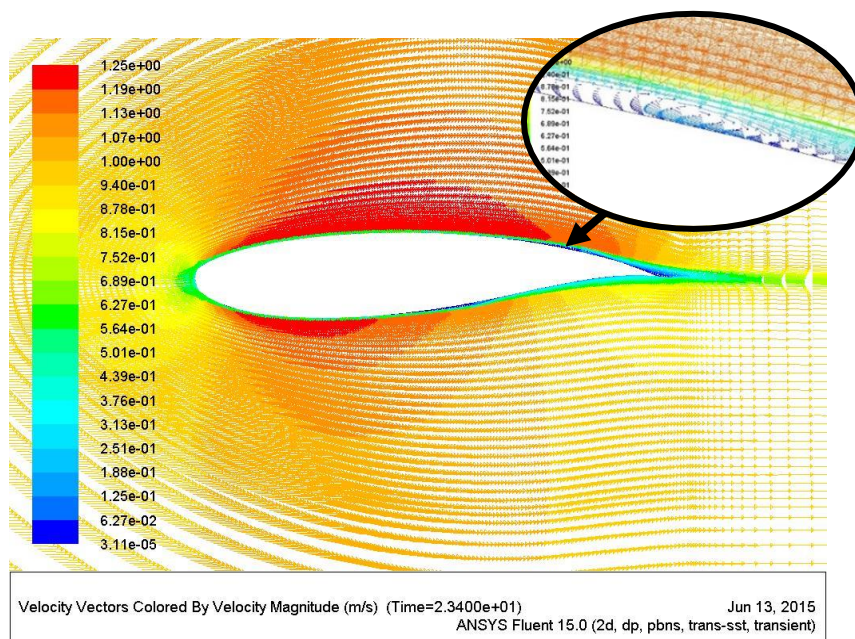


Figure 3. Separation bubbles near the airfoil trailing edge at 0° AoA.

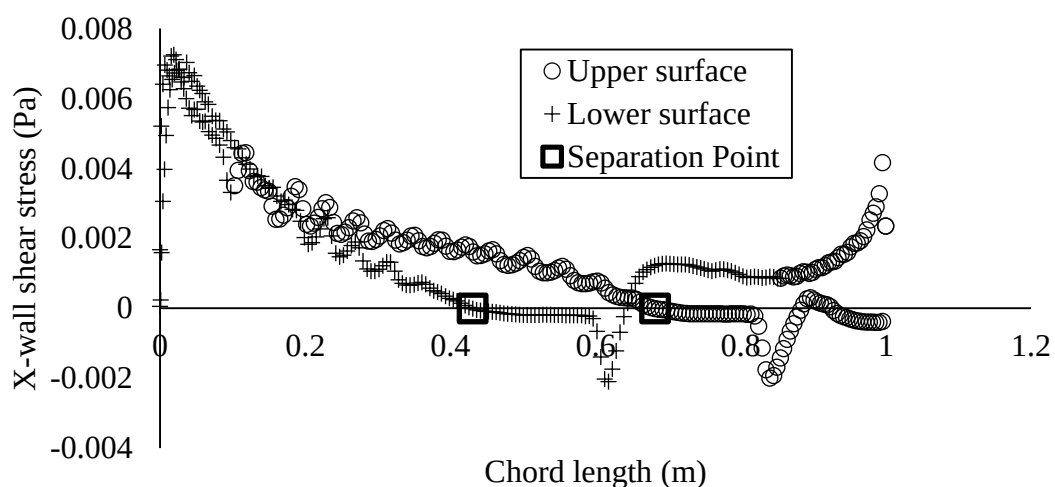


Figure 4. Mean wall shear stress in X-direction of the S833 airfoil at 0° AoA.

3.4 The dimple effect on S833 airfoil

The dimpled airfoil was compared with the plain airfoil by the simulated coefficient of lift and drag. The simulated results shows that the coefficient of lift and drag of the dimpled airfoil have a steady grow from 0° to 14° Angle of Attack (AoA). For both dimpled and plain airfoil, stall occurred at about 14° AoA. Stall is the maximum lift which an airfoil can achieve, beyond that point the performance of the airfoil will deteriorate. However, dimpled airfoil had shown sign of delay of deterioration which the generated coefficient of lift is higher than the plain airfoil from 14° to 16° AoA. The coefficient of drag for dimpled airfoil was decreased at point 16° AoA. From 0° to 14° AoA, the dimpled airfoil shows little or no change of coefficient of lift and drag compared to the plain airfoil. At 17° AoA, the vortex shedding behind the trailing edge of the dimpled airfoil started to oscillate vigorously and thus affected the coefficient of lift and drag. The instability of wake generated at 17° AoA had led to the increasing of drag which is not feasible to apply on harvesting wind energy. The oscillated wake (vortices) may also imply stress and strain to the turbine blade which eventually lead to blade failure. Therefore, the optimum AoA for the dimple to bring positive impact to the wind turbine was the AoA in between 14° to 16° . Figure 4-3 and Figure 4-4 show the coefficient of lift and coefficient of drag respectively against the different angle of attack (AoA). The maximum increased percentage of lift coefficient is 8.5 % when both dimpled and plain airfoil were compared.

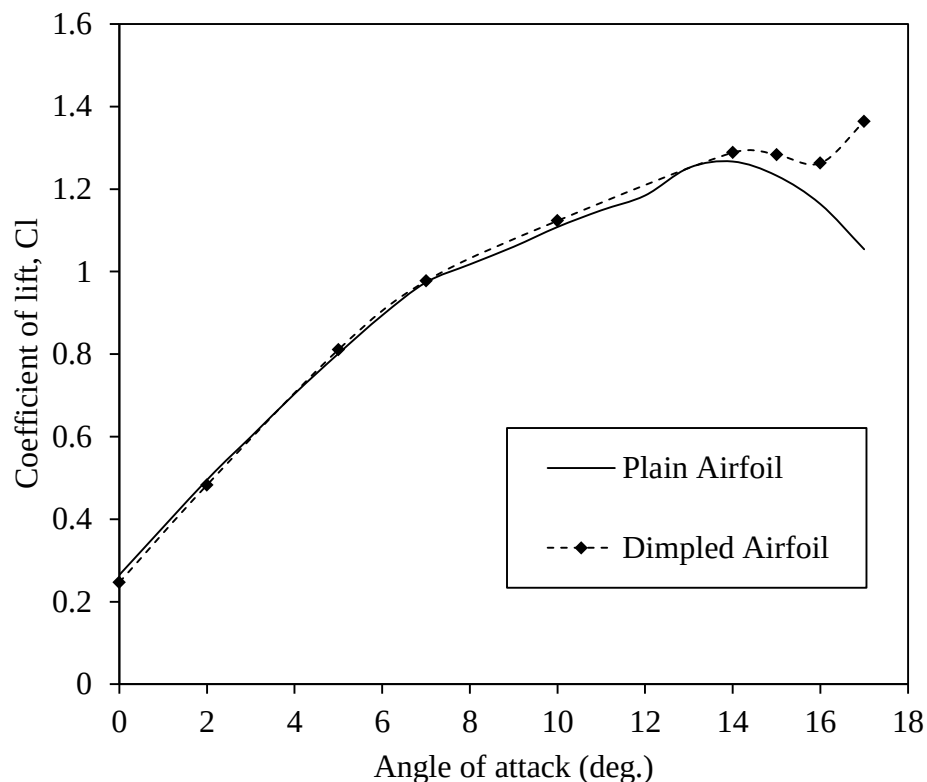


Figure 5. The comparison of coefficient of lift with respect to different AoA for both plain and dimpled airfoil.

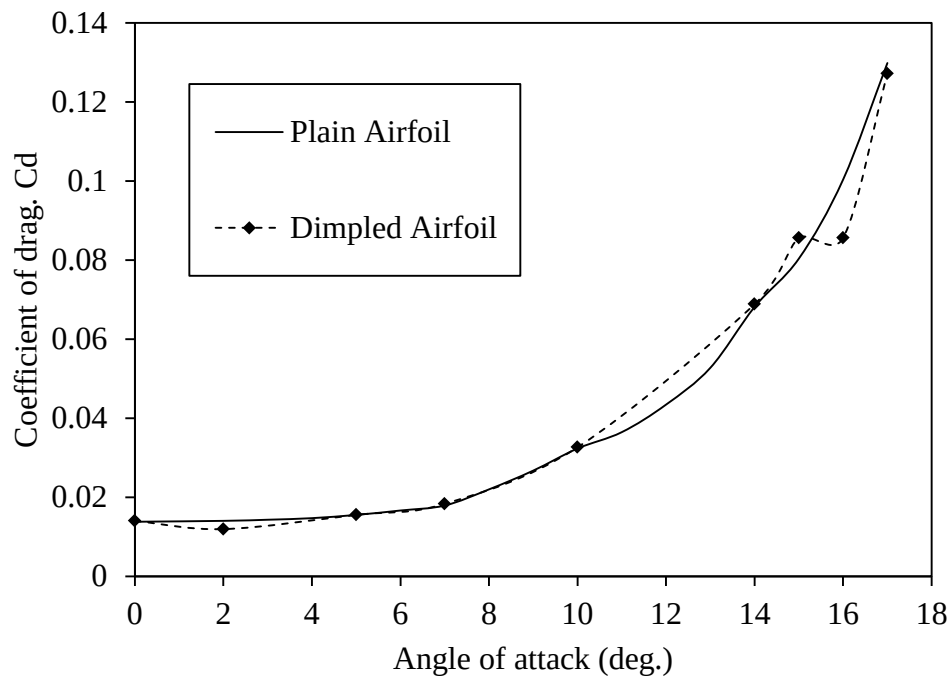


Figure 6. The comparison of coefficient of drag with respect to different AoA for both plain and dimpled airfoil.

4. Conclusion

This research is concluded with 149,544 element size of meshing are used to simulate the 2D fluid flow over the airfoil. The simulated results from ANSYS fluent are verified with another airfoil simulator XFOIL. The ANSYS simulated results stalled at 15° angle of attack whereby XFOIL stalled at 18° angle of attack which is higher than the coefficient of lift predicted by XFOIL. Separation point was identified on the upper airfoil surface that occurred at about 0.67 m of chord length. Last but not least, dimpled airfoil shows improvement by increased the coefficient of lift up to 8.5 % when compare with the plain airfoil.

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Optimization of Process Variable for a Biosorption of Heavy Metals from Wastewater using Response Surface Methodology (RSM)

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Abstract

In this research project, it is to find the most common agricultural waste that produce in Malaysia to help the reduction on the amount of waste as well as help to treat waste water by adsorption process of heavy metals before discharging to the sewage system. Besides, the sorbent used in this project is rice husk because the properties of the rice husk can help in achieving high level of adsorption of heavy metals in waste water. In addition, the adsorption behavior of Zn (II) and Cu (II) ions on the rice husk in removing the metal ions from the aqueous solution by using batch method. The initial and final concentration of the metal solutions will be tested with Atomic Adsorption Spectrophotometer (AAS) after the adsorption process of the rice husk. The major parameters studied in this project are pH level and concentration of the metal ions of the samples. The weight of the sorbent used to treat the heavy metals are 1g and 2g of rice husk at metal solution. Furthermore, the pH level of the sample was tested at the range of 6 to 9. Hence, the optimum value of each parameter will be determined in the end of this project by the help of Response Surface Methodology (RSM) software. In brief, the adsorption of capacity and percentage of the rice husk can be achieved efficiently.

Keywords: Rice husk, Heavy metals, Adsorption, RSM

1.0 Introduction

Over the centuries, humans discover a lot of ways in treating the wastewater from the industrial plants. In Malaysia, environment is one of the important sources to be kept safe. There are rules and regulations in building industrial places. Besides, department environment of Malaysia had stated the rules in discharging waste to the environment this are to avoid pollution towards the flora and fauna. Heavy metals are the common hazardous materials and it is a challenge for majority of the industrial plants to evade the decontaminations of these hazardous materials from water and soil ground of the environment.

Furthermore, environmental problems are increasing each year and heavy metals pollution is one of the critical issues in the world. This is because the development of industrial plants has been increasing rapidly every year and by this, the high volume of wastewater being discharged into the environment will cause very bad environmental pollution.

Moreover, there a lot of methods in removing heavy metals from the wastewater which are membrane processes, ion exchange, electroplating, evaporation, precipitation and etc. In choosing the methods for the wastewater treatment, there are several experiments need to be carried out. However, minority of the methods have its disadvantages such as generation of sludge, high reagent requirement, unpredictable metal ion removal and etc.

The treatment process of wastewater has evolved to be more affordable and excellent tool by using biosorption process. Biosorption process is a biotechnological innovation using natural biosorbent to adsorb heavy metals and toxic metallic ions. Therefore, the process of biosorption will prevent pollution and adsorb unwanted heavy metals from the wastewater without using any addition of chemicals.

1.1 Objectives

The objectives of this research project are:

- To choose and determine the best biosorbent for the process of biosorption of heavy metals of heavy metals from the wastewater. (eg. Rice husks, papaya wood and etc).
- To develop and determine the best parameters settings (eg. Concentration, pH, temperature agitation and etc) that can achieve high capacity biosorption of heavy metals
- To do analysis and experiment based on the response surface methodology based on the biosorbent used for the biosorption process.

Scope

Area of study

- a) Biosorbent is an active component that helps in saving energy and waste. Recent study shows that rice husk has a high potential in becoming a good biosorbent. It is important to study the amount rice husk being produce in Malaysia. Besides, Malaysia owns a very large area of paddy fields; this will help in reducing the amount of waste from the production of rice.
- b) Methods of the response surface methodology of the biosorption of the heavy metals using rice husks as the biosorbent.
- c) Optimization of the biosorption process. Experiments are conducted to determine the best process parameter for the biosorbent used

Expected Outcome

- a) Besides, it could decrease the amount of waste in the production of rice.
- b) The best method on the response surface methodology of the biosorption process
- c) Process conditions and parameters that can give the best optimization biosorption results can be determined.
- d) The percentage of heavy metals can be adsorb by the biosorbent of rice husks

Limitations

- a) There are several ways in improving the biosorbent to be more active in removing the heavy metals. The procedure and chemicals is complicated whereas it is also depends of the availability of the equipment in the lab to conduct this experiment. However, in this project, pure rice husks will be used for the analysis in biosorption process.
- b) The chemicals such as heavy metals solution are limited in the laboratory as well as the cathode lamp which is used for the AAS machine. Besides, the knowledge on operation Design Expert 2.0 is limited as the parameter tested was not enough for the software to analyze and the software is not available in Taylor's University.

2.0 Theoretical Framework

2.1 Properties of rice husk

The theoretical framework for this project research is on the adsorption capacity and percentage of the heavy metals that can be achieved by using rice husk as a sorbent in a waste water treatment plant. The properties of the rice husk is very important to be identified the components that can adsorb the heavy metals efficiently.

In this era of globalization, it is important for mankind to reduce the effect towards environment and humans. The environment can easily be effected by heavy metals as it can cause pollution. By this, it will give negative impact towards the humans in terms of health. There are several ways in removing heavy metals from the industrial waste water. There is a new sustainable and environmental friendly method which is called biosorption method.

Furthermore, the biosorbents are the components that need to be study in choosing the suitable biosorbent for the process of biosorption to occur. In many countries, rice husk is widely produce and the availability is high as globally 600 million tons of rice paddy has been produce each year. In recent studies, rice husks has been used widely as a biosorbent in removing heavy metals because it has suitable properties that helps in adsorbing the heavy metals from the wastewater. [1]

The amount of organic matter in rice husk contains approximately around 75-90% for example lignin, cellulose and etc. The remaining percentage is the minerals such as alkalis, silica and etc [2]. The properties of the rice husks also depend on the geography, location, soil chemistry and conditions of the climate. [3] The table below shows the analysis of the rice husks:

Table 1: The analysis of rice husk [4]

Properties	Range (%)
Ash	22-29
Carbon	Approximate 35
Hydrogen	4-5
Moisture	8-9
Sulphur	0.04-0.08
Nitrogen	0.23-0.32
Bulk density (kg/m ³)	96-160

In Malaysia, there are about 408,000 of metric tons each year being produced. This shows that, there are a lot of rice husk produced and it is often being process or burn as a waste because it can cause air pollution. However, this can be preventing as rice husk can be used alternatively as a biosorbent for the process biosorption of heavy metals. Foo and Hameed (2009) stated that rice husk can provide twofold benefits towards management of environment. This is generally because the rice husk waste reduction, converted to adsorbent and it can be developing to a useful low cost adsorbent to prevent pollutions to occur. [5]

2.2 Heavy metals

Over decades, world is facing a lot of challenges in avoiding pollutions such as air, water, sound and environment pollution. The most concern pollution is caused by the heavy metals. This is because the toxicity of the heavy metals can caused diseases to the community and environment. Besides, the pollution caused from these heavy metals is from these common industries such as ceramic, mechanic, chemicals and petrochemicals. There are ways in calculating the amount of heavy metals in the wastewater in order for bio sorption process to take places. This procedure can determine the type of heavy metals and by this the suitable bio sorbent enable to adsorb the heavy metals at the high efficiency and capacity.

2.2.1 Electroplating Industry

In this era of globalization, industrialization zone increase dramatically in the world which causes the surface as well as ground water to change as the contamination from the heavy metals waste water. [6].The identification of properties for each of the heavy metals is important because majority of the heavy metals are not biodegradable. Hence, it can affect the health and environment problems towards human and nature. In Malaysia, there are a lot of industrial places such as food industry, electroplating industry, cosmetic industry and cement industry. However, in this project, electroplating industry was chosen to determine the amount of heavy metals in the waste water. Example of electroplating company which is EL- AHLIA Company produced $750 \text{ m}^3/\text{day}$ amount of waste water that discharged in the sewer system in Abozabal. [7] Besides, in Kuala Lumpur and Klang there are various forms of electroplating industries such as chromium, silver and zinc. It is stated that majority of the electroplating has no facilities for the waste water treatment. [8] It is dangerous to the health and environment as it exceed its allowable limit from the Department of Environment (DOE) Malaysia. [6] The table below shows the common initial amount of heavy metals in the waste water of the electroplating industry.

Table 2: Initial Concentration of the Heavy Metals in Wastewater [9], [7]

Heavy Metals	Initial Concentration	
	mg/L	ppm
Lead (Pb)	1.17	1.1713
Zinc (Zn)	17.40	17.420
Copper (Cu)	43.50	43.550
Cadmium (Cd)	0.48	0.4805
Nickel (Ni)	1.74	1.7420

Parameter		Unit	Standard	
	(1)	(2)	A	B
i.	Temperature	°C	40	40
ii.	pH Value	–	6.0-9.0	5.5-9.0
iii.	BOD ₅ at 20°C	mg/L	20	50
iv.	Suspended Solids	mg/L	50	100
v.	Mercury	mg/L	0.005	0.05
vi.	Cadmium	mg/L	0.01	0.02
vii.	Chromium, Hexavalent	mg/L	0.05	0.05
viii.	Chromium, Trivalent	mg/L	0.20	1.0
ix.	Arsenic	mg/L	0.05	0.10
x.	Cyanide	mg/L	0.05	0.10
xi.	Lead	mg/L	0.10	0.5
xii.	Copper	mg/L	0.20	1.0
xiii.	Manganese	mg/L	0.20	1.0
xiv.	Nickel	mg/L	0.20	1.0
xv.	Tin	mg/L	0.20	1.0
xvi.	Zinc	mg/L	2.0	2.0
xvii.	Boron	mg/L	1.0	4.0
xviii.	Iron (Fe)	mg/L	1.0	5.0
xix.	Silver	mg/L	0.1	1.0
xx.	Aluminium	mg/L	10	15
xxi.	Selenium	mg/L	0.02	0.5
xxii.	Barium	mg/L	1.0	2.0
xxiii.	Fluoride	mg/L	2.0	5.0
xxiv.	Formaldehyde	mg/L	1.0	2.0
xxv.	Phenol	mg/L	0.001	1.0
xxvi.	Free Chlorine	mg/L	1.0	2.0
xxvii.	Sulphide	mg/L	0.50	0.50
xxviii.	Oil and Grease	mg/L	1.0	10
xxix.	Ammoniacal Nitrogen	mg/L	10	20
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Figure 1: Environmental Quality Act 1974, Environmental Quality Regulations 2009

The figure above shows the standard amount of each heavy metal that is allowed to be discharged in the sewage drain in Malaysia. These rules of regulations apply to every industry in Malaysia which takes considerations of the effluent discharge to the environment. Furthermore, the design and construction for the waste water treatment system need to be acceptable conditions for the industrial and environmental safety.

2.3 Adsorption of heavy metals

2.3.1 Concentration of heavy metals

Moreover, there are a lot of techniques to determine the heavy metals in the waste water such as ETAAS, FAAS, ICP-OES, ICP-MS and LIBS. The steps of operating the AAS machine it requires precaution steps because to avoid high potential of errors. It also requires pretreatment for the waste water before it can be test as a sample in a lab. This is because it might contain organic or particulate components [10]. The procedure is to determine the types of heavy metals in the effluent by atomic adsorption spectrophotometer (AAS). It is stated that two general types of AAS that have been used throughout determining the heavy metals which are flame and electro thermal atomizers [11]. There are 2 types of flame used for the flame atomic absorption spectrometry which is nitrous oxide and acetylene flame. However, this technique has advantages and limitations as the temperature is insufficient to break down the composition of the elements. The figure of the block diagram of the FAAS and GAAS below shows the procedure on determining the heavy metals from the water sample [10].



Figure 2: The process flow of the spectrometry [10]

The dissolved metals are analyzed if there is a present of particulates. This shows that the particulates of the heavy metals will be further determine by the differences of the wavelength. Every metals excites at a different wavelength and this will be detect by the detector as well as amplify for the signal to be process [11].

It has been stated that the amount of heavy metals concentration in herbal cosmetic need to be control and determined the acceptable limits. The toxic effects of each heavy metal can be identified by knowing the types as well as the concentration of the heavy metals such as, Mg, Cr, Fe, and etc. This can indicate the amount of heavy metals and the content of the cosmetic product

The parameters are pH values, sorbent dosage, temperature, contact time and agitation rate. The beaker used is shaken according to the length of time by magnetic stirrer and it will be filtered by the filter paper. The remaining amount of heavy metals ion in the wastewater will be further determined by AAS. The balance amount of heavy metal ions can be calculated by [12]:

$$\% \text{ Adsorption} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

Where:

C_0 = initial concentration of adsorbate

C_e = equilibrium concentration of adsorbate

From the equation above, the heavy metals adsorbed calculated in per kilogram of the biomass.

$$Q_e = \frac{(C_0 - C_e)V}{M} \quad (2)$$

Where:

Q_e = adsorption of metals on the sorbent

M = weight of the sorbent

V = volume of metal solution

C_0 = initial metal concentration

C_e = metal concentration at any time

2.4 The Response Surface Methodology

The purpose of this study is to optimize as well as model the process of adsorption of heavy metals by using rice husks by using the Design Expert software of RSM. The investigation will be made on the parameters which are contact time, temperature, pH, initial concentration and agitation rate.. The behaviour of the biosorbent can be seen in a three dimensional view of response surface contour plots. Besides, maximal amount of the adsorption can also be determined by using the response surface software. From the results, the software will be able to draw a three dimensional surface contour plot [12]. Therefore, best yield can be obtained from the analysis. The figure below is the example of surface contour plot shows the effect of parameters on the adsorption of the rice husks:

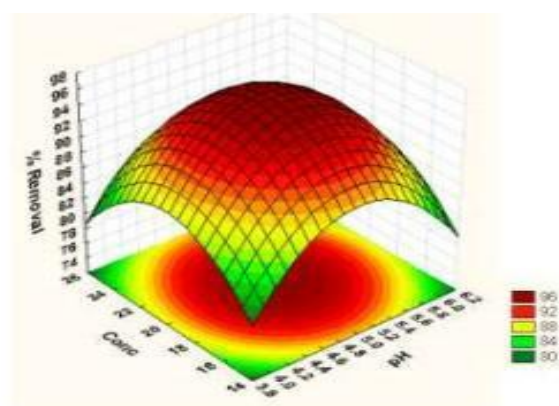


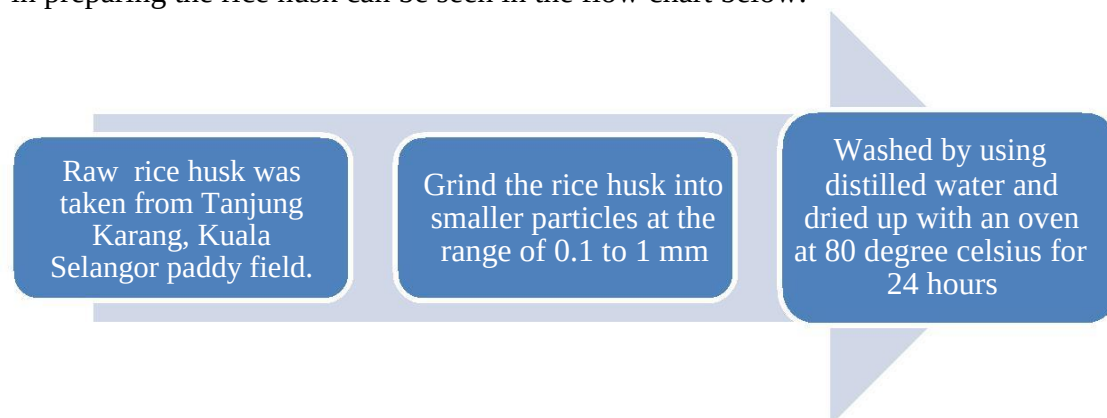
Figure 3: The surface contour of pH and initial concentration effects on rice husk [12]

3.0 Methodology and Data

In this research project, it is important to read and compare the journals as it can help in discovering new ideas as well as exploration. The research of finding the right sorbent to adsorb heavy metals from waste water and the parameters of pH value and sorbent dosage that needs to be control to achieve high adsorption capacity is the foundation of assessment for this project need to be done. Besides, from the results obtained in this experiment can improve the development in removal the heavy metals of Zn (II), Pb (II), and Cu (II) by using rice husk. The experiment procedures for the rice husk are divided into 2 stages. At the first stage, it involves on the preparation of the raw rice husk for the experiment need to be done. The second stage, it is about adsorption studies on the percentage of capacity and adsorption of metal ions and graph will be drawn by using Response Surface Methodology (RSM) software for each parameters tested.

3.1 Experimental procedures

The procedure for the preparation of this raw rice husk are proposed by Abdul, R (2008) and Taha at al (2010). Besides, in the preparation of this raw rice husk is basic because the objective of this project is to ensure the suitable parameters for the rice husk to work in the adsorption of the heavy metals in the waste water. The stages in preparing the rice husk can be seen in the flow chart below:



The procedure of this project is proposed by Taha at al (2010). However, there are changes had been made referring to the concentration of the metal solution tested for the adsorption using rice husk [13] [14].

Preparation of rice husk

1. Rice husk is washed by distilled water several times to remove any unwanted components
2. The rice husk is then dried in an oven at 80 °C for the whole day which is 24 hours in order to remove the moisture content as well as the volatile components in the rice husk.
3. Lastly, the rice husk is grinded and blended into smaller particles into 1mm size of rice husk.

Preparation of heavy metals for the adsorption studies

1. Solution of 5 ppm of Zn (II) ions is prepared by mixing the suitable amount zinc oxide (ZnO) with distilled water
2. This same procedure are applied for the preparation of 5 ppm of Cu (II) ion solution from copper sulfate
3. 1 g and 2g of rice husk mixed with 25 ml of 5 ppm Zn (II) ion solution in a beaker and it was stirred at 150 rpm.
4. The concentration of Zn (II) ion is filtrate and analyze by using atomic adsorption spectrophotometer (AAS).
5. The calibration for the AAS machine was done by using the standard solution for Zn (II) ion at the range of (2 and 10 ppm).
6. Steps 3 to 5 were repeated by using, Cu (II) ion.

The percentage of the adsorption and capacity can be obtained from the AAS machine

Preparation of the sample by increasing the number of pH value by using nitric acid

1. Solution of nitric acid will be used to adjust the pH of the sample at the pH range of (6 to 9) by addition of 0.1 M of NaOH
2. 30 ml of 5 ppm metal solution of Zn (II) ions is prepared by mixing the suitable amount zinc oxide (ZnO) with distilled water.
3. The sodium hydroxide need to be added in the samples in each of the heavy metals solution tested prior to the experiment
4. Step 1to 3 are repeated by using Cu (II)
5. The rice husk was filtered and the remaining heavy metals solution will be test using AAS machine
6. The percentage of the adsorption and capacity can be obtained from the AAS machine and equation (1) and (2)

4.0 Research Outcomes and Discussion

4.1 Effect of metal ions concentration in different amount of sorbent dosage

Initial Concentration = 5ppm of metal solutions

Volume of solution= 25 mL= 0.025 L

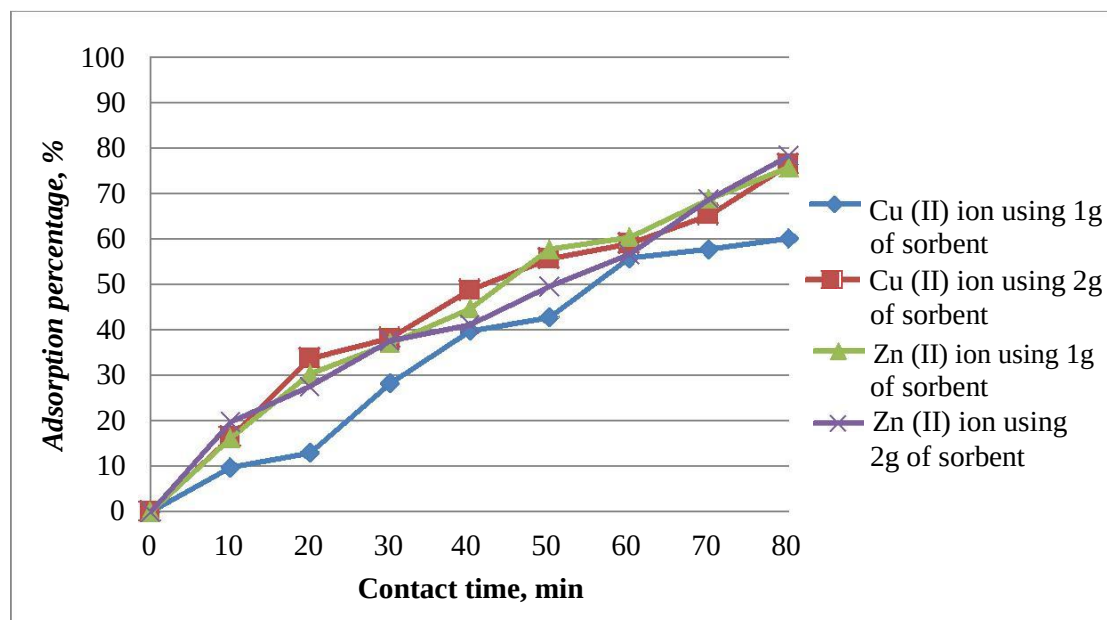


Figure 4: The adsorption percentage of metal ions

In this segment, the graphs show that the increase in adsorption percentage in different amount of adsorbent used. The adsorbents used were 1g and 2g of rice husk. It was tested to analyze the increment of adsorption percentage equilibrated at contact time of 0 to 80 minutes. The increase in surface area of adsorbent will increase the adsorption percentage respectively. Besides, the initial metal ions concentration in solution decreases when the sorbent amount increase from 1g to 2g. Thus, the results show an increasing amount of adsorption as the adsorbent provides more surface area. [15]

The effect of contact time also can be achieved in this experiment. The initial metal ions concentration decrease as increase in contact time. The efficiency of adsorption showed in the figure 15 above, the adsorption rate is initially fast for Cu (II) ion at 10% and approximately 20% of Zn (II) ion were adsorb by 1g of sorbent. It reaches it equilibrium adsorption capacity within 80 minutes and the adsorptions slowly decrease after 80 minutes of this experiment. This is because it has reach its optimum agitating time for the process of adsorption to occur which accepted as 80 minutes for 1g of rice husk used. It can be seen from the figure, adsorption percentage increasing dramatically because the large number of vacancy for the sorption site to adsorb the metal ions solutions. Therefore, it shows slower adsorption rate due to the saturation of active site on the rice husk surface.

4.2 Effect of metal ions concentration in different pH value

Sorbent amount = 1g of rice husk

Volume of solution= 30 mL= 0.030 L

Equilibrium time = 5 minutes

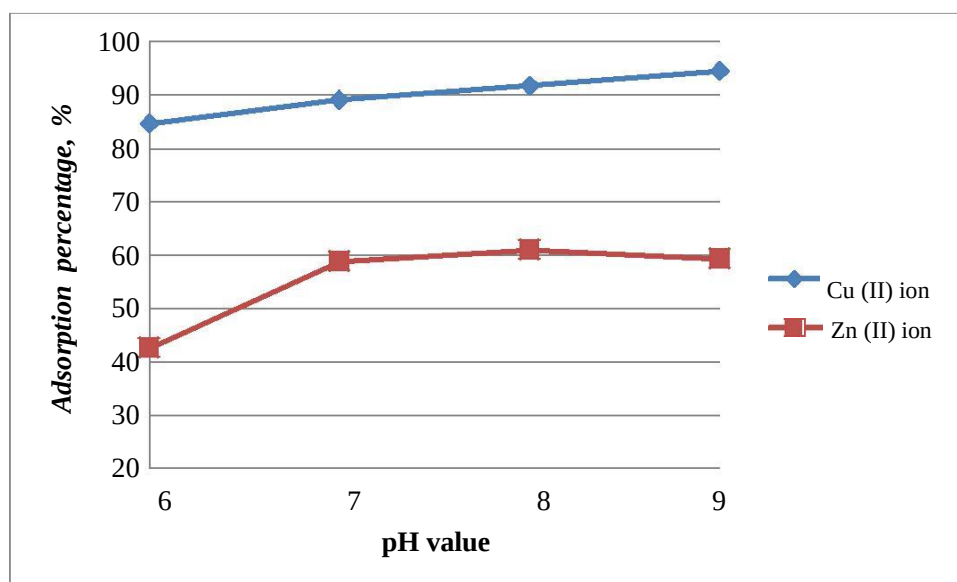


Figure 5: Comparison of adsorption percentage in different amount of pH value

The effect of pH towards the adsorption of rice husk was investigated by increasing the pH at the range of 6-9 pH level. The solution is at 30 ml and the sorbent used is 1g of rice husk at 5 minutes equilibrium time. From the graph shows that, it is dependent on the pH value as it increase from 6-9 pH level. it can be seen in the figure above, shows the reaction of rice husk on the adsorption of heavy metals solution in different pH value.

At higher pH the deprotonated groups are triggers which increase the adsorption percentage that involve in Cu (II) and Zn (II) ion adsorption. It reaches maximum adsorption percentage at 94.6% for Cu (II) ion and 60.9% for Zn (II) ion at the pH of 9 and 8. By this, it is prove that the sorption process is dependent of the pH of the solution. It also stated that increase in pH can activated the properties of carbon in the rice husk for it to adsorb the heavy metals ion more rapidly. However, the journal stated that by decreasing the amount of pH level of the solution will decrease the adsorption percentage as it will triggers the heavy metals cation at extreme acidic conditions. [16]

Moreover, metal biosorption is considered as a complex process that can be affected by various factors. There are several factors that involve in this mechanism of biosorption process such as, chemisorption, adsorption on surface and pores, ion exchange and heavy metal hydroxide condensation on the biosurface. [17]

5.0 Conclusion

In conclusion, this project is to enhance the development of low-cost biosorption of heavy metals from industrial waste water. Rice husk is the selected alternative source as it is a high amount of agricultural waste in Malaysia. The aim of this project is to conserve chemicals as well as energy for the waste water treatment without affecting the environment. The rice husk used for this project is raw rice husk because it is to avoid treatment as it can save more time and cost. It is to study the potential of the rice husk properties without changing the structural properties before the experiment is done. It is stated that, the used rice husk can be further reused for regeneration as well as re used in generating electricity and from the process of adsorption the rice husk produce less sludge which can make it to be more reliable as an adsorbent. [18] The characterization of raw rice husk is used in 3 types of parameters such as sorbent dosage, contact time and pH value of the samples. The potential of this rice husk can be seen in the results collected from the data calculated by Atomic Adsorption Spectrophotometer (AAS) machine. The maximum adsorption can be achieved sorbent dosage of 1g of rice husk at 60.2% and 2g of rice husk at 76.4% for Cu (II) ion. Besides, for 1g of rice husk the maximum adsorption for Zn (II) ion is at 75.8% and 2g of rice husk is at 78.4%. Furthermore, the increase of pH maximum amount of adsorption percentage can also be determined by batch process experiment. The value of pH 9 has the highest value of adsorption percentage at 94.6% of Cu (II) ion and pH 8 is at maximum adsorption for Zn (II) ion is 60.9%. In addition, isotherm adsorption has been studied to see the properties of rice husk in adsorbing the metal ions that shows it is correlated well with the Langmuir isotherm model. Therefore, it shows that the properties of rice husk are reliable for the adsorption of heavy metals solution.

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Release Dynamic study for Controlled-released-fertilizer by Starch-derivative-alginate based formulation

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Abstract

Controlled release fertilizer had been developed to minimize harmfulness to environment and increase delivering efficiency by controlling the release rate of fertilizer. However, conventional Controlled release fertilizer will acidify or left residue in soil which affect the growth of agricultural crops. This research is to synthesis Controlled release fertilizer with sodium alginate and cassava starch with performs of release dynamic studies to overcome the drawbacks of conventional type of Controlled release fertilizer. The synthesis of starch derivative alginate fertilizer is by crosslinking starch, alginate and urea mixture with calcium chloride solution and this Controlled release fertilizer is further used to undergo release studies. Release dynamic study is carry out in static condition by immersing Controlled release fertilizer in distilled water for duration of one month with measuring amount of urea released according to absorbance value obtained from UV-Vis Spectrophotometer under wavelength of 210nm. Starch derivative alginate fertilizer provide significant decrement in release rate where conventional fertilizer is fully release to water in two days but Starch derivative alginate fertilizer spent twenty one days to have full release; besides that, through data analysis the release rate can be reduced through high level (0.2667g/ml) of sodium alginate, high level (1M) of Crosslinker concentration and low level (0.1g/ml) of urea content.

Keywords: *Controlled-release-fertilizers, starch-alginate formulation, release dynamic study.*

1. Introduction

The growth of worldwide population outdistances global agricultural production and this lead to shortage of food supply; achieving higher agricultural yield is necessary to overcome the problem. Therefore, agricultural chemicals and fertilizers are introduced to control pests and supply nutrients to agricultural crops and increases the production of crops [1]. In the real life phenomena, only 30% of agrochemical and fertilizer applied on the agricultural crops reach the target region and produce desired biological responses. The reason of having low delivering efficiency is due to excess application, leaching due to rainfall and irrigation water, and degradation of active ingredients[2-4]. Besides that, improper application of agricultural chemicals and fertilizers is causing environment pollution and water pollution which affected the natural, animals as well as human life [5]. Furthermore, overdose of urea fertilizer will having reaction with bio-enzyme in soil which accounting 24% of global annual emission of N_2O and NH_3 [6,7].

To overcome leaching of fertilizer and increase the efficiency of delivering nutrients towards target, Controlled Release Formulations (CRF) is introduced to assure the delivering [7,8]. Controlled release formulation has been applied in many region such as pharmaceutical, biotechnology and agricultural region. Coating active ingredients with material that reduces the release rate of active ingredients (medicine, agrochemical or tissue) is the basic principles of CRF. Efficiency of delivering active ingredients to the target area will increase as controlled release formulation applied ensures the utilization of active ingredients by agricultural crops with reduction of leaching percentage. The primary standards for choosing coating material are low cost, having good coating property and degrade in soil without forming harmful toxic substances [5,9].

As Controlled Release fertilizer to the market and research still on-going to further improve the delivering mechanism and reduce the leaching of fertilizer. The coating material for Controlled Release fertilizer can be classified to three types that included organic, inorganic compound and polymer or matrix of polymer[10, 11].Moreover, the most widely applied controlled release fertilizer; sulfur coated fertilizer and polymer encapsulated fertilizer caused pollution to the soil where sulfur coated acidified the soil and polymer only degraded after a long period of time [10].

Starch derivative alginate based controlled release formulation is biodegradable and preparing through natural resources that showed a potential to be applied on controlled release fertilizer. Besides that, few researches have been done on pesticide, herbicide and fungicide; the release rate of starch derivative alginate formulation on these agrochemical is showed in Figure 1 which support the applicability of this formulation on fertilizer[5,12-13].

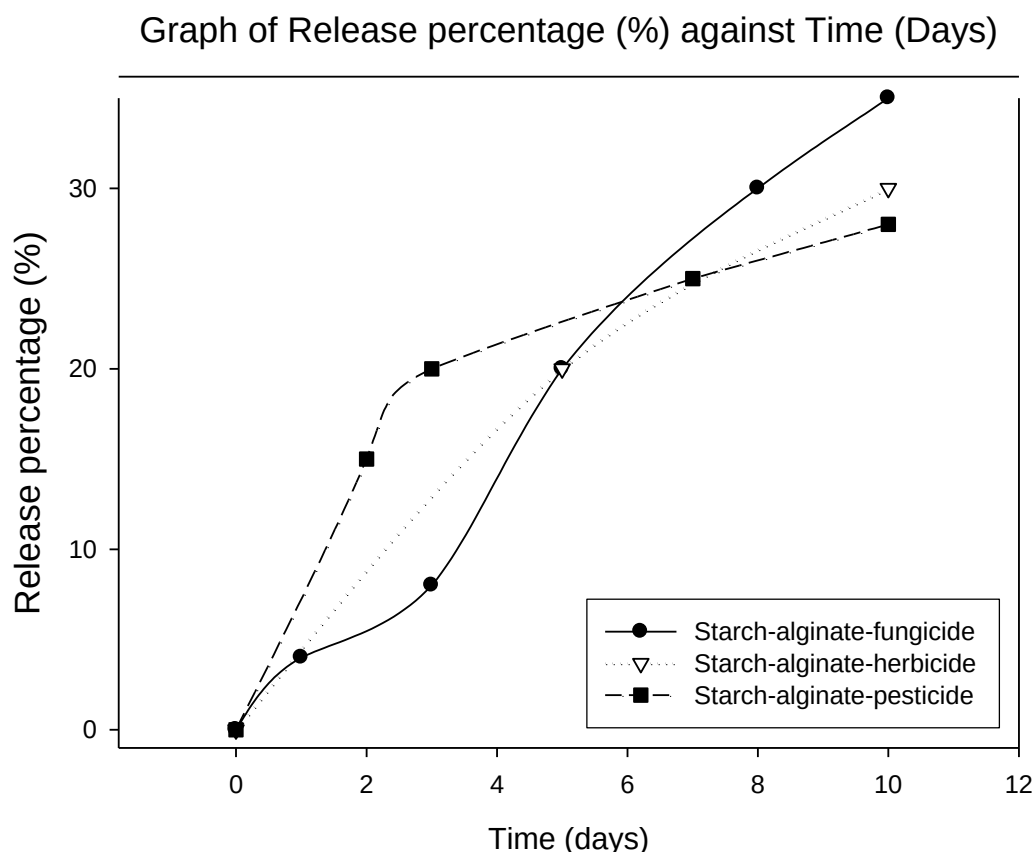


Figure 1. Graph of Release Percentage(%) against Time (days)

Alginate, an unbranched binary copolymer consists of 1,4 linked α -L-guluronic acid and β -D-mannuronic acid obtain from brown sea weeds that with non-toxic, fast gelling and simple handling properties [14]. The release of active ingredient encapsulated by alginate occurs after swelling of alginate granule as alginate is hydrophilic. Alginate beads that encapsulated with active ingredients can easily formed by dropping alginate-active ingredient solution to divalent ion solution as alginate will crosslink with divalent ion (refer to Figure 2) [15]. The drawback of alginate coating is due to macrospores presence in alginate molecular which enhances the diffusion of hydrophilic molecules and reduces physical stability of alginate beads to environment condition. Other polysaccharides is then applied on alginate formulation to improvise the physical properties and release dynamics of alginate [16,17]

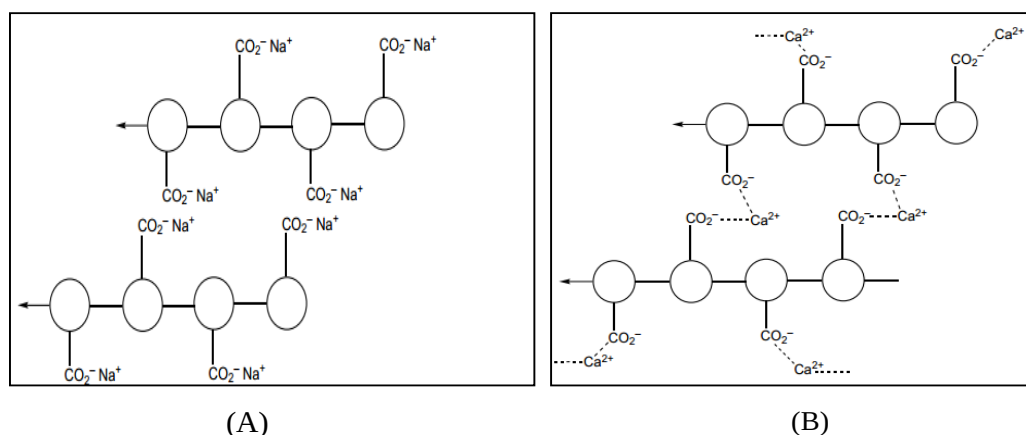


Figure 21. Crosslinking Sodium alginate solution with Calcium Chloride (A) Before crosslinking (B) After Crosslinking [15].

Starch, a natural polysaccharide that consists of repeating 1,4- α -D-gulucopyranosyl unit with naturally discrete granules. In compared with other carbohydrate, starch discrete granules are relative dense, immiscible and lightly hydrate in cold water which enforced the reduce in release rate [13]. Besides that, starch is easily found from crops and biodegradable by microorganism.

This research is to conduct release dynamic study of starch derivative alginate based fertilizer by first synthesis the controlled release fertilizer with three levels of 4 parameters- Starch, Sodium alginate, Crosslinker (CaCl_2) concentration and Urea content. With the controlled release fertilizer, release dynamic experiment is undergo to evaluate the encapsulation efficiency of controlled release fertilizer and the effect of each parameter to the release rate of urea to water.

2. Research Methodology

2.1 Materials

Sodium alginate (R&M) the gelation material for controlled release formulation was obtained from Evergreen Engineering & Resources Sdn.Bhd. Cassava starch or tapioca starch as filler for alginate formulation to improve the mechanical and physical properties of Controlled release formulation was obtained from Thye Huat Chan Sdn.Bhd. Urea (Duchefa, Netherlands) the active ingredient to be encapsulated in controlled release formulation was obtained from Saintifik Sdn.Bhd. Calcium Chloride anhydrous (Alpha) was purchased from Saintifik Sdn.Bhd. and used as crosslinking agent for starch-alginate-urea mixtures for synthesis of Controlled release fertilizer.

2.2 Design of Experiment

The experiment is conducted on three levels four parameter design; with application of Taguchi method, L9 arrays are applied to evaluate the effect and interaction of each parameter and 9 samples are required for the different parameter and level involved. The four parameters are cassava starch, sodium alginate, calcium chloride and urea content in the formulation. Three levels for cassava starch and sodium alginate are 0.0067, 0.2000 and 0.2667g/ml respectively for determination the

interaction of different levels. For concentration of crosslinking agent- calcium chloride solution, three levels are 0.2M, 0.5M and 1.0M. Lastly, for active ingredient-urea, the low, medium and high are 0.1, 0.1667 and 0.2333g/ml respectively. The formulation using Taguchi method was tabulated in Table 1.

Table 1. Composition and Crosslinker concentration for controlled release fertilizer

Experiment	Starch (g/ml)	Alginate (g/ml)	Calcium Chloride concentration (M)	Urea (g/ml)
1	0.0067	0.0067	0.200	0.1000
2	0.0067	0.2000	0.500	0.1667
3	0.0067	0.2667	1.000	0.2333
4	0.2000	0.0067	0.500	0.2333
5	0.2000	0.2000	0.200	0.1000
6	0.2000	0.2667	0.500	0.1667
7	0.2667	0.0067	0.500	0.1667
8	0.2667	0.2000	1.000	0.2333
9	0.2667	0.2667	0.200	0.1000

2.3 Synthesis of Controlled Release Fertilizer

Synthesis of starch-derivative-alginate based fertilizers is based on gelation properties of sodium alginate. Different formulation is prepared by mixing sodium alginate, starch and urea in distilled water according to concentration shown in Table 1. These mixtures are then stirred until homogeneous mixture formed. This alginate mixture is then dropped wisely into different concentration of Calcium Chloride solution by using syringe with needle size of 1.2mm diameter. Sodium alginate mixture will then crosslinked with Ca^{2+} ion to produced beads [18,19]. The beads are left inside the CaCl_2 solution to ensure completed gelation. Beads are then removed from the solution and rinsed with distilled water to remove CaCl_2 content. Beads are dried at room temperature and further dried in oven operating at 50°C until constant weight achieved [20]. The dried beads are then use to carry out release dynamics experiment. The resulted formulation is label sample 1-9 according to Table 1.

2.4 Calibration curve for pure urea

A calibration curve of pure urea is prepared for determination of amount of urea release to water in release dynamics studies; the calibration curve is done by first dissolving 5mg to 2g of urea in 100ml of distilled water. Absorbance of these pure urea solution is then measured with Thermo Scientific™ GENESYS 10S UV-Vis Spectrophotometer with wavelength of 210nm and a curve of absorbance value against concentration of urea solution is plotted for further release dynamic experiment.

2.5 Release dynamic study of Controlled Release Fertilizer

Release dynamic study is to evaluate the effect of parameter to release rate of urea and conclude the interaction between these parameters. The release dynamic study is

carry out in water; dry controlled release fertilizer is added to 100ml of distilled water. At different time interval, 3.5ml of sample is removed for determination of urea by using Thermo Scientific™ GENESYS 10S UV-Vis Spectrophotometer under wavelength of 210nm which follows the literature review done [21]. 3.5ml of distilled water is then added to the beaker to maintain constant level.

Determination of urea concentration is done with absorbance value obtained by referring to predetermined calibration curve.

3.0 Results and discussion

3.1 Release study of urea

Release dynamics study is the key experiment of this research; it was done by measuring amount of urea release to water over a period of 28 days by using UV-Vis Spectrophotometer. A sample of pure urea was also performed as a comparison to starch-alginate controlled release fertilizer. Figure 3 shown the amount of urea release of sample 1 to 9 and also a reference of pure urea; from Figure 3 can observed that the release rate of sample 1 to 9 were respectively lower than pure urea where the urea was totally release to water within 2days and sample 1 to 9 showed a reduction in release rate.

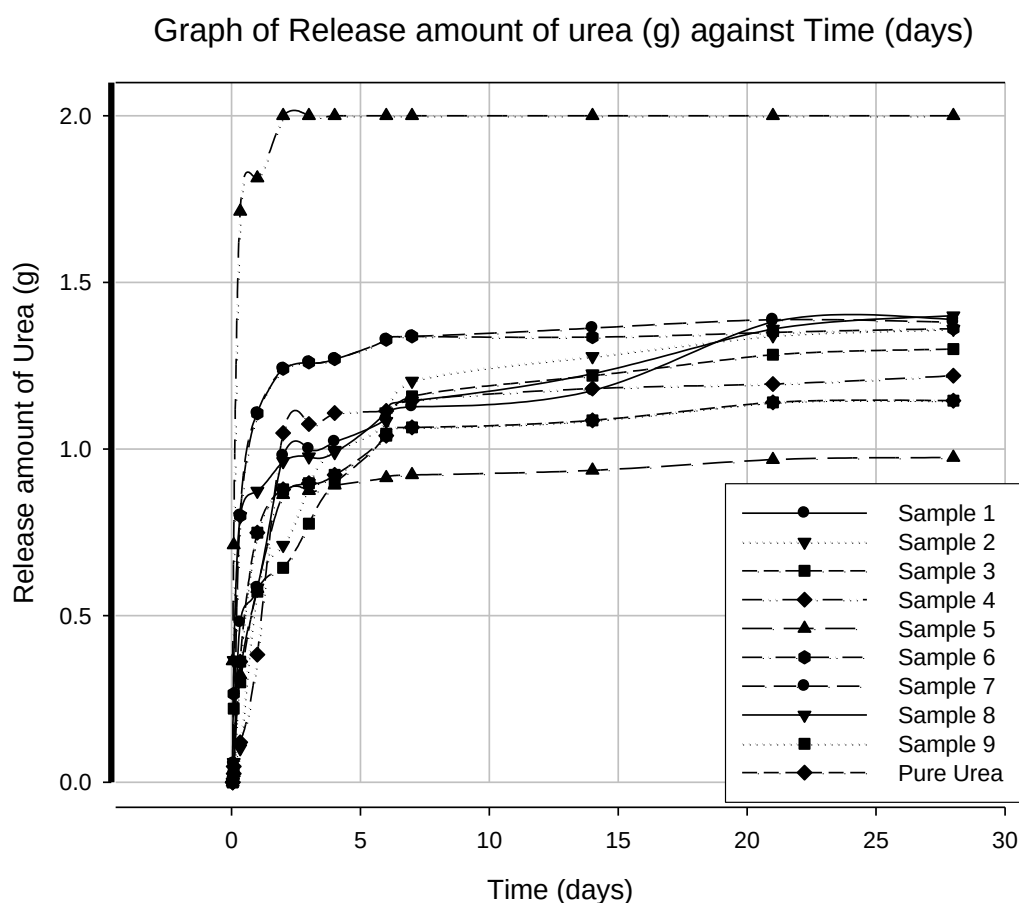


Figure 3. Graph of Release amount of urea (g) against Time (days)

3.2 Main effect of parameter to release rate of urea

Based on the main effect plot obtain from Minitab 17 with using Taguchi L9 array; the effect of each parameter to release of urea was showed as Figure 4.

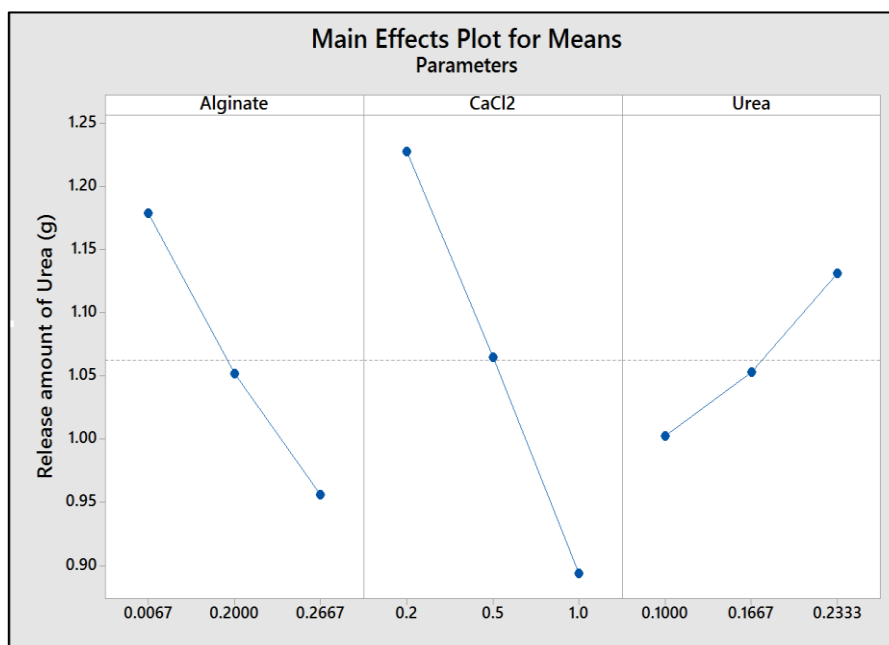


Figure 4. Main Effect of Alginate, CaCl₂ and Urea concentration to Release rate

3.2.1 Effect of Sodium Alginate to Release Rate of Urea

From Figure 4, when sodium alginate concentration increased from 0.0067g/ml to 0.2267g/ml in alginate mixture for synthesis of controlled release fertilizers, the release rate of urea to water decreased. The same effect was also described by Baljit et al. on encapsulated thiram fungicide by using starch derivative alginate based controlled release formulation [12]. The effect of sodium alginate to release rate of urea can be explained as increase of sodium alginate content resulting in higher polymer compound was developed to encapsulate urea which increased the path of diffusing [12]. The effect can further describe by Figure 5, where the average release rate of controlled release fertilizer prepared with low, medium and high level of sodium alginate content was showed with respect with time.

Graph of Release amount of urea (g) against Time (days) for alginate

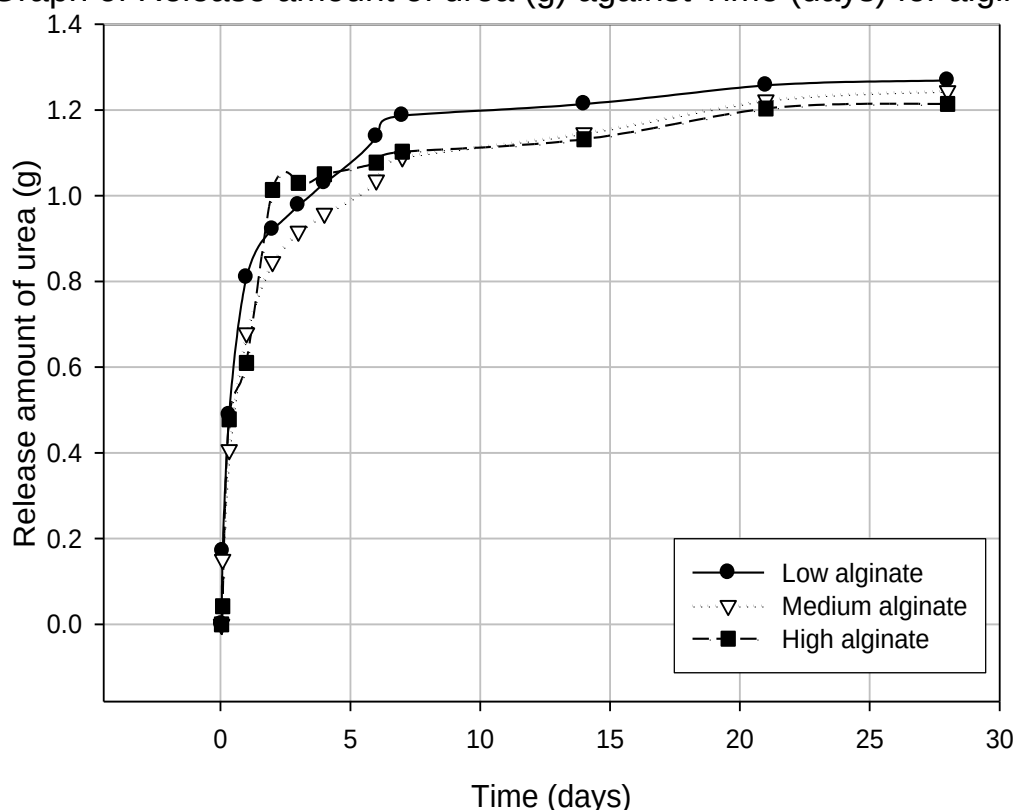


Figure 5. Graph of Release amount of urea (g) against Time (days) for alginate

3.2.2 Effect of CaCl_2 concentration to Release Rate of Urea

Crosslinking agent (CaCl_2 solution) showed a large effect towards the release rate of urea to water. The effect of CaCl_2 solution was done by varying the concentration from 0.2M to 1M when preparing the controlled release fertilizer. Effect of CaCl_2 solution is showed in Figure 4 where increased of concentration resulting in reduction in release rate of urea to water; Pepperman et al. and Roy et al. on alginate based controlled release formulation showed the same effect which supported the finding of this research[13,22]. This phenomenon can be explained as crosslinking agent CaCl_2 increase the crosslink between sodium alginate with calcium ion which strengthen the structure of the polymer and reduced the distance between each bonding and reduced the diffusion rate of water into controlled release fertilizer. Figure 6 showed the release of urea on low, medium and high level of CaCl_2 solution over time.

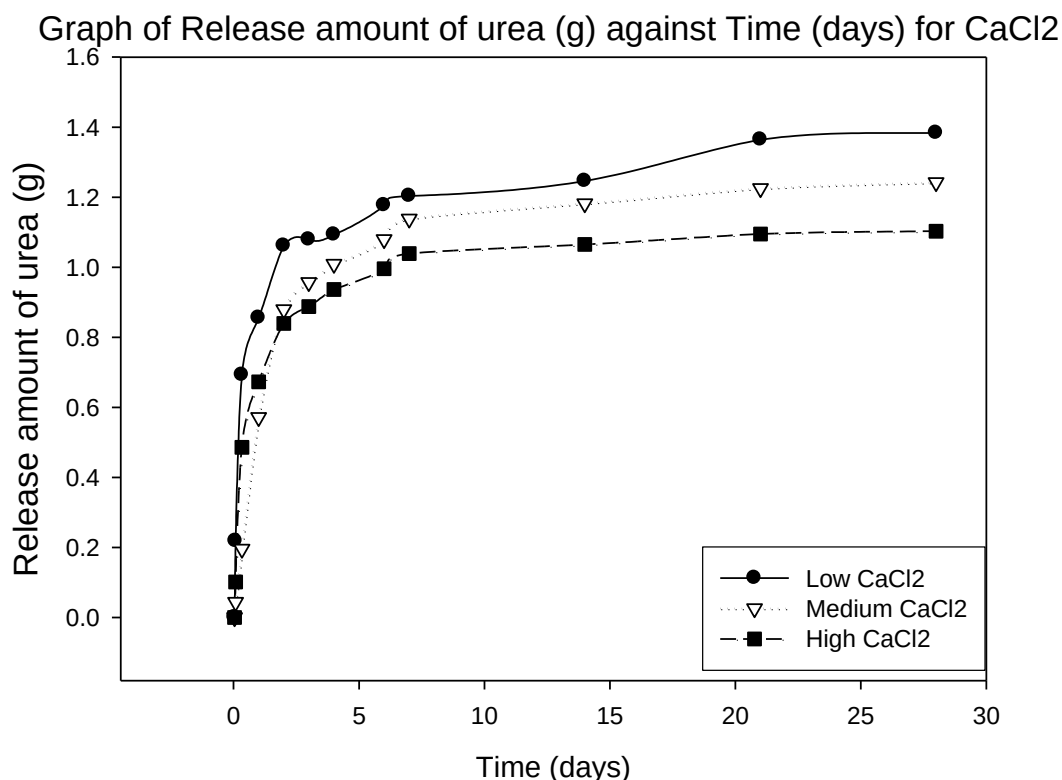


Figure 6. Graph of Release amount of urea (g) against Time (days) for CaCl₂

3.2.3 Effect of Urea to Release Rate of Urea

Urea the active ingredient which encapsulated in starch derivative controlled release formulation showed effect to release rate. Based on Figure 4, the increased of urea content increased the release of urea; from Roy et al. research, the loading of active ingredient also gave the same phenomenon which support the result of this research [13]. Increased in active ingredient concentration resulting in higher content encapsulated which increase the gradient of diffusion between controlled release fertilizer with water and resulting in increase in release rate. Figure 7 showed the effect of three level of urea to release rate over period of 28days.

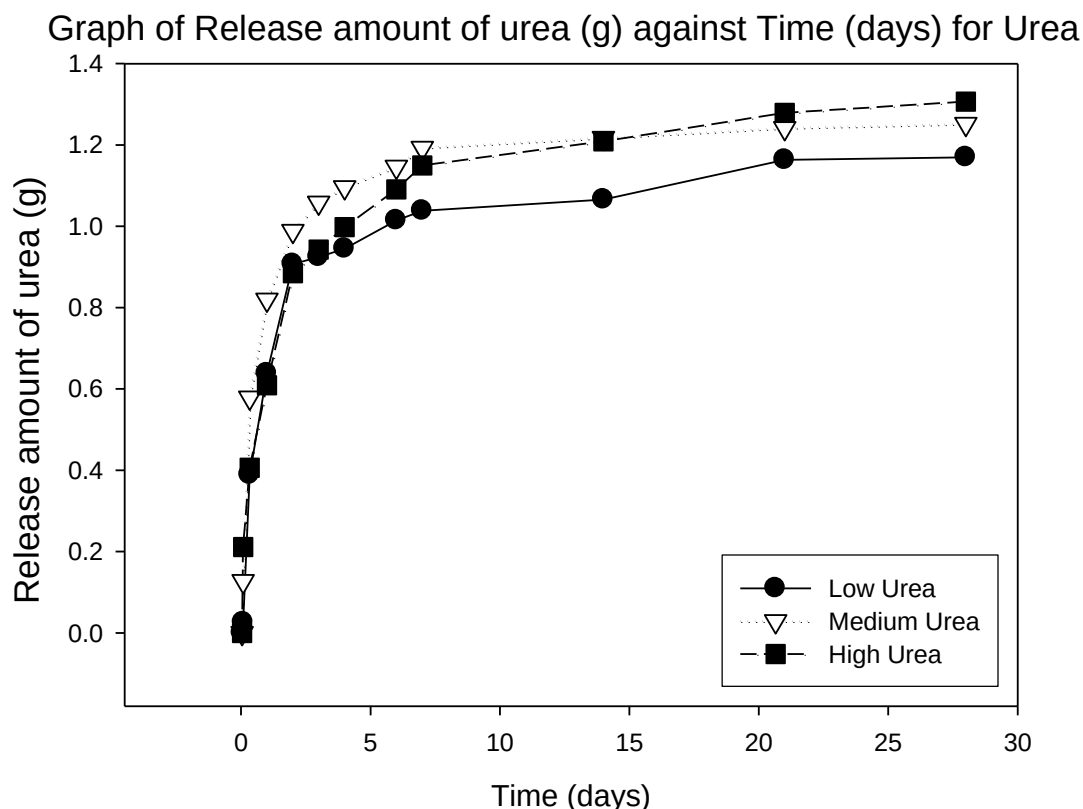


Figure 7. Graph of Release amount of urea (g) against Time (days) for urea

4.0 Conclusions

In the conclusion, this research successfully demonstrated the new Controlled Release Formulation on Fertilizer. Release dynamic of starch derivative alginate based fertilizer is done in water and results are analysed. Parameters- alginate, Crosslinker (CaCl_2 solution) and urea concentration showed effect to release rate of urea where increase in sodium alginate and crosslinker concentration reduced the release rate of urea but in opposite situation, increase in urea concentration in formulation increase the release rate of urea. With the results from this research, different combination of fertilizer can be prepared for usage in different region and benefit to agricultural field and reduce pollution towards environment. Further work such as analysis of release under different region, temperature and also biodegradability study can also proceed to identify applicability of this formulation.

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Optimisation of *Hibiscus Sabdariffa* as a Natural Coagulant to Treat Wastewater

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Abstract

The process of coagulation is commonly practiced in water and wastewater treatment to reduce level of dissolved chemical, turbidity and so on. Aluminium sulphate (alum) is the common coagulant used in wastewater treatment. However, recent studies show that residual aluminium in drinking water and sludge may induce Alzheimer's disease and environmental issues. Natural coagulant which is environmental friendly and non-toxic is developed as an alternative to overcome these issues. In this work, *Hibiscus Sabdariffa* was studied as natural coagulant to treat dye wastewater containing Congo red. The seeds were extracted with different solvent such as distilled water, 0.5M NaCl and 0.05 M NaOH to extract the coagulation agent. The working parameters were optimised using Response Surface Methodology (RSM). 0.5 M NaCl was found to have highest colour removal of 95.1 % among the solvents. In addition, *Hibiscus Sabdariffa* seed was found to be an effective coagulant that has 91.2% colour removal at the optimal working condition of pH 2, 190 mg/L coagulant dosage at 400 ppm of dye concentration. In this case, the pH was determined to be the most significant parameter affecting the colour removal. It was also been identified that the performance of natural coagulant is comparable with conventional coagulant, aluminium sulphate with colour removal of 91.2% and 92.3% respectively.

Keywords: *Hibiscus Sabdariffa*, Natural Coagulant, Coagulation, Wastewater Treatment.

1. Introduction

Dyes are widely used in many industries such as textile dyeing industry, cosmetic industry, and fabric industry. Most of the dyes used are synthetic or chemical dye that are available in different colours [1]. During the process of dyeing and painting, it generates large amount of complex chemical constituent in the form of wastewater[2]. Direct discharge of dye wastewater into environment induces aesthetic problem such as change in colour of river and water streams [2]. This interrupts the penetration of sunlight into the river hence disturbing the biological process of aquatic life[3]. Several dyes are proven toxic to aquatic life with their decomposition derivatives[4]. As environmental protection has become a main concern in global, wastewater produced must be treated using proper treatment method before discharge to reduce the level of damage to the environment. However, synthetic origin and complex aromatic molecular structures of dye leads to difficulty in wastewater treatment. Many techniques have been developed for dye removal from wastewater such as physico-chemical treatment, adsorption, advanced oxidation, electrochemical degradation and so on [5].

Among the processes mentioned, coagulation is the most common physico-chemical treatment practiced due to its simplicity and effectiveness[6]. Coagulation is a process to neutralize negatively charged colloid and dissolved solid present in wastewater which causes turbidity and colour by chemical coagulant. The neutralized particles will combine with each other and form large particle called floc. This floc is separable and their removal is facilitated by sedimentation[7]. Hence, level of turbidity, colour and contaminates in wastewater will be reduced. Commercially available coagulant such as aluminium sulphate, ferric sulphate and ferric chloride are most commonly used. Despite this, usage of these coagulants has several disadvantages. The treated water containing residual Aluminium from water treatment consumed by human will result in health issue. In addition, disposal of sludge generates from wastewater treatment containing aluminium leads to soil pollution.

Possible solution to these problems may be developing new coagulants which are derived from natural. Nowadays, great attention has been focused on natural coagulant to replace conventional coagulant. Natural coagulant derived from plants and animals which are high biodegradable, non-toxic is more environmental friendly and safe for human consumption. Besides, plants can be grown locally hence it is more cost effective than chemical coagulant. Several natural coagulants have been studied for water and wastewater treatment including *Moringa oleifera* [8–10], Nirmali seed [8] and *Jatropha curcas* [11,12]. Present of water-soluble protein in the seeds of these plants may contribute to coagulation process. Another potential natural coagulant which is *Hibiscus Sabdariffa* have been studied for turbidity removal for water treatment [13,14]. However, there is lack of further study of this plant as natural coagulant to treat dye wastewater.

In this project, *Hibiscus Sabdariffa* also known as Roselle is studied as a natural coagulant to treat dye wastewater. *Hibiscus Sabdariffa* is widely available in Malaysia and the production is about 240 tons yearly. This plant has been used widely for food and medical purpose. However, the capsules containing the seeds are usually discarded as a waste and by-product after the processing process[15]. Nutritional study of *Hibiscus Sabdariffa* shows that the seeds are found to have highest protein content compared with the flower and calyces which is 31.02% and the seed could be used as a potential source of proteins[16–19]. In addition, the protein present in seed of *Hibiscus Sabdariffa* is expected to have the ability for coagulation.

Therefore, in this project the performance of *Hibiscus Sabdariffa* as natural coagulant to treat dye wastewater is studied. The objectives of this work are to compare the performance of *Hibiscus Sabdariffa* as natural coagulant extracted by different solvent. Parameters such as pH, coagulant dosage and concentration of dye are also optimized using Response Surface Methodology (RSM). Lastly its performance is compared with conventional coagulant, aluminium sulphate (alum).

2. Methodology

2.1 Preparation of coagulant from *Hibiscus Sabdariffa* seeds

Hibiscus Sabdariffa was obtained from Raub, Pahang. The seed husk was removed and the good quality seeds were washed with water and dried at 60 ± 2 °C for 2 hours in an oven[20]. The dried seeds were then pulverised using a grinder into powder form and was used for each experiment. 5 g of seed powder was blended with 100 ml of solvent which were distilled water, 0.5M sodium chloride (NaCl) and 0.05 M sodium hydroxide (NaOH) to extract its coagulant agent. The extraction was done by using a household food blender for 2 minutes. These solvents were chosen based on previous researches [10,11]. The coagulant was filtered through muslin cloth to remove impurities and used in the subsequent jar test. In order to prevent microbial decomposition of organic compound present in the coagulant, the coagulant was prepared and used on the same day for optimum performance.

2.2 Preparation of synthetic dye wastewater

Stock solution of synthetic dye wastewater was prepared by dissolving accurately weighed Congo Red ($C_{32}H_{22}N_6Na_2O_6S_2$; molecular weight: 696.66 g/mol) in distilled water to concentration of 1000 ppm. The stock solution was diluted with distilled water to achieve different concentration of dye wastewater for the jar test. The pH of the wastewater was adjusted using concentrated hydrochloric acid (95%) or 1.0 M sodium hydroxide (NaOH) to the desired pH value.

2.3 Jar test

The coagulation process was performed to evaluate the performance of natural coagulant using jar test. 500 ml of dye wastewater was added with coagulant and the mixture was mixed for 4 minutes at 100 rpm for rapid mixing enhance floc formation. The sample was stirred at 40 rpm to allow flocculation for 25 minutes and then settle for 30 minutes. The colour removal after the coagulation was measured using a UV-Spectrophotometer (Model HALO RB-10-5110026) with wavelength of 500 nm[20]. The colour removal percentage was calculated using the following equation:

$$\text{Colour removal (\%)} = \frac{Abs_0 - Abs}{Abs_0} \times 100 \quad (1)$$

Where Abs_0 is the absorbance value before treatment and Abs is the absorbance value after treatment process. Each experiment was conducted in triplicate.

2.3.1 Effect of using different solvents for extraction of coagulation agent

Jar test for different solvent used for extraction process was done to identify the best solvent for extraction. The experiment was conducted at pH 2, coagulant dosage of 150 mg/L and concentration of dye wastewater at 100 ppm based on research done by Beltran-Heredia et al[21]. The coagulant with highest colour removal was chosen to carry out the optimization of working condition for coagulant in next experiment.

2.3.2 Optimization of coagulant activity using Response Surface Methodology (RSM)

Optimization of working condition for *Hibiscus Sabdariffa* as a natural coagulant was carried out using Response Surface Methodology (RSM). RSM is a popular and economical statistical technique in evaluating the influence of parameters on treatment response [22]. Three-factors and three level Box-Behnken response surface design (BBD) was employed in this work. The variables and the level selected are given in Table 1. Colour removal was analysed as the response.

Table 1. Experimental factors and levels of independent variables.

Factors	Range and levels		
	Low (-1)	Medium (0)	High (1)
pH	2	7	12
Dosage (mg/l)	100	200	300
Concentration (ppm)	100	250	400

Design Expert Version 6.0.8 (Stat-Ease Inc. Minneapolis) was used in this work. A total of 17 experiments were generated from Design Expert and the results were analysed and presented using 3D contour plot. Optimization was performed by the software and analysis of variance (ANOVA) was utilised to study the significant factor that affects the output of experiment.

2.3.3 Comparison of *Hibiscus Sabdariffa* and Aluminium Sulphate as a coagulant

Optimum combination of parameters was generated from RSM and jar test was performed for both natural and chemical based coagulant with the optimised working condition. In this study, aluminium sulphate (alum) was compared as chemical based coagulant as it is widely used in conventional water and wastewater treatment. The results would indicate the ability of natural coagulant to treat dye wastewater over chemical based coagulant.

2.4 Limitation of study

In this research, purification of coagulant extracted from the seed is not performed. Purification of seed extract such as dialysis, ion-exchange, precipitation and lyophilisation is rarely done in natural coagulant. This process would increase the overall process cost during commercialisation. Most research studies employ method of drying and pulverising of plant seed into fine powder and extract using solvent to use for experiments. Without purification, coagulation performance will decrease. Hence, future study can be done to discover the effect of purified seed coagulant on treatment process.

3. Results and Discussion

3.1 Effect of using different solvents for extraction of coagulation agent from *Hibiscus Sabdariffa* seeds

Determining the best solvent to extract coagulation agent from *Hibiscus Sabdariffa* seeds is able to improve the coagulation process. In order to identify the best solvent to be used, the effects of distilled water, 0.5 M NaCl and 0.05 M NaOH were compared. Figure 1 shows the colour removal of synthetic dye wastewater using three types of solvents at condition of pH 2, dosage of 150 mg/L and concentration of dye at 100 ppm.

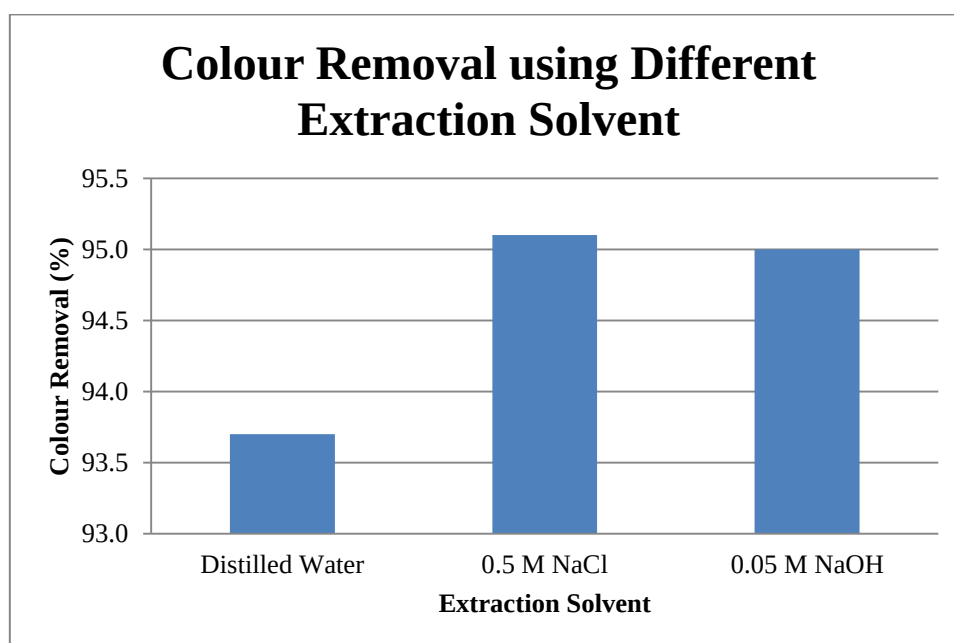


Figure 1. Effect of using different solvent for coagulant agent extraction from *Hibiscus Sabdariffa* seeds.

Based on Fig. 1, the highest percentage of colour removal obtained is 95.1% by using 0.5 M NaCl as extraction solvent while distilled water has the lowest percentage for colour removal at 93.7%. Protein solubility is dependent on the ionic strength of the solvent. When the ionic strength of solvent increases, dissociation of proteins will be enhanced and the solubility of protein will increase as well. During the extraction, protein interacts with the molecules of sodium chloride which allows it to form H-bonds with the surrounding molecules. When the protein surface is hydrophilic enough, the protein will dissolve [23]. After extraction, an odourless and milky coagulant solution was obtained using distilled water and 0.5 M NaCl. However, a greenish solution with rotten smell was obtained using 0.05M of NaOH. This might be due to the denature of protein and the seed content as NaOH is a strong base with pH 12. This observation eliminates NaOH as a solvent to be used for extraction although it shows similar result with NaCl. Similar result was reported by several researchers that 0.5 M NaCl gives highest coagulation activity using natural

coagulant compared to NaOH and distilled water[8,11]. Hence, 0.5 M NaCl was chosen to continue with next experiment.

3.2 Optimization of working parameter using RSM

Performance of natural coagulant can be affected by parameters such as pH, coagulation dosage and dye concentration. Hence, it is important to identify the suitable working condition for coagulant to perform optimally. The results obtained from experiment runs (colour removal) were correlated using the second-order polynomial shown in Eq. (2)

$$\begin{aligned} \text{Colour Removal (\%)} = & -1.70 - 46.62A + 0.18B - 2.93C + 49.82 A^2 - \\ & 1.03 B^2 + 1.58 C^2 + 0.3AB - 3.2 AC \\ & + 0.7 BC \end{aligned} \quad (2)$$

Where A, B and C are the coded values of the parameters pH, coagulant dosage and concentration of dye. Different models were compared using statistical analysis. The quadratic model was chosen based on high R^2 statistics. The R^2 value for colour removal was 0.9982 and the plot of predicted versus actual result for colour removal in Fig 2 indicates that the experimental result is similar with the predicted result. This shows that the prediction of experiment result is satisfactory using this model.

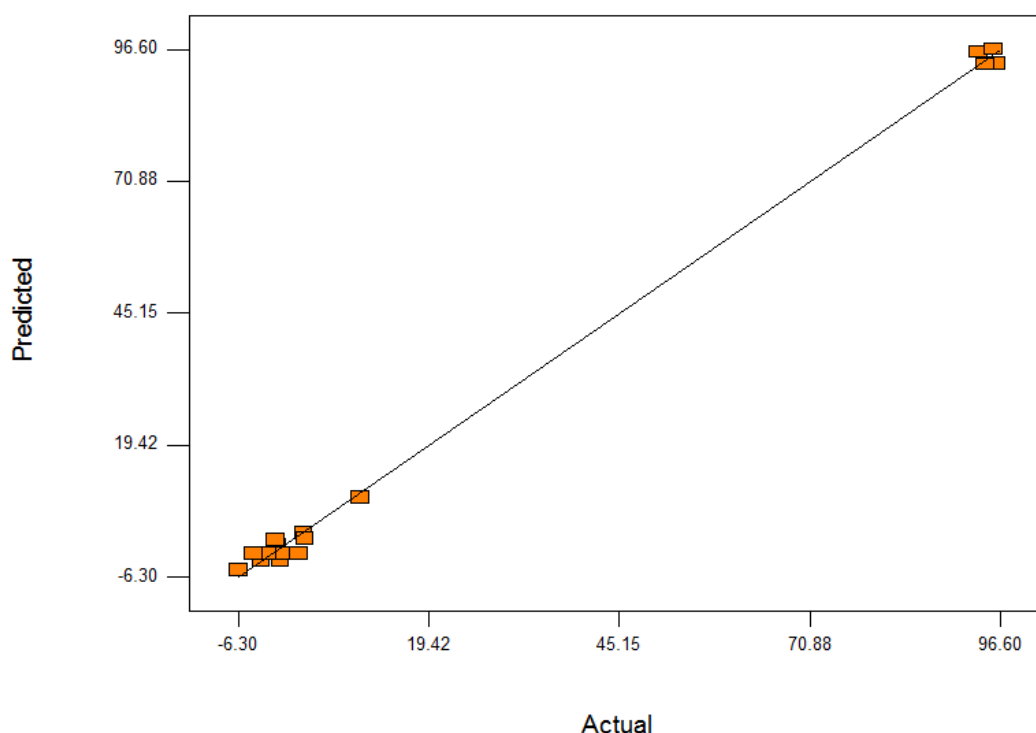


Figure 2. Predicted vs. actual result for colour removal (%)

This model was used to study the effects of the factors on the response and presented by 3D surface graphs and contour plots generated by Design-Expert software in Fig 3 to Fig 5.

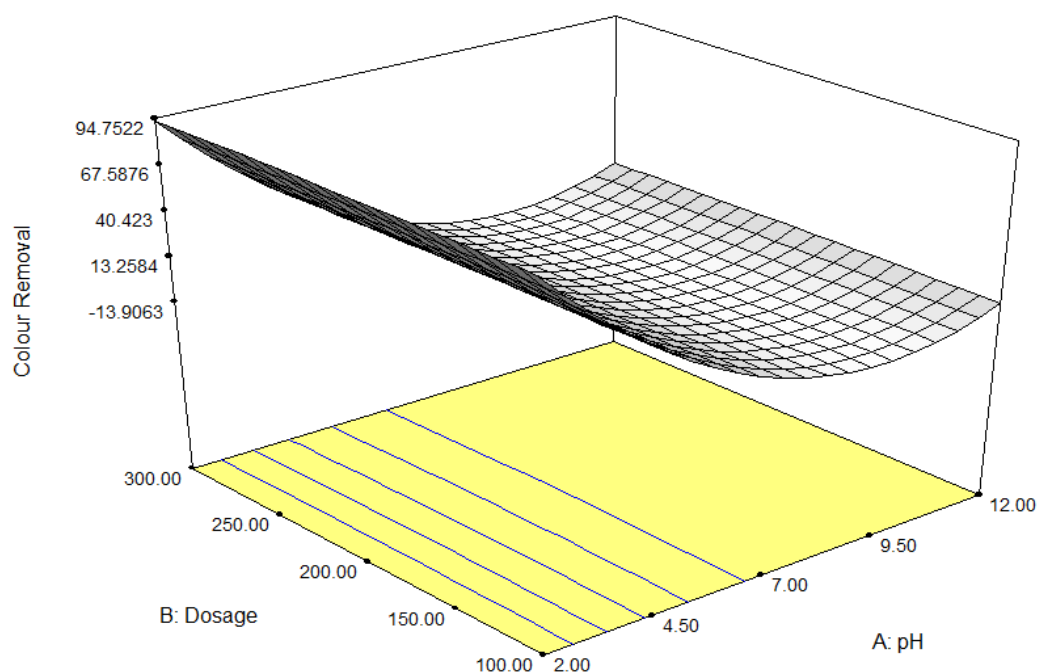


Figure 3. Effect of coagulant dosage and pH on colour removal.

Fig. 3 shows the 3D response surface plot for the effect of coagulant dosage and pH at concentration of dye at 250 ppm. Colour removal increases when the pH decreases. A significant reduction in colour removal was observed when the pH was increased beyond 2. Besides, highest colour removal was obtained at pH 2 regardless the amount of coagulant dosage. This shows that coagulation process was highly pH-dependent and *Hibiscus Sabdariffa* works efficiently under acidic condition.

The coagulant activity happens in acidic condition due to the amino acids that make up the protein as the key component for coagulant protonated at pH 2. Amino acid of protein present in *Hibiscus Sabdariffa* has isoelectric point range from 3.2 to 11 [24]. When the protein is subjected to pH lower than the isoelectric point, it carries a net positive charge. Hence at pH 2, all the amino acids carry positive charge and give protein its overall charge. This protein acts as a cationic coagulant to remove negatively charged sulfonic group of Congo Red. This can be explained as the coagulation occurred effectively at pH 2.

According to ANOVA shown in Table 2, pH is the most significant parameter that affects the colour removal. *F* value of this factor (2345.85) with *P* value less than 0.0001 indicates this factor was significant at 95% confidence level. This proves that coagulation process using *Hibiscus Sabdariffa* as natural coagulant is highly pH-dependent.

Table 2. ANOVA for Quadratic Model used for analysis of colour removal.

Source	Sum of Squares	DF	Mean Square	F Value	Prob>F
Model	28044.43	9	3116.05	420.32	< 0.0001
A, pH	17391.12	1	17391.12	2345.85	< 0.0001
B, dosage	0.24	1	0.24	0.033	0.8609
C, Concentration	68.44	1	68.44	9.23	0.1890
A ²	10452.76	1	10452.76	1409.95	< 0.0001
B ²	4.42	1	4.42	0.60	0.4651
C ²	10.44	1	10.44	1.41	0.2740
AB	0.36	1	0.36	0.049	0.8319
AC	40.96	1	40.96	5.53	0.0510
BC	1.96	1	1.96	0.26	0.6230
Residual	51.89	7	7.41		
Lack of Fit	28.45	3	9.48	1.62	
Pure Error	23.44	4	5.86		
Cor Total	28096.33	16			

However, identifying the optimum dosage of coagulant is important for optimum performance with minimum amount of coagulant required. This can minimize the cost of coagulant in treatment plant and reduce the sludge formation [25]. Thus, choosing a low amount of coagulant dosage with high percentage colour removal of dye is preferable. In this case, dosage required to treat 250 ppm of dye wastewater is found sufficient at range from 100 mg/l to 200 mg/l with colour removal of 94%. Nevertheless, the dosage required depends on the initial dye concentration. The higher the concentration of dye, the more the negative charged dye particle presents hence it requires more cationic coagulant to neutralize it. The coagulation process could not be initiated if the dosage is too low while overdose of coagulant confers positive charges on the particle surface would result in re-disperse of dye particle hence low colour removal [26].

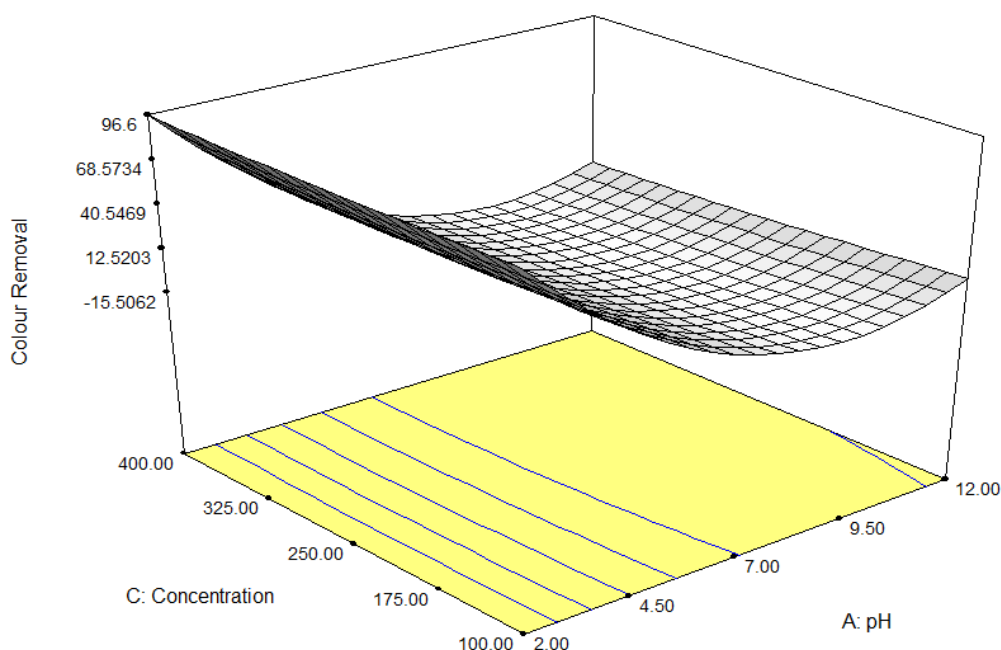


Figure 4. Effect of initial concentration of dye and pH on colour removal.

Fig. 4 shows the effect of different concentration of dye and pH at coagulant dosage of 200 mg/L. Coagulation was performed efficiently with dye concentration varied from 100 ppm to 400 ppm. This indicates that 200 mg/L of coagulant was sufficient to treat dye wastewater up to 400 ppm with approximate 96.6% colour removal. This suggests that *Hibiscus Sabdariffa* can be used to treat dye wastewater with this range of concentration.

On the other hand, maximum colour removal was again observed at pH 2 regardless of the initial concentration of dye due to the coagulant is highly pH-dependent. Colour removal reduced significantly when pH increases beyond 2 to 9.5. This is due to the formation of positive and negative charged amino acid when subjected to this pH. This mixture of different charges of amino acid would have decreased the cationic ability of the coagulant, hence reduce the performance of coagulation. The colour removal was slightly increased to 10%-12% at pH range from 11 to 12. This may be due to the present of arginine in protein with isoelectric point of 11[24]. Arginine which has high percentage in total protein present in seed of *Hibiscus Sabdariffa* might have the responsibility in the coagulation process at this pH. However, the ability of colour removal is low and not significant. Hence it is not consider as optimum pH for coagulant process.

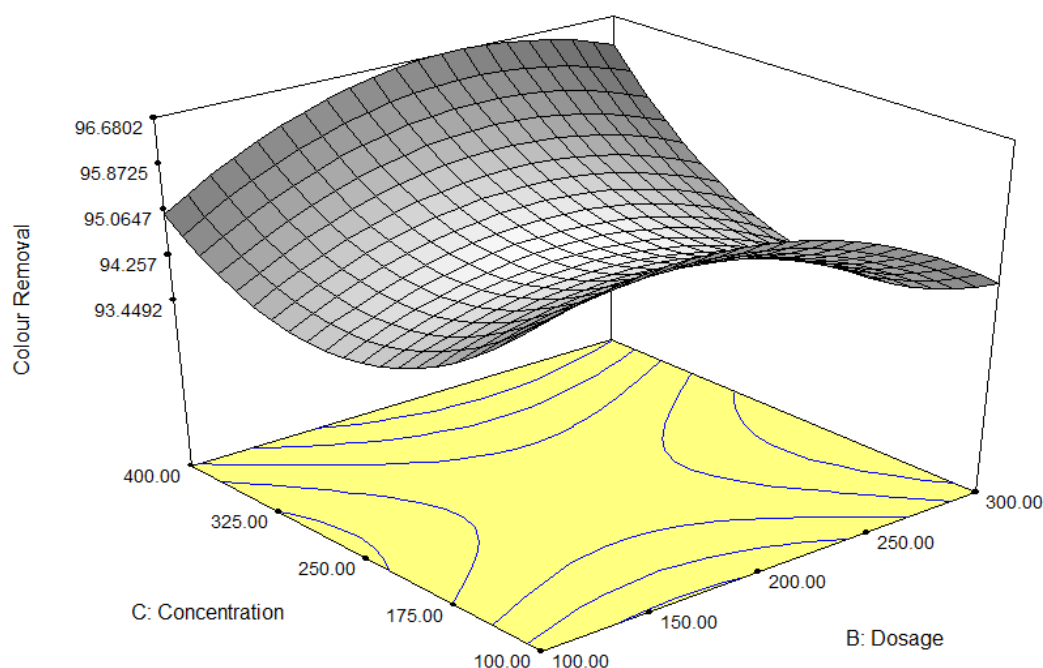


Figure 5. Effect of initial concentration of dye and dosage on colour removal.

pH was determined as the significant factor that affect the output of the experiment. The relationship between concentration of dye and dosage of coagulant is also important to study. The effect of initial concentration and coagulant dosage at pH 2 was shown in Fig. 5. The plot shows that colour removal increases with increment of dosage from 100 mg/L to 200 mg/L. Wastewater consists of more negative charged sulfonic group requires higher dosage of coagulant in order to achieve complete neutralization. In spite of this, colour removal decreased when dosage increased from 200 mg/l to 300 mg/l. This is explained as overdosing of coagulant. Excess amount of

coagulant causes the floc formed to re-disperse thus colour removal decreased[27]. This should be avoided to ensure the performance of coagulation.

The working condition was optimized by using the numerical optimization of Design-Expert based on the experimental results obtained and the model selected. The maximum colour removal with 96.1% was predicted at pH 2, initial concentration of 400 ppm and dosage at 190 mg/L. This can be seen from Fig. 5, maximum colour removal was achieved at the range of 325ppm to 400ppm of dye concentration and dosage at 150 mg/L to 200 mg/L. Experiment was conducted at this condition and the actual value obtained was 91.2% with 4.2% deviation. This result showed that the model developed from Eq. (2) was well fitted to the experimental result. Thus, the optimum value of the factors was finalized at pH 2, initial concentration 400 ppm and dosage of 190 mg/L.

3.3 Comparison of *Hibiscus Sabdariffa* and Aluminium Sulphate as coagulant

Optimum working condition for *Hibiscus Sabdariffa* was obtained using RSM as pH 2, initial concentration 400 ppm and dosage 190 mg/L. Jar test was performed using *Hibiscus Sabdariffa* and aluminium sulphate at this condition for comparison purpose.

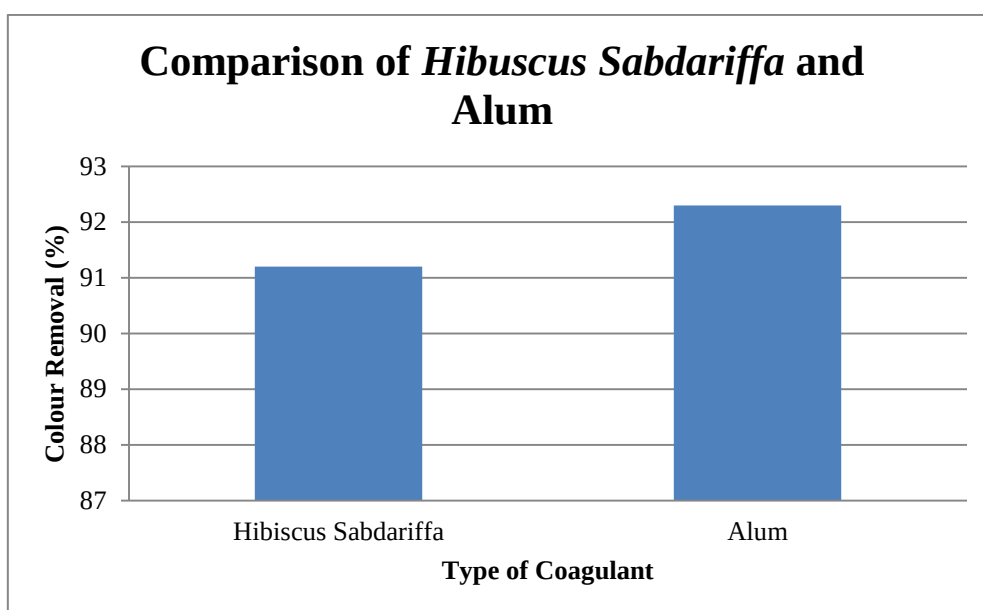


Figure 6. Comparison of *Hibiscus Sabdariffa* and Aluminium Sulphate.

Performance of *Hibiscus Sabdariffa* was found comparable to alum based on Fig. 6. 91.2% colour removal was achieved by *Hibiscus Sabdariffa* while alum recorded a percentage colour removal of 92.3%. This shows that the cationic protein of *Hibiscus Sabdariffa* has the ability for coagulation similar to alum. Hence, *Hibiscus Sabdariffa* can be used to replace alum as a commercial coagulant. By using natural coagulant, the drawback of using alum related to health and environmental can be prevented.

4. Conclusion

In this study, *Hibiscus Sabdariffa* seed was found as a highly effective colour removal agent for coagulation of Congo Red dye. Present of cationic protein in this plant is the key component contributed to coagulation process. Extraction of coagulation agent from the seed using 0.5 M NaCl solution was found to have highest colour removal of 95.1% compared to seed extracted by distilled water and NaOH. Working conditions such as pH, initial dye concentration and coagulant dosage was evaluated using Response Surface Methodology and pH was found as the significant factor that affects the output for colour removal. The coagulation process was also modelled and optimized and the optimum working condition was found at pH 2, 400 ppm of initial dye concentration and 190 mg/L of dosage. Lastly, *Hibiscus Sabdariffa* also showed a relatively good and comparable performance with aluminium sulphate to treat synthetic dye wastewater. This can be concluded that *Hibiscus Sabdariffa* can be used to replace aluminium sulphate as a coagulant in the industry, which is cost-effective, biodegradable and environmental friendly.

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The Fundamental Study of Anti-microbial Activity of *Piper Betle* Extract in Toothpaste

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Abstract

The leaves of *Piper Betle*, also known as betel leaves, that belongs to the piperceae family, is known to possess many medicinal properties such as gastro-protective, wound healing as well as prevailing oral health by hardening of the gums and removing bad breath. In recent years, the extract of betel leaves has also gained much attention for its abilities to inhibit microbial growth due to the presence of bioactive compounds. Hence, the extraction of these bioactive compounds is essential if these properties are to be utilized in real life applications. In current research, the effects of various solvents (ethanol and water) on the extraction of these bioactive compounds are investigated. It was found that ethanol (95%) has the highest phenolic content of 840 mg GAE/g followed by ethanol (50%) and water of having values of 460 mg GAE/g and 200 mg GAE/g respectively. The use of *Piper Betle* extract in real life applications is very much still limited. Keeping all of the beneficial properties of this medicinal plant such as its highly effective antimicrobial abilities in mind, the idea of combining its extract with an existing oral product (toothpaste) for the enhancement of its antimicrobial properties is investigated in this study. The minimum concentration of the three solvents, ethanol (95%), ethanol (50%) and aqueous solvent, required to inhibit *Escherichia coli* was found through the minimum inhibitory concentration (MIC) assay. The MIC values for the three solvents were found to be 2 mg/ml, 7 mg/ml and 19 mg/ml respectively. Since 95% ethanolic extract was found to contain the highest phenolic content, it was also introduced to *Staphylococcus aureus* which gave an MIC of 2 mg/ml. The ethanolic extract combined with a conventional toothpaste, containing both fluoride and triclosan, were subjected to the same bacterial pathogens, *Escherichia coli* and *Staphylococcus aureus* as well as *Candida albicans* via agar well diffusion assay. An increase in the zone of inhibition of 5.3 mm and 9.7 mm for the bacterial pathogens and 5.4 mm for the fungal pathogen was observed showing the potential of using herbal extracts as antimicrobial agents in oral products such as toothpastes.

Keywords: Betel leaves extract, anti-microbial activity, toothpaste.

1. Introduction

Oral hygiene is an important part of the overall health that is generally overlooked when it comes to diseases caused by microbes. Saliva, excreted by the salivary glands, can serve as a key component for the inhibition of bacterial and fungal growth. Saliva contains 99% of water and 0.5% of other substances including enzymes, electrolytes and antimicrobial agents. Its primary function is to break down food particles inside the oral cavity [1]. In a normal clean oral cavity, around 350 species of commensal microorganisms can be found given that the mouth is warm and moist providing the perfect breeding ground for it [2]. These microorganisms are not only present in the tooth's surface but it can also be found in every corner such as on the tongue and oral fluids. Hence, if not much needed attention is paid to oral hygiene it can give rise to diseases such as dental caries [1].

Toothpaste is one such vital tool for oral hygiene. Even though the history of toothpaste stretches back almost 4000 years ago, it wasn't until 1950 a dental surgeon named Dr. Washington Wentworth Sheffield first invented toothpaste [3]. Regular toothpaste contains thickening agents, abrasive agents, humectant, detergents, coloring agents, flavoring and antimicrobial agents. However, among all of these ingredients, fluoride and triclosan are the main active antimicrobial agents present in toothpaste. According to World health organization (WHO), triclosan together with fluoride are considered the most effective components in the prevention of oral diseases such as dental caries due to their antimicrobial effects [4]. It is also WHO's recommendation to use fluorinated toothpastes since fluoride maintains the mineral balance of the outer enamel layer of the teeth intact [4]. Although, fluoride is one of the widely known key active components in toothpaste that provides protection against microorganisms, excess use can lead to a disease called dental fluorosis, a disease that causes the disturbance of the outer enamel layer [5]. Even though triclosan is deemed less harmful due to lower toxicity than fluoride, it still can have perverse effects such as skin irritation according on a chemical assessment report by the Australian government's department of health and ageing [6]. Thus, the usage of these chemicals and their acceptable levels are already fixed due to health reasons.

The use of herbal extracts in toothpaste is not an uncommon practice and recently is gaining attention for their effectiveness in inhibiting microbial growth. Few studies in the past show that toothpaste containing herbal components exhibited better antimicrobial activity when compared to toothpastes containing fluoride [3], [7]. It was deduced based on the zone of inhibition that the antifungal activity of the toothpastes containing plant extracts was double than that of a fluoride toothpaste [3]. Though triclosan is still the best antimicrobial agent among the components, herbal or otherwise, the amount that can be present in oral products is a constraint. For a vital oral product such as toothpaste that gives the primary protection against pathogens, there is no limitation of its antimicrobial activity. Thus, this leaves room for the addition of herbal extracts to enhance the toothpaste's ability to inhibit microorganism.

Piper betle, more commonly known as betel leaves, are the leaves of a plant that belongs to the piperaceae family. It is cultivated widely in Asians regions Sri Lanka, India, Malaysia, Thailand are some of the countries among them [8]. This

plant is known to possess many medicinal properties such as gastro-protective, wound healing and also hepato-protective abilities due to the presence of bioactive compounds which are also known as phenolic compounds [9]. These phenolic compounds are known to be very effective antimicrobial as well as antioxidant agents through various studies [10]–[12]. Although betel leaves and its extract are mainly known for its anti-oxidant property, recently it has gained much attention for its antimicrobial abilities as well [8], [11]. Thus, the extraction of these compounds from the plant material is crucial in further utilizing these properties. Hence, the most effective solvent for the extraction of phenolics are explored in this study through the total phenolic content analysis. Moreover, the effectiveness of the plant extract in the toothpastes is studied through agar well diffusion assay.

2. Materials and Methods

2.1 Pre-treatment of *Piper Betle* leaves

Piper betle leaves were purchased from a local farmer from the area of Banting, Malaysia. The leaves were thoroughly washed to remove any dirt particles and were dried in the air forced convection oven (FAC-350, Protech, USA) at a temperature of 50°C for 3 days to ensure the moisture content is reduced to low levels for better preservation of the bioactive compounds and prevention of microbial contamination [13]. The dried leaves were crushed into fine powder by means of an electric bender and passed through a sieve to eliminate the larger leaf particles.

2.2 Chemicals, Reagents and Microorganisms

The chemicals used in all the experiments were Ethanol (95%), Gallic acid, Fast blue BB reagent, and NaOH which were all bought from Sigma-aldrich (St. Louis, MO, USA). The nutrient media and chemicals including nutrient agar and nutrient broth were bought from Sigma-aldrich (St. Louis, MO, USA). The McFarland standards as well as the microorganisms strain, *Escherichia coli*, *Staphylococcus aureus* and *Candida albicans* were provided by bioscience laboratory (School of Bioscience, Taylor's University).

2.3 Extraction of Phenolic Compounds

For every batch of experiment 8 g of the dried *piper betle* leaves powder was weighed using weighing balance (TX423L, Shimadzu Corporation, Japan) and soaked in 240 ml of the respective solvent in a beaker which was placed in the water bath (Copens scientific Sdn. Bhd, Malaysia) for an hour. A temperature of 50°C was maintained throughout the whole extraction process. An electric stirrer was used to ensure uniform mixture of the powdered leaves and the solvent. The solvent from the extract was evaporated by using the rotary evaporator (RV 10 Basic, Lee Hung Scientific SDN. BHD, Malaysia) until the crude extract was obtained.

2.4 Total Phenolics Content using Fast Blue BB methods

Gallic acid standards were prepared in the concentrations of 50, 100, 200, 500 µg/ml. 1 ml of the respective standards were pipetted to small beakers. 0.1% of FBBB reagent was prepared by mixing 0.1 g of the reagent with 99.9 ml of DI water. 5% of

NaOH was prepared in the same manner. 0.1 ml of FBBB reagent was added to the standards and mixed for 1 minute followed by 0.1 ml of NaOH. The standards were kept for 90 mins for the reaction to reach completion. 200 µl of the standards were transferred to cuvettes and their absorbance was measured at 410 nm in the UV spectrophotometer (Genesys 10S, ApLab scientific Sdn. Bhd, Malaysia). Gallic acid standard calibration curve was prepared by plotting the absorbance against concentrations with a correlation coefficient of 0.9646.

The extract solutions were prepared by mixing 0.15 g of the crude extract with 3 ml of DI water for each solvent. As explained in 1.2, 0.1% of FBBB was added to the extract solutions followed by 5% of NaOH. The absorbance of the extract solutions were measured at 410 nm in an UV spectrophotometer (Genesys 10S, ApLab scientific Sdn. Bhd, Malaysia). Based on the absorbance, the total phenolic content was extrapolated from the Gallic acid standard curve and expressed in mg Gallic acid equivalence/g of dried extract.

2.5 Preparation of Bacterial and Fungal Suspensions

Bacterial and fungal strains were grown over nutrient agar medium which were always maintained at 4°C. Prior to all the antimicrobial susceptibility assay, a loopful of the cells from the agar medium were grown in nutrient broth overnight at 37°C.

2.6 Determination of Minimum Inhibitory Concentration

Different concentrations of the crude extract for the various solvents were prepared. 1 ml of the extract with different concentration was poured into test tubes followed by 4 ml of nutrient broth. 0.1 ml of the bacterial suspension matched with 0.5 McFarland standard was introduced to each of the sample. One control was used for each batch of experiment conducted which is the growth medium with the inoculum and without the extract. All the samples are incubated overnight at 37°C in the orbital shaker incubator (LM-400D, Lee Hung Scientific Sdn. Bhd, Malaysia). The turbidity of the samples were compared with the control. The concentration with no visible turbidity gives the MIC. All experiments were duplicated for better accuracy.

2.7 Agar Disk Diffusion Assay

Agar plates were prepared by pouring 15 ml of nutrient agar onto sterile plates and kept until solidified in the incubator. Bacterial and fungal suspensions were grown overnight in nutrient broth at 37°C in the incubator and was matched with 0.5 and 1 McFarland standard respectively. The plates were inoculated with 100 µL of the microbial suspensions and kept in the incubator to dry for an hour. Wells were punctured into the agar using a sterile borer of 6 mm diameter and 4 mm deep. 0.5 mg of the toothpaste samples, with and without the toothpaste, were introduced into the wells. The agar plates were incubated for 24 hours at 37°C in the incubator (BCR-240, CNG Instruments Sdn Bhd, Malaysia). After which the diameter of the zone of inhibition was measured using a capiler in mm. All experiments were duplicated for better accuracy.

3. Results and Discussions

3.1 Physical Characteristics and Extraction Yields

Table 1 gives a summary of the physical traits of the extracts obtained using the three solvents. Various results has been reported over the years that certain phytochemicals are extracted by specific solvents based on their properties which is the most likely reason behind the different extract colors. [13], [14] both reported of dark green and brownish green for their ethanolic extracts. [14] also reported the same colour for their aqueous extract whereas [15] had a dark brownish color for the same solvent. The second study is more similar to this current research as a dark green color and dark yellow color extracts were obtained for ethanol (95%) and water respectively. It is suggested that the green color is most likely due to the presence of chlorophyll showing the possibility of the presence of different compounds in the extracts [15]. Previous phytochemistry studies has shown that certain solvents leach out different compounds [15], [16]. Phytochemicals such as carbohydrates, flavonoids were detected in both aqueous and ethanolic solvents but protein and steroids were only found to be in the ethanolic extracts [15], [16]. This shows that a complete extraction of the phytochemicals by any one solvent is not achievable. Depending on the solvent type and properties, the phytochemicals are being extracted.

Table 3. Physical characteristics of the different extracts

Solvent used	Color	Odor	Consistency
Ethanol (95%)	Dark green	Pungent	Solid-thick
Ethanol (50%)	Dark brown	Pungent	Solid-thick
Water	Straw	Pungent	Solid-thick

Figure 1 shows the different extraction yields obtained for the three solvents: water, ethanol (50%) and ethanol (95%). Highest extraction yield was obtained using water as the solvent which has 27% of extract yield. Ethanol (50%) gave a yield of 24% while ethanol (90%) has the least yield of 6%. Similar results were reported in another study where the *piper betle* extraction yield using water as the solvent was 26%, almost twice than that of the ethanolic extract (11%) [32]. A second study also reported similar findings with the solvent water having an extraction yield of 26.2% whereas the 50% ethanolic and 100% ethanolic extracts to have yields of 22.5% and 11.6% respectively [15]. Majority of the phytochemicals in *piper betle* extract are highly polar for which the solvents are able to form hydrogen bonds with them during extraction process [15]. Polar compounds dissolve better in solvents with high polarity due to their ability to form more hydrogen bonds [15]. The polarity index of water is twice than that of ethanol making it easier for the phytochemicals to form more hydrogen bonds with water. Thus, they can easily dissolve in them and be extracted out resulting in a higher extraction yield.

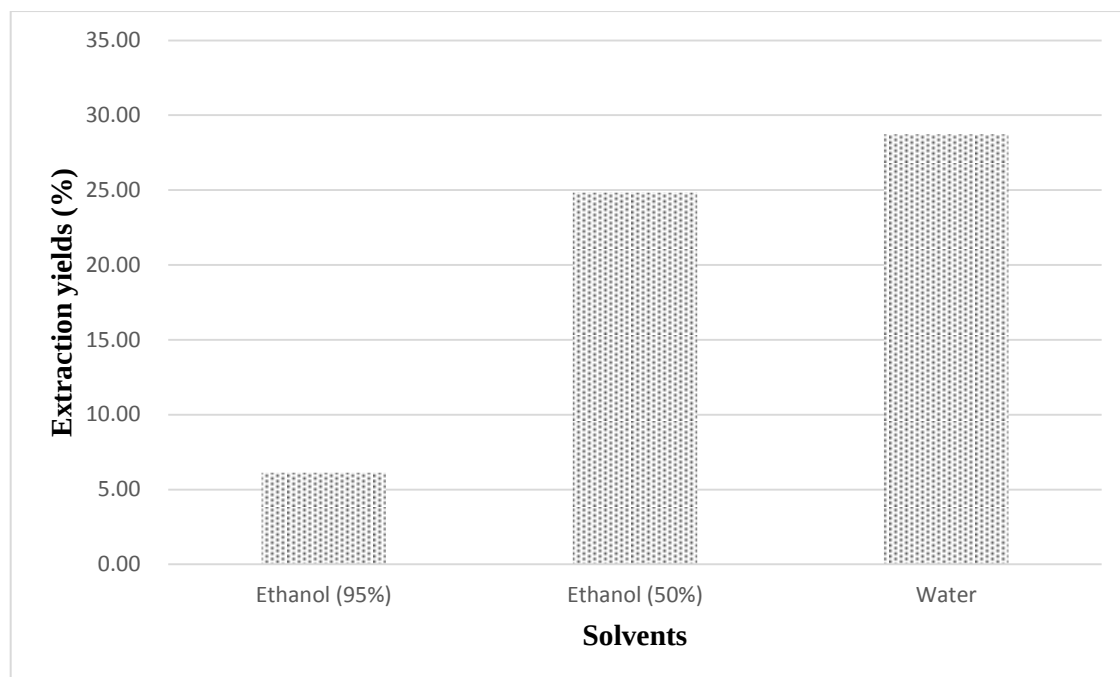


Figure 2. Various extraction yields for the different solvents

3.2 Total Phenolic Content of the Extracts

Table 2 gives the total phenolic content for all the three solvents of *piper betle*. The highest phenolic content was found in the ethanolic extract (95%) of 840 mg GAE/g followed by ethanol (50%) and water with values of 460 mg GAE/g and 200 mg GAE/g respectively. Phenolic compounds, a type of phytochemicals, are organic polar compounds with a hydroxyl molecule attached to the aromatic ring [18]. This hydroxyl compound forms hydrogen bond with the electronegative oxygen of the polar solvent, thus, being extracted from the plant material [19]. The extraction of these phenolic compounds are essential as they are the ones responsible for the antimicrobial properties. [17] reported that the total phenolic content of 95% ethanolic extract was almost three times than that of aqueous extract. It was suggested by [15] that together with polarity, other properties of the solvent can determine the solubility of the phenols such as the size of the solvents [15]. In comparison to the phenols, water is a relatively smaller molecule for which the polar component gets masked easily forming weaker hydrogen bonds which not the same in case of ethanol as it is a much bigger molecule [18]. The extraction is not only influenced by the polarity of the solvents but also the polarity of the phenols alike. According to the “like dissolve like” principle, phenols dissolve more easily in solvents with polarities similar to theirs [20]. Hence, it can be assumed that the phenols present in the extract has polarities more closely to ethanol than to water.

Table 4. Total phenolic content

Solvent	Total Phenolic content (mg GAE/g)
Water	200
Ethanol (50%)	460
Ethanol (95%)	840

[21] predicted that the solubility tendency of natural phenols were more towards intermediate polarity solvents. Using an UNIFAC model the solvent activity coefficient were determined which gave an overall highest figure for the alcohols, ethanol and methanol. It was further reported that this tendency is due to the stereochemistry of the phenols and intermolecular forces. The hydroxyl group of the alcohols can form hydrogen bonds with the oxygen atom present inside the aromatic ring of the phenol whereas the hydroxyl group of the benzene ring can form hydrogen bonds with the alcohol's electronegative oxygen atom [21]. This is a little harder to achieve in case of water given its smaller size.

The “like dissolve like” theory further explains the nature of the solvents and solute interaction. Phenols are considered organic matter [20]. Provided that alcohols are an organic solvent and water is an inorganic solvent, the solubility of the phenols in ethanol should be higher. Due to this organic nature, ethanol is able to denature polyphenol oxidases. In turn the cell wall of the plant degrades more efficiently, extracting the constituents from inside the cell with much ease unlike water [22]. Thus, resulting in a higher phenolic content for the ethanolic extracts.

3.3 Minimum Inhibitory Concentration Assay

The minimum inhibitory concentration (MIC) of the different extracts against the two pathogens are summarized in Table 3. The MIC for 95% ethanolic solvent was lowest, 5mg/ml, followed by 50% ethanol and water with 7 and 19 mg/ml, respectively for gram negative bacteria, *Escherichia coli* (*E.Coli*). To further solidify the results, the 95% ethanolic extract was tested against gram positive bacteria, *Staphylococcus aureus* (*S. aureus*) and the MIC was found to be 2.0 mg/ml. The results are in alignment as section 3.2 showed that 95% ethanolic extract had the highest total phenolic content for which a lower concentration was able to inhibit the bacterial growth. Similarly, the water extract has the lowest phenolic count resulting in a higher concentration to inhibit the bacterial growth. The MIC value of the ethanolic extract for *E. coli* is slightly lower than *S. aureus*. [23] reported the MIC values of methanolic extracts of *piper betle* to be 8.196 mg/ml and 0.0021 mg/ml respectively for *E. coli* and *S. aureus*. [14] reported the MIC for *Streptococcus mutans* (*S. mutans*) to be 5 mg/ml and 10 mg/ml for ethanol and water extracts respectively. [5]

MIC is highly dependent on the amount of phenolic compounds extracted which is in turn dependent on the extraction parameters and the type of solvent used. [11] reported that the total phenolic content was highest for 95% ethanol. After subjecting this extract to the agar disk diffusion assay, the zone of inhibition (ZOI) for this extract was found to be 10.6 and 14.5 mm for *E. coli* and *S. aureus* respectively. This was considerably higher than the ZOI of the aqueous extract, which were 7.0 and 11.5 mm for the same pathogens. The results further solidifies the findings in this research that firstly the more phenolic compounds present in the extract the better its antimicrobial properties will be. Secondly, it is much easier to inhibit gram positive bacterial pathogens, *S. aureus*, than gram negative pathogens, *E coli*.

Gram positive bacteria contains a thicker cell wall membrane consisting of two layer of polymers of sugar and amino acids together with a layers of proteins [23], [24] unlike the gram negative bacteria which contains only one. Nonetheless, gram positive bacteria are more susceptible to inhibition agents as they contain more proteins which can be denatured due to the formation of hydrogen bonds by the antimicrobial agents. On top of that, the outer membrane is not an effective barrier when it comes to permeability. Extensive damage to the cell wall weakens the bacteria and causing the fluids from the cytoplasm to seep out [26]. Moreover, gram negative bacteria consists of an outer phospholipidic membrane including structural lipopolysaccharide components that is highly impermeable making them less susceptible to antimicrobial agents [27]. Hence, during the MIC assay, a lower concentration of the extract was able to inhibit *S. aureus* while *E. coli* needed a much higher concentration.

Table 5. Minimum inhibitory concentration for bacterial pathogens

Micro-organism	Solvent	MIC value (mg/ml)
<i>Escherichia coli</i>	Ethanol (95%)	5.0
	Ethanol (50%)	7.0
	Water	19
<i>Staphylococcus aureus</i>	Ethanol (95%)	2.0

3.4 Agar Disk Diffusion Assay

The zone of inhibition of the toothpaste are summarized in Table 4. Even without the extract the toothpaste showed a considerable ZOI of 40.7 and 39.3 mm for both of the bacterial pathogens and 26.3 mm for the fungal pathogen. The toothpaste used in this study contains sodium fluoride (0.32% w/w, 1450 ppm) and triclosan (0.3%) as the active ingredients. These two components are the most effective antimicrobial agents present in the toothpaste [27], [28]. For this reason, even without the extract such a high zone of inhibition was expected. Triclosan and fluoride exhibits antimicrobial activity in multiple ways. Triclosan interferes with the enzymes required for fatty acid synthesis which in turn kills the microbes [29]. It was reported by [28] that the highest zone of inhibition came from the toothpastes containing triclosan even though all of them contained fluoride as well. A reason behind this conclusion was because the toothpastes containing only fluoride has a considerably lower ZOI so it was deduced that the major antimicrobial activity was due to the presence of triclosan.

Fluorinated toothpastes also does inhibit microbial growth to some extent as it acts as an enzyme inhibitor thus directly effecting the bacterial mechanism and preventing the growth of bacteria [29], [30]. Fluoride also reduces the acid tolerance of bacteria, thus preventing glycolysis, the conversion of glucose to provide energy, and the bacterial metabolism altogether [31]. Both of these components are known to cause damage to the inner membrane of bacteria. However, much focus is on fluoride due to the part it plays in the mineralization process. It takes part in the demineralization process by enhancing the mineralizing of the tooth's surface by effecting the mineral phases of the teeth. In this manner it protects the tooth's surface

and prevents it from further destruction at the same time [30]. With a combined action of antimicrobial activity and mineral phase effect fluoride together with triclosan and other agents provides protection against microorganisms to the oral cavity. However this being said the concentration and amount is a constraint given excess of any of these two components can lead to adverse effects. Excess of fluoride has known to cause a disease called dental fluorosis that causes mineral imbalance in the outer layer of the teeth [5]. Even though it is WHO's recommendation to use a fluorinated product [4], it's amount has limitations while the antimicrobial activity of a toothpaste has no such barriers.

Table 6. Zone of inhibition of toothpaste

Microorganism	Mean zone of inhibition (mm)	
	Without extract	With extract
<i>Escherichia coli</i>	40.7	46
<i>Staphylococcus aureus</i>	39.3	49
<i>Candida albicans</i>	26.3	31.7

The antimicrobial activity of *piper betle's* extract has been reported several times over the past few years [11], [12], [14] due to the presence of phenolic compounds. Based on the results obtained in Table 4, the zone of inhibition is considerably higher after the addition of the toothpaste. An increase of 5.3 and 9.7 mm in the ZOI was observed in case of bacteria and 5.4 mm increase in case of fungus. Gram positive bacteria are easily inhibited due to their less resistance towards antimicrobial agents as previously stated in section 3.3 which is the reason behind the bigger ZOI unlike the gram negative bacteria. As very limited research has been done on the applications of the extract, comparisons are drawn between researches that has already been done on toothpastes involving other plant extracts.

The use of natural extracts as antimicrobial agents is not uncommon and in recent years has been gaining a lot attention. [28], [31] and [32] have reported antimicrobial activity of toothpastes containing herbal extracts. There are commercial toothpastes already in the market that solely relies on herbal extracts as the primary components for the inhibition of pathogens. [32] reported findings that showed the toothpaste Paradontax, containing plant extracts to have a higher ZOI than Sangonil, containing triclosan and fluoride, against three bacterial pathogens, *S. mutans* and *S. sobrinus*. *P. aeruginosa*. On the otherhand it had a lower ZOI for four different bacterial pathogens, *E. coli*, *S. aureus*, *K. rhizophila* and *E. faecalis*. The antimicrobial activity of the toothpaste, Paradontax, is for the presence of a number of herbal components including sage, rhatany, chamomile and myrrh which as all deemed as natural antiseptics together with the oil of peppermint, known to possess antimicrobial properties [32]. Interestingly enough, the same study reported that the ZOI of the toothpastes for the fungal pathogen, *Candida albicans* to be very close to each other. This further solidifies the abilities of the phenolic compounds in the plant extracts to retain their ability to inhibit microorganism in the product after the addition of other components.

Another study done on commercial toothpastes found an even more interesting results as the toothpaste with the biggest zone of inhibition for the fungal pathogen, *Candida albicans*, was for the toothpaste containing both fluoride and herbal extracts

[34]. Even without triclosan it has a better antifungal activity than Paradontax even though both toothpastes share the same plant extracts with the exception of peppermint oil. Even so, this shows the potential of combining plants extracts with toothpastes containing active ingredients like fluoride and triclosan. This is consistent with current study as the toothpaste used contains both triclosan and fluoride. Nevertheless, the extract was able to not only retain its antimicrobial activities but also enhance the overall antimicrobial potential of the toothpaste.

4. Conclusion

The extraction of bioactive or phenolic compounds is crucial for their utilization in applications. In this research, the effect of the different solvents, ethanol and water on the extraction of the phenolic compounds were investigated. The highest extraction yield was found for the aqueous extract. On the contrary, the highest phenolic content was found to be in the 95% ethanolic extract. The lowest MIC value for *E. coli* was found for 95% ethanolic extract of 5 mg/ml which was expected since it had the highest phenolic content. Similarly the highest MIC was found to be for the aqueous extract which was a value of 19 mg/ml. Furthermore, this research explores the possible application of *piper betle*'s extract in toothpaste by studying the antimicrobial activity of a commercial toothpaste combined with the extract. A significant increase in the ZOI was observed in case of both bacterial and fungal pathogens after the addition of the extract. This research was conducted with a few limitations involving the extract's amount and concentration which needs to be looked into on a broader and detailed scope. Nevertheless, the increased antimicrobial activity suggests the potential of using this plant's extract as an antimicrobial agent in toothpastes.

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Densification Behavior and Properties of Iron Oxide Doped Y-TZP Ceramics

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Abstract

The effect of small addition of Fe₂O₃ (up to 1 wt%) on the densification behaviour and mechanical properties of commercially available 3 mol% Ytria Tetragonal Zirconia Polycrystals (Y-TZP) sintered from 1250°C to 1500°C was investigated. Tests were carried out in order to determine the bulk density, Vickers hardness, Young's Modulus and fracture toughness of the sintered samples. Based on the work carried out, it is revealed that the amount of dopants and sintering temperature influences the mechanical properties of Y-TZP. The results showed that even sintering at low temperature at 1250°C, relative bulk density ~98% of theoretical density could be achieved with the addition of 0.3 wt% Fe₂O₃. The additions of small amounts of Fe₂O₃ from 0.05 wt% to 1.0 wt% was found to be beneficial in enhancing the matrix stiffness and hardness of the sintered bodies when compared to the undoped counterpart sintered at same temperature. However, the fracture toughness was found to be unaffected by the additions of small dopant amounts except for the case of 0.5 and 1 wt% Fe₂O₃ when sintered above 1400°C.

Keywords: Y-TZP, Zirconia, Iron Oxide, Densification, Mechanical Properties

1.0 Introduction

Yttria Tetragonal Zirconia Polycrystalline, also known as Y-TZP, have become an important advanced material as it exhibits excellent combination of mechanical properties, thermal properties and high wear resistance. Zirconia has been used in various applications. Such applications include the use of zirconia to strengthen the silicon carbide ceramics [1] fuel cell's oxygen sensor, heating elements and extrusion dies [2-5]. Besides zirconia has been widely used in the biomedical field as orthopaedic femoral head implant and as a replacement tooth due to its biocompatibility [6].

There are three polymorphs that are known to exist in pure zirconia which are the monoclinic (m), tetragonal (t) and cubic (c) [7]. Pure undoped zirconia exhibits the following phase transition depending on the temperature as shown in Fig. 1.

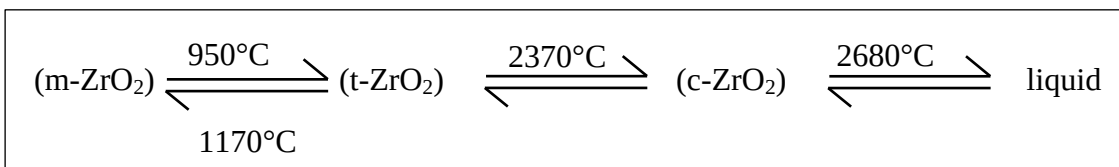


Figure 1. Phase transition of a pure undoped zirconia [7]

The (t)→(m) phase transformation in zirconia is a reversible isothermal martensitic transformation and there will be large temperature hysteresis approximately 200 K are involved in this transformation. In addition, this (t)→(m) transformation is also accompanied by 4-5% volume change and a shear strain of 14-15% [6-7]. Large amount of stress are induced by this transformation hence lead to destruction of pure zirconia when it is sintered above 1170°C [8]. In the last few decades, there have been many researches focusing on manufacturing structural ceramics with excellent mechanical properties such as high toughness combined with high strength [9]. A few authors has suggested that one of the main issues in developing a high toughness ceramics is the microstructural design. One of the main features of zirconia is the phenomenon called transformation toughening [10].

Higher zirconia's fracture toughness can be achieved by enhancing its microstructure through introducing a non-linear crack shielding zone crack tip [10] or by stopping or delaying the motion of the crack front. These sequences of events leads to a phenomenon known as the stress induced transformation toughening. Transformation toughening involves zirconia's phase transformation from the metastable (t) phase to the stable (m) phase around an advancing crack. As the phase transformation involves 4-5% volume expansion, a net compressive stress is introduced in the process zone around the crack tip as shown in Fig. 2. In order to obtain optimum results from transformation toughening, it is best to retain maximum amount of metastable (t) phase at room temperature or at the application temperature. According to various transformation toughening literature, the terms transformability usually refers to easiness which the t-ZrO₂ transforms to m-ZrO₂ around the crack tip stress field [11-15].

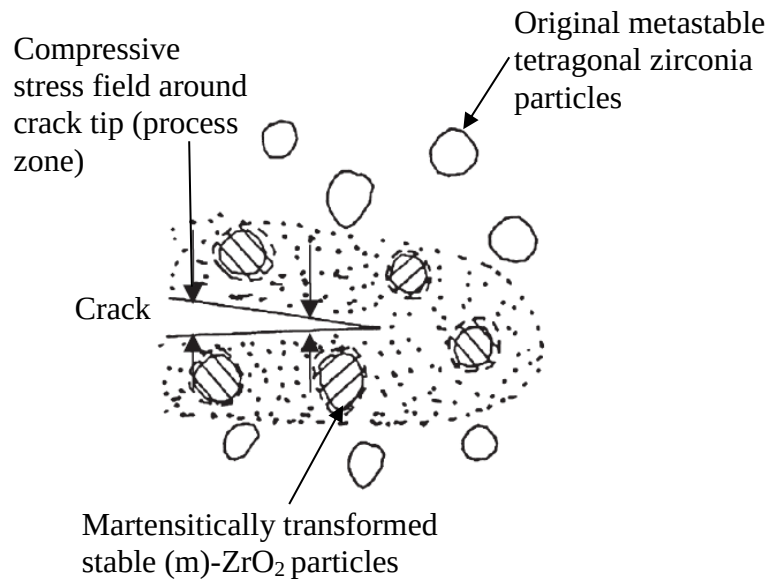


Figure 2. A schematic diagram showing stress induced transformation in the compressive stress field of a propagating crack. [7]

Although Y-TZP has excellent mechanical properties, it also has an Achilles heel. When there is (t)→(m) transformation due to propagating crack, the results will be transformation toughening. However, when the free surface is exposed to moist temperature usually around 100°C to 600°C, the Y-TZP will suffer properties degradation due to the autocatalytic surface-initiated transformation from the metastable (t)-ZrO₂ phase to the stable (m)-ZrO₂ phase counterpart [16]. The autocatalytic transformation is also known as the low temperature degradation or LTD and this phenomenon has been extensively studied for three decades. The underlying LTD mechanism is still yet to be resolved [17-18].

Researches has been done by many authors [19-25] to study the effect of doping transition metal oxides such as Nb₂O₅, SiO₂, Al₂O₃, CuO, Nd₂O₅ and MnO₂ in improving the LTD properties. In most of the cases, with the addition of the transition metal oxides as sintering additives, it was revealed that the additives would segregate at the grain boundary forming a Y₂O₃ and ZrO₂ rich grain boundary glassy phase [19-26]. For instance, Kenellopous & Gill [27] has reported that Y-TZP doped with CuO exhibits enhanced densification due to the liquid-phase sintering mechanism due to the low melting point of CuO in the ZrO₂ matrix. In addition, Golieskardi *et. al.*, [16] has also reported that with small addition of Al₂O₃ and CeO₂ would improve Y-TZP densification and also improving its mechanical properties. The authors have attributed it to the presence of glassy phase that could have suppressed the grain growth and also sealed the grain boundary. Therefore, doping transition metal oxides such as Fe₂O₃ are likely to influence the LTD properties if the dopant is able to aid sintering at low temperature (i.e. 1250°C) resulting in densification without significant grain growth.

The aim of this research is to study the effect of small amounts of iron oxide (from 0.05 wt% to 1 wt%) on the densification and mechanical properties of commercially available 3 mol% Y-TZP.

2.0. Experimental Setup

3 mol% Y-TZP powder, supplied by Kyoritsu Japan, manufactured through the co-precipitated method was used. This powder had a total impurity concentration of approximately 0.1 wt%. The major impurities were found to be SiO_2 , Fe_2O_3 , TiO_2 and Al_2O_3 . High purity iron oxide powder manufactured by Sigma-Aldrich, US with weight concentrations (wt%) of 0.05, 0.1, 0.3, 0.5, and 1 wt%, was doped with Y-TZP powders. The dopants were introduced through wet milling methods, employing zirconia balls and ethanol as the milling media and the mixing medium respectively. The resulting slurry was dried in an oven and subsequently sieved to obtain soft, ready-to press powders. Green samples consisting of discs with 20 mm diameter and rectangular bars sized 4 mm $\times$ 13 mm $\times$ 32 mm were compacted at 0.3 MPa before undergoing cold isostatic pressing at 200 MPa. Pressureless sintering was chosen as the method to consolidate the powder in air using a rapid heating furnace manufactured by ModuTemp, Australia. Pressureless sintering was performed at various temperatures ranging from 1250 to 1500°C with 2 hours holding time before subsequently cooling down to ambient temperature. As-sintered specimens were subjected to grinding on one face by silicon carbide papers ranging from grades 120 to 1200. Post grinding, these specimens were polished with diamond paste of 6 μm and 1 μm . This procedure a shiny surface is obtained on one face of all specimens.

Densities of as-sintered samples were determined using Archimedes's principle. Rectangular bars were used to determine Young's Modulus by physically tapping the samples. The tapping physically induced vibration with a frequency that was detected and measured by a commercially available testing instrument (GrindoSonic: MK5 "Industrial", Belgium) using [28]. The values of Young's modulus obtained through this method were been found to be consistent and independent from the number of tests performed for each samples.

Vickers indentation method was performed by a machine manufactured by Future tech, Japan and was used on polished samples to determine the Vickers hardness of the samples. The values obtained from the hardness measurements were then subsequently used to obtain the fracture toughness (K_{IC}). During the hardness measurements, indentation load was kept constant at 98.1 N with a 10 s loading time. Fracture toughness' values were computed using the equation derived by Niihara *et al.*, [29]. Average values were taken from five measurements. X-ray diffraction (Geiger-Flex, Rigaku Japan) was used for phase analysis of the powders. The phase analysis measurement was conducted under ambient conditions using Cu-K α as the radiation source. The amounts of monoclinic (m) phase present in the ceramic matrix were determined using the method proposed by [30]. Micro-scale changes in the structure and morphology were examined using scanning electron microscopy (Phenom ProX).

3.0 Results and Discussion

The XRD results of the undoped (0 wt%) to 0.3 wt% Fe_2O_3 doped Y-TZPs shows that the samples consists of 100 % tetragonal (t) phase regardless of the sintering temperature employed. This is an indication that tetragonal phase stability of the zirconia matrix are unaffected by the addition of dopant up to a maximum limit of 0.3 wt% Fe_2O_3 . However, the tetragonal phase stability of 0.5 wt% and 1 wt% Fe_2O_3 -doped Y-TZP was affected when sintered at 1450°C with the formation of 2.6 % monoclinic (m) phase in the zirconia matrix and this monoclinic (m) phase was found to increase up to 4.5 % for the case of 1 wt% Fe_2O_3 .

The effect of varying sintering additives (0 to 1 wt%) on the variation between bulk density and sintering temperature for undoped and Fe_2O_3 -doped Y-TZP are shown in Figure 3. Assuming the theoretical density (T.D.) of Y-TZP as 6.1 Mg m^{-3} , it is revealed that Y-TZP samples containing $\geq 0.3 \text{ wt}\%$ Fe_2O_3 exhibited higher relative densities $\sim 97\%$ of the T.D. when sintered at 1250°C as compared to the undoped Y-TZP which achieved only 92.2 % of the T.D. when sintered at same temperature. The bulk densities of the 0.5 and 1 wt% were found to increase slightly from 97.87% to 98.36% and from 97.30% to 97.60% respectively when sintered within a temperature range of 1250°C to 1400°C , before reducing to 98.52% and 96.20% respectively at 1500°C . The bulk densities of all other samples (undoped, 0.05 and 0.1 wt%) all followed a similar trend which may be describe as a significant increase between a temperature range of 1250°C to 1350°C . Subsequently the density of these samples were found to fluctuate between (98.03% to 98.69%) in the temperature range of 1350°C to 1400°C before steadily decreasing with an increase in the temperature up to 1500°C .

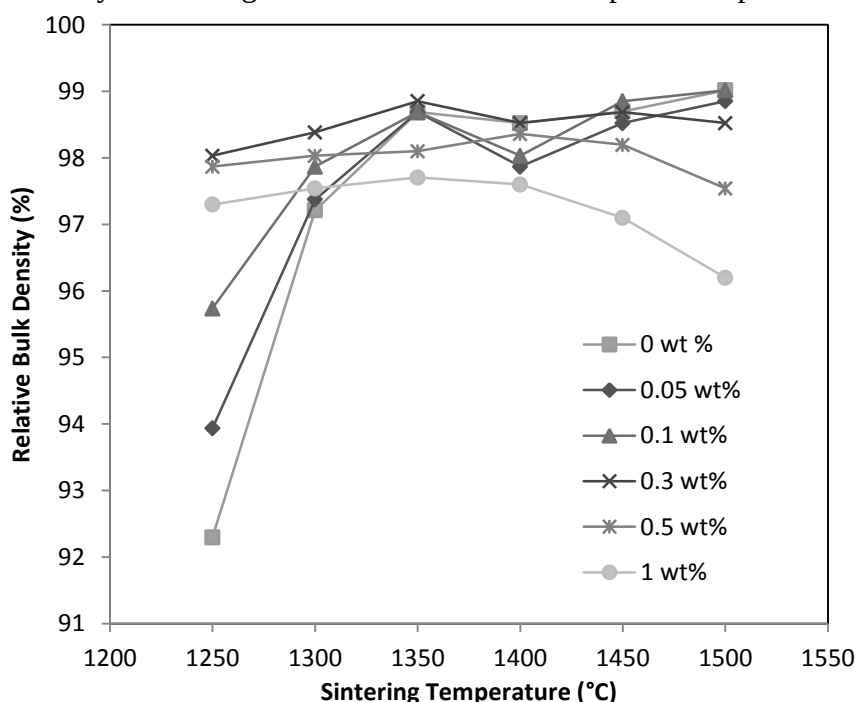


Figure 3. Effect of sintering temperature and Fe_2O_3 on the bulk density of Y-TZP sintered at various temperatures.

The bulk density of Y-TZP containing 0.3 wt% sintered at 1250°C was among the highest in all samples as it achieved $\sim 98\%$ of the T.D. Subsequently the bulk density

increased from 98.03% to 98.85% with increasing sintering temperature up to 1350°C before reducing to 98.52% at 1500°C. In the case of 1 wt%, the addition of sintering additives does not aid the densification of Y-TZP when sintered above 1350°C. The relative bulk density was observed to be around 97.3% T.D. when sintered at 1250°C, increasing to a maximum value of 97.7% T.D. at 1350°C before decreasing gradually when sintered at 1400°C and finally undergoing significant reduction from 97.6% to 96.2% T.D. when sintered at 1500°C. The significant reduction of density when sintered at 1400°C to 1500°C may be attributed to the formation of cubic grains. This phenomenon is in agreement with the works of [31].

The effects of iron oxide addition on the Young's modulus of Y-TZP are shown in Figure 4. In agreement with the results obtained for bulk density, it is found that the additions of 0.3 wt% Fe_2O_3 was beneficial in improving the stiffness of the zirconia matrix when sintered at 1250°C to 1300°C. Using the results obtained for 1250°C, samples with 0.3 wt% Fe_2O_3 , exhibited a Young's modulus of 212 GPa which is 12.8% higher when compared to the corresponding Young's modulus value of 188 GPa for the undoped sample. Based on Fig. 4, undoped Y-TZPs require sintering at higher temperatures *i.e.* 1350°C in order to achieve values of $E > 200$ GPa.

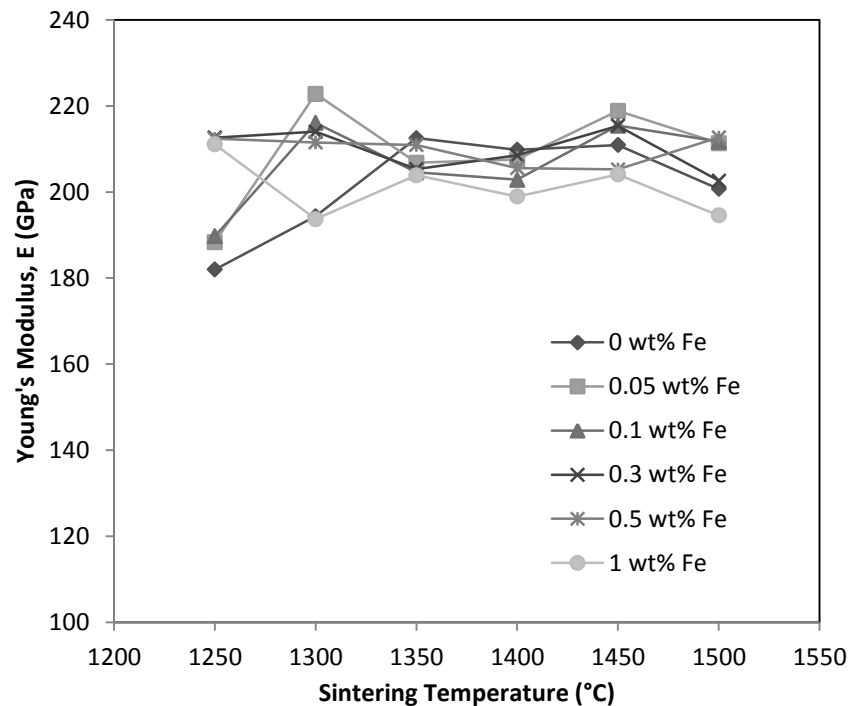


Figure 4. Effect of sintering temperatures and Fe_2O_3 on the Young's modulus of Y-TZP sintered at various temperatures.

Based on the current work, it is also revealed that there is a linear relationship between the Young's modulus and the bulk density of the sintered Y-TZP bodies as shown in Fig. 5. It was revealed that regardless of the amount of dopants employed, the sintered body exhibited Young's modulus of more than 200 GPa when the relative bulk density was more than 98 % T.D. Therefore, it can be inferred that the matrix stiffness deeply influences the bulk density.

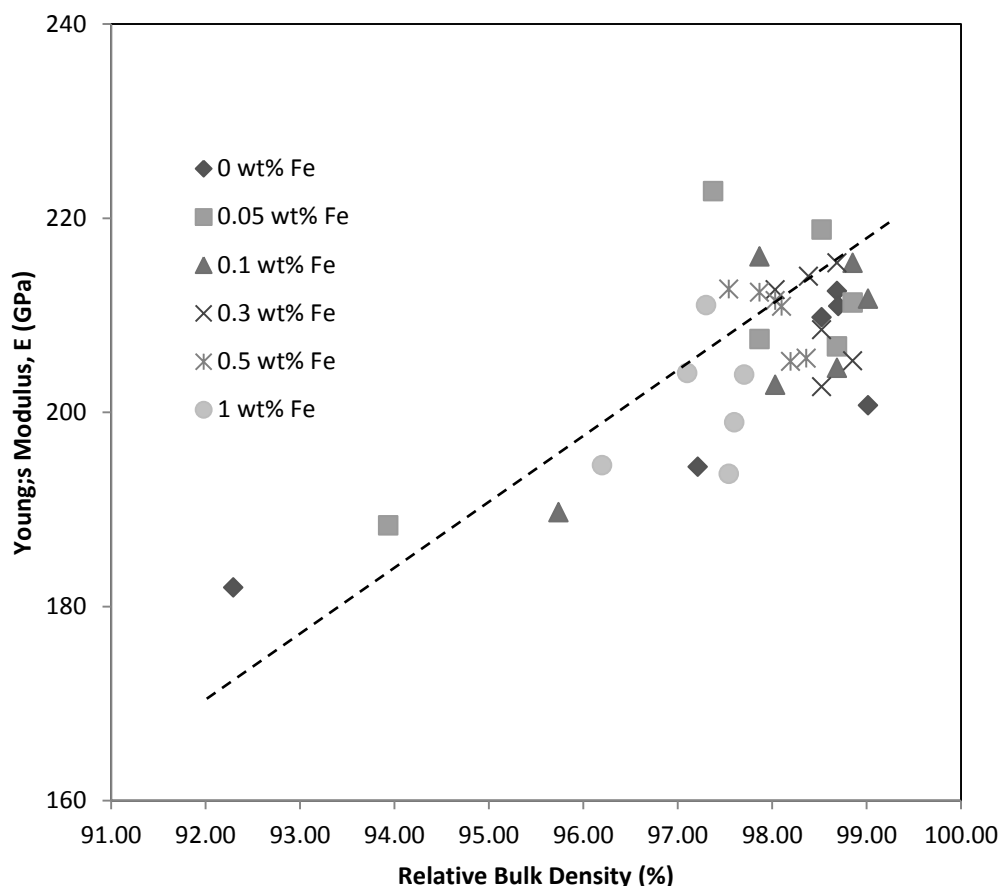


Figure 5. A linear relationship exists between the Young's modulus and bulk density of Y-TZP regardless added amounts of Fe₂O₃.

Figure 6 shows the effect of iron oxide as dopants on the fracture toughness of Y-TZP sintered bodies. It has been revealed that up to 0.3 wt% Fe₂O₃, sintering additives had negligible effect on the fracture toughness as the values of fracture toughness fluctuated in the range of 4.54 to 5.03 MPam^{1/2}. Since the transformation toughening mechanism is dependent on the phase stability of the (t) grains, the values of fracture toughness can be used as an indicator for the degree of stability of the (t) grains in the zirconia matrix. Generally, a high value of fracture toughness would indicate that the (t) grains are in a metastable state. Based on the current work, up to 0.3 wt% Fe₂O₃, there is no sign of fracture toughness enhancement. This is in agreement with the theory that the tetragonal phase stability is not affected by the dopant concentration [GGGG]. However, for the case of 0.5 wt% and 1 wt% Fe₂O₃-doped Y-TZP, at temperature above 1400°C, there is an increase in fracture toughness of these sintered bodies. In the case of 0.5 wt% Fe₂O₃, there is an increase in fracture toughness from 5.01 to 5.1 when sintered at 1450°C followed by rapid increase to 5.81 when sintered at 1500°C whereas for the 1 wt% Fe₂O₃, the fracture toughness increased from 5.02 to 5.72 MPam^{1/2} when sintered at 1450°C followed by significant increase to 7.34 MPam^{1/2} when sintered at 1500°C. The results obtained is in agreement with the XRD phase analysis where small amount of monoclinic (m) phase about ~4.5 % were detected in this sample.

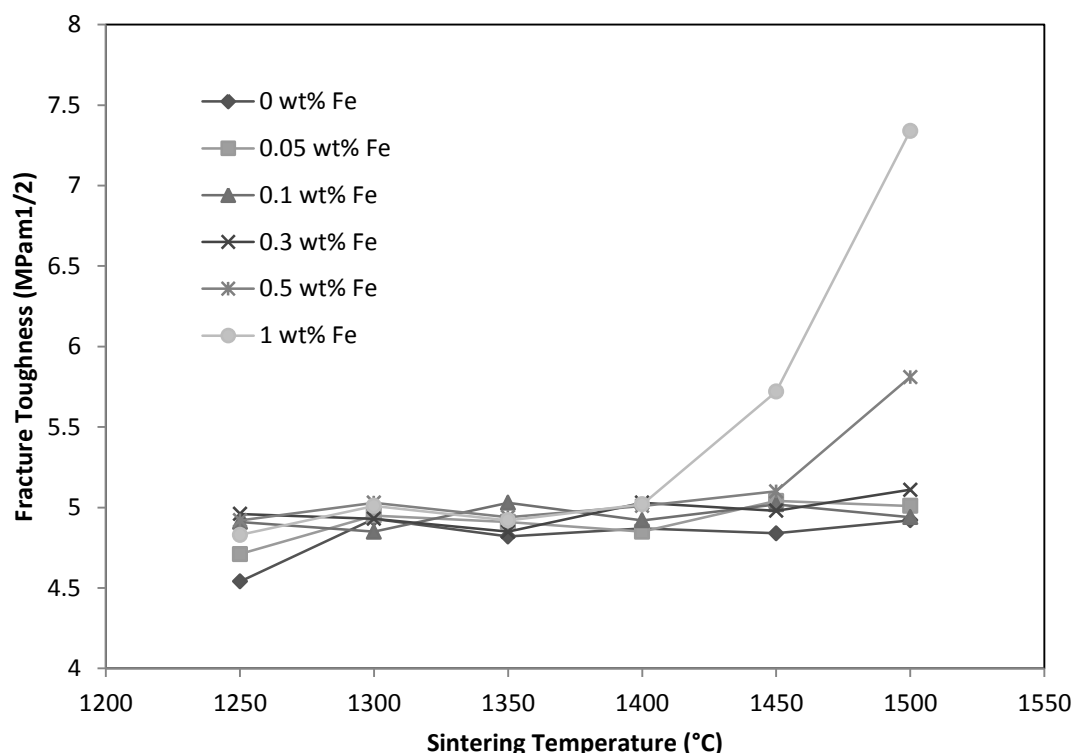


Figure 6. The effect of Fe_2O_3 on the fracture toughness of Y-TZPs sintered at various temperatures.

Based on these observations, it can be inferred that there might be a mechanism that is triggered causing yttria segregation in the Y-TZP matrix. The mechanism suggested is as described in the following. During sintering, large amounts of yttria surround particular tetragonal grains hence causing the tetragonal grains to be over-stabilised leading to significant grain growth. Due to the non-uniform segregation of yttria, a number of tetragonal grains which lack yttria would undergo a spontaneous (t) to (m) phase transformation upon cooling to room temperature. This is in agreement with the data obtained from the XRD phase analysis where small amounts of monoclinic phase was detected in the 1 wt% Fe_2O_3 samples when sintered at 1500°C. On the other hand, tetragonal grain which have the optimum amount of yttria required for transformation toughening would remain in a metastable state. These tetragonal grains would readily undergo transformation toughening when stress is induced resulting in higher values of fracture toughnesses as shown in Figure 6.

The effect of sintering temperatures and additions of Fe_2O_3 on the Vickers hardness of Y-TZPs are as shown in Fig. 7. It may be shown that addition of Fe_2O_3 on Y-TZP has beneficial effect on the Vickers hardness of Y-TZPs especially at low temperature sintering such as 1250°C. The undoped Y-TZP exhibits the lowest hardness at ~9.5 GPa when sintered at 1250°C then followed by rapid increase to ~12.8 GPa when sintered at 1300°C before reaching a maximum hardness of ~13.7 GPa when sintered at 1400°C. However, as the sintering temperatures increases beyond 1400°C, the hardness for these samples reduced to ~13.1 GPa when sintered at 1500°C. On the other hand, at low temperature sintering of 1250°C and 1350°C, all the Fe_2O_3 samples exhibited higher hardness as compared to the undoped samples. Similar trend were observed for Y-TZPs doped with 0.05 wt% and 0.1 wt% Fe_2O_3 . The hardness of these samples starts out low when sintered at low temperature of 1250°C. As the sintering temperature increase, the hardness of these samples increases

rapidly from 11.4 and 12.6 GPa to 13.3 and 13.4 GPa respectively when sintered at 1300°C. When the samples were sintered beyond 1300°C, these samples exhibit hardness trends which were quite similar to the hardness trend for the undoped Y-TZP.

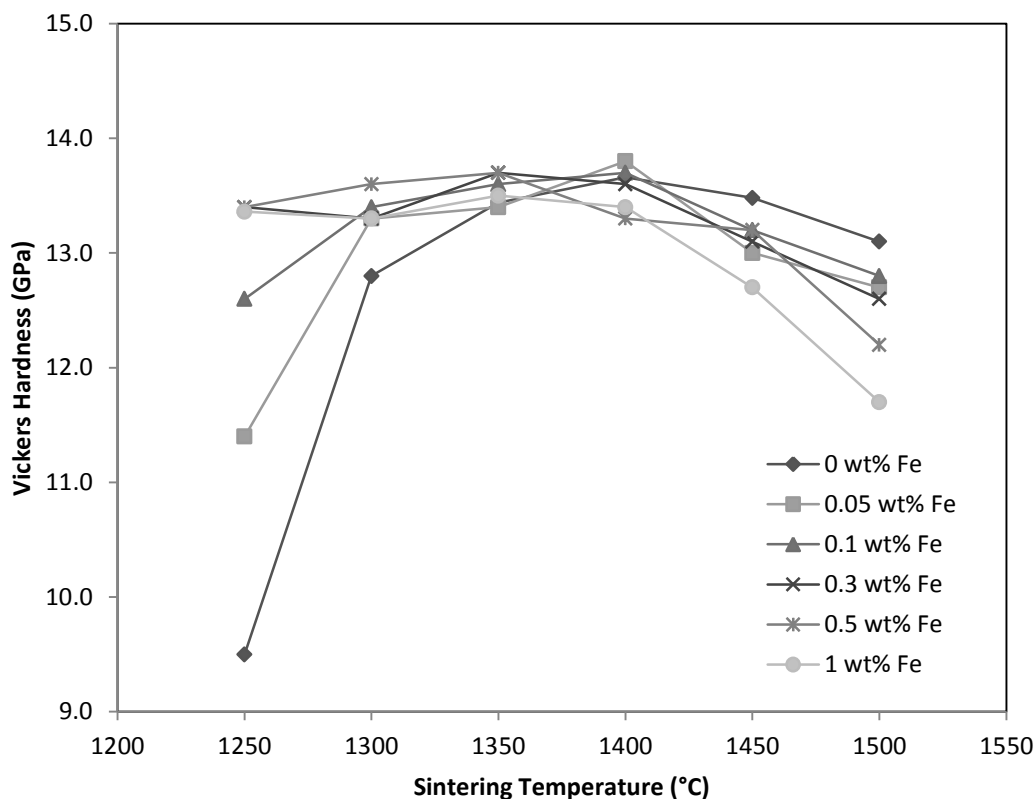


Figure 7. The effect of Fe_2O_3 on the Vickers hardness of Y-TZPs sintered at various temperatures.

The hardness trend of 0.3, 0.5 and 1 wt% Fe_2O_3 were found to be similar. These samples show very high hardness at low temperature sintering of 1250°C. As the temperature increases from 1300°C to 1350°C, these samples have almost the same hardness ~13.3 GPa except for 0.5 wt% Fe_2O_3 which was found to be around 13.6 GPa. As the sintering temperature increases further to 1400°C, it is found that the hardness value decreased rapidly with a decrement that was more evident in the 1 wt% Fe_2O_3 -doped samples from. The hardness value decreased from ~13.4 GPa to ~11.7 GPa when sintered at 1400°C and 1500°C respectively. The rapid decrease in the hardness value when the sintering temperature was increased from 1450°C to 1500°C for these samples may be attributed that the formation of monoclinic (m) phase detected in these samples.

4.0 Conclusions

The densification behaviour of Fe_2O_3 -doped yttria tetragonal zirconia polycrystals and the effect on the mechanical properties of Y-TZP has been investigated. Based on the results obtained, it has been revealed that small additions of Fe_2O_3 was effective in promoting

densification and also enhancing Y-TZPs mechanical properties especially when sintered at low temperature of 1250°C. The Young's modulus and bulk density has been shown to have a linear relationship regardless of dopant additions. Up to 0.3 wt% Fe₂O₃, the tetragonal phase stability were unaffected by the addition of Fe₂O₃. On the other hand, the Y-TZP matrix started to lose its stability when sintering temperature increased above 1400°C. This phase instability is associated with the decrement in the bulk density and the Vickers hardness, but caused an increase in the fracture toughness.

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Education of Engineers for Sustainable Development – Localising the Global Agenda

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Abstract

Engineering Education for Sustainable Development (EESD) emphasizes how education for engineers should be oriented towards sustainable development with increase in environmental awareness and ethical responsibility. However, the situation globally highlights transitional issues from implementing EESD and emerging call in deriving better understanding on integration of SD with a current curriculum.

Localising the agenda is an important qualitative experience that would interest educational researchers since adoption of practices oriented towards SD is not widely reflected in educational practice. Although literature highlights various factors for institutions disregarding implementation of EESD, some institutions have embarked on unique journeys of localizing the agenda for their own context. Taylor's University is an example of an institution that is looking into efforts for incorporation and integration of SD into their current curriculum.

This article is written based on the findings of action research done as part of PhD in Engineering Education at SOE. This article sets out to inform readers on the issues discussed on implementation of EESD within the contemporary engineering education curriculum in a global setting. A review in terms of the current practice and relevant literature with regards to incorporation of SD is undertaken using a soft systems approach. The findings are used to implicate the direction and scope of work for contextualizing and integrating SD with the current curriculum at SOE. The efforts to transition SD into the current curriculum through educational research is also discussed in terms of the various actions considered which is intended to raise consciousness on what it means to improve educational practice for EESD.

Keywords: engineering education, sustainable development, action research

1.0 Introduction

Technical problem solving has always been a territorial activity of engineers. The philosophy of “who is an engineer” is closely tied to the involvement of the self in this activity which reveals the social or “work” dimension of engineers identifying themselves with a problem, technology and the respective solution. In a keynote address, Downey [1] presents how engineers historically perceived as technology based problem solvers are now contended by other profession who are also pro-technology [1]. Downey [1] brings to the attention of the engineers community through his keynote how identifying with technology has made engineers vulnerable and the relationship with problems should not be focused at technical problem solving but rather at problem definition and solution to reduce this vulnerability. His concern is well founded with the advent of technology based courses like biotechnology which requires the need to validate his suggestion.

Referring to problems that Downey addresses, they are not simple technical challenges that can be easily dealt with or dealt alone. The challenges referred are that which are multidimensional, multiple realities for multi-actors; it suggests complexity in representing it with the structure that engineers are used in prior as problem solvers. Many of such challenges are applied industrial challenges which strongly suggest social implication and questions on how the engineers identify themselves in response to these challenges to gain social trust. What Downey is concerned with is reflected in the global concern for responsible engineering.

Current reality in terms of whether society trusts engineers do not suggest a positive image, particularly in the intention to represent the powerless, be it nature or society [3]. Examples of such incidences can be traced in history and relevant powerful messages (i.e Rachel Carson’s *Silent Spring* on pesticides, Earthjustice and WWF for engineering environmental disasters and empowering public voice, BP’s oil spill accident in Alaska and Gulf of Mexico) that does not condone the solutions provided is portrayed numerously to society. For example, Bell [4] in her message on the identity crisis of engineers questions the handling of such challenges and blames it on the lazy identity construction of engineers for responsible actions.

The professional conditions for engineering has changed, propagated as the need to address global challenges using technological in responding to SD globally. Based on this premise, new challenges are posed for the education of engineers. Engineering Education for Sustainable Development (EESD) represents such efforts in correspondence to the Decade of Education for Sustainable Development (DESD) by the United Nations from 2005-2014. A representation of the commitment of engineering educators for DESD is the Declaration of Barcelona which highlights the envisioned attributes of graduates for sustainable development to be change agents.

Research into implementation of EESD has started since 2002 and after a decade, there is still concern in terms of lack of fundamentals with regards to sustainability and how it is taught in terms of content and context. Vare & Scott [5] highlights the concerns of education for that is a product of what environmentalists are pushing forward but not based on emancipatory decision based on biases a community holds for. If attributes of graduates mention development of action competent citizens, this would require more than being environmentally aware and establishment on what sustainable engineering education implicates. Conceptualization of sustainable development and engineering education has to move away from coordinating the environmental elements with technology and focus on

integration. This creates more working dimension and more meaningful employment and eventually happier engineers [6].

Theoretical research into educational practise of EESD is evidently more advanced than actual implementation of EESD, where the focus has shifted from professionalization alone and to include the addressing of personal needs as well. However translating theory into practice is a challenge from the global engineering community for educational institution which has research value for better implementation and integration of EESD into current curriculum setting of any institution.

Huntzinger et.al [7] describes the efforts of various institutions who incorporate sustainable development through bolting on, building in or redesigning the concept of sustainable development for integration into the curriculum. The description enumerates the various consideration required as an implication on the practise and its sustainability. The article also gave an insight to the challenges arising, moving on from 'bolt on' to redesigning which had implication for various aspects of educational practise.

Any educational effort has to consider in terms of its implication to society as well as to the value of the profession. Delving into initiatives of various engineering education efforts provided insights on what could be done locally and the challenges to be addressed in developing the identity as change agents.

This article is written based on the findings of action research done as part of PhD in Engineering Education at SOE. This article sets out to inform readers on the issues discussed with regards to implementation of EESD within the contemporary engineering education curriculum in a global setting. A review in terms of the current practice and relevant literature with regards to incorporation of SD is undertaken using a soft systems approach. The findings are used to implicate the direction and scope of work for contextualizing and integrating SD with the current curriculum at SOE. The efforts to transition SD into the current curriculum through educational research is also discussed in terms of the various actions considered which is intended to raise consciousness among readers on what it means to improve educational practice for EESD.

2.0 The global challenge in incorporating sustainable development (SD) into engineering education

The challenge to incorporate SD has been translated as efforts of linking professional education with technical education and sustainable agency [9]. These suggestions have brought changes to educational practices in a number of institutions. The engineering education community is embracing this notion with committed action through use of problem oriented pedagogies such Project Based Learning (PjBL) and Problem Based Learning (PBL) [10, 11, 12].

The actions show a trend towards multidisciplinary - transdisciplinary design educational setting in engineering education. Transdisciplinary related work was evident in engineering research but is now a recognized reality for professional engineers as well [9]. Transdisciplinarity is foremost a mental view which would influence how students value sustainable development as an organizing principle to work together for better decision making. Professionals from water industry as noted in the article by Mollinga [13] are required to be prepared for a transdisciplinary professional requirement and learning and therefore, it has a bearing on the educational practise. Moving on from multidisciplinary to

transdisciplinary is an affective outcome of scientific community reaching out to the social science [14]. However, bringing together aspirations that questions tradition is a critical and challenging task and how it can be integrated for educational development is a question of sustainability itself.

However, moving towards transdisciplinary approach may be hampered as the positive trend of using multidisciplinary design education to address SD have also been coupled with notifications of barriers and challenges which may potentially discourage the practice. Ashford [15] questions the current setup of engineering departments which are pro-traditional discipline which may prohibit this new trend to integrate easily. He also argues that academicians may prefer to teach using the traditional approaches due to challenges that might arise from the intervention for a multidisciplinary setting. He also argues for developmental efforts as required for students as well as academics in allowing these practices to progress for better implementation of EESD.

Apart from problems in the setup of the academics, learning in a multidisciplinary in engineering education curriculum also represents its own challenges when implemented. Wolff [16] emphasizes on the conceptual and contextual elements that underpin a multidisciplinary engineering curriculum which requires its nature and relationship to be understood for effective educational experience. Ratcheva [17] states how integration of knowledge is challenging due to knowledge diversity of participants in a multidisciplinary context although it can be mediated with use of various other interventions that may result in other operational constraints for the educational practise.

Based on this, it can construed that the implication for educational practise has to considered as to what it means to use a multidisciplinary approach and proceeding towards a transdisciplinary vision in educating aspiring engineers for sustainable development. Azapagic, Perdan & Shallcross [18] states from the findings of an international survey, significant knowledge gaps exist and if it is evident in the multidisciplinary setting that we are promoting, how are we addressing them when the knowledge and value base for sustainable development is variable [6] ?

The question addressed here is mainly on how we approach and promote learning that would allow students to experience utility of SD in a disciplinary context as well, working with boundaries as proposed for transdisciplinary education [13]. However, this can be difficult to implement due to the diversity to be addressed as well disciplinary content which will be the core science in the case of engineering education. Alternatives solution suggested include transboundary exposure for competence building [19], sustainability and ethics as decision making paradigm [20], sectoral integration [14] and transdisciplinary sustainable development [21].

In another perspective, how the multidisciplinary design education is fitting with the rest of the subjects in terms of the developing decision making capacity and capability is addressed also needs to be considered. Views on sustainability thinking and holistic education, especially on the multi-dimensional aspects of sustainability suggests shifting of opportunity to address sustainable development should be given to other subjects which are more suitable platform due to its contextual approach [20]. However, it has not been discussed widely on how should the multidisciplinary design education be approached or supplemented to form a holistic educational experience while fitted with the rest of the subjects [21].

With regards to these issues, the ESD Toolkit highlights 12 issues that become barriers for change and limits the progress for the infusion of ESD [22]. Furthermore, each institution present challenges unique to their context, which requires delving into the practise of a local context to understand what and how, various factors are contributing to the success or failure of the response for EESD. If multidisciplinary design education is not sufficient for valuing sustainable development, what else can be done practically?

The question upholds the reality of students, practitioners and practise to value SD. Wals & Jickling [6] discuss extensively on various realities and how a continuum has to be considered, from utilitarian to emancipatory, focusing on development of action competent citizens who critically participate in decision making as well as respect alternative views. This requires for students to be exposed beyond multidisciplinary design but yet, moving through a continuum where at the end is a transparent society. Integrative translation is a requirement to consider for re-designs or improvement of curriculum compared to a bolt-on approach of teaching sustainable development using design.

As highlighted previously, this is not an issue of improving one module but attempting to improve holistically in terms of technical (holding the status quo) to emancipatory (questioning the status quo) [23] ; for allowing proposed educational intervention by educators rather than recommendations by environmentalists for engineers [5]. Borrego & Newswander [24] highlights how positive attitude development could be considered using socio-scientific context provides opportunities which also provides for successful engineering education collaboration. Nevertheless, considering the process through the continuum towards transdisciplinarity would requires attention to highlight, possibly not only knowledge and learning as a transformative outcome but also biases [24] that engineers might uphold for variable yet, valid reasons [6].

3.0 Translating the global challenge to local challenge

In the previous section, a number of issues encompassing the educational practice and learning with regards to the global agenda on integration of SD into curriculum is discussed.

Localising or contextualizing the agenda is an important task to done in order to

- i. provide an overview for the researcher to fit the research agenda into the a specific context
- ii. build a case to convince the community of a operational practise on necessary direction for improvement to substantiate any restructuring or remodeling of operations [25]

The effort to localise the agenda is due to the call for sustainable education which emerges around the poles of holism, systematic thinking, sustainability and complexity [26]. This perspective was necessary as from the initial, the question was, why do SOE need to disrupt the current arrangements which already requires much coordination and commitment? In order to ensure the attempts address in the overview results in a sustainable effort for education, the findings are concluded based on the descriptors as tenets of sustainable education [26]

- a. that which helps sustain people, communities and ecosystems
- b. that is tenable where the ethical dimension is considered through integrity, justice, respect and inclusiveness
- c. that which is a healthy system where it is viable and nurtures the relationship

- d. within the context
that which is durable in terms practise to continue doing it

3.1 Product Design Education, Conceive-Design-Implement-Operate Framework and EESD

Product design education forms the global trend in accommodating the needs of the industry for engineers familiar with multidisciplinary situations [27]. The situational context it provides becomes an advocated choice of teaching and learning approach where the context is embedded in the content that was intended to be taught. Contemporary design perspective which condones transition from problem/solution to systems approach benefits from the approaches of product design as it promotes cognitive apprenticeship where student knows what to design (i.e content) and who is a product designer and what do they do (context) [27].

These approaches are taught separately through individual courses but integrative efforts to bring the dimension of work into the classroom has resulted in integrated design experience through well thought initiatives such as the Conceive Design Implement Operate (CDIO) initiative conceived at MIT in 1990's and now, also adopted by SOE [28]. CDIO is not only an initiative but also a networked concept of educational practice with standard and implementing procedures that a significant number of institutions around the world have adopted starting from 2000 [28]. It focuses on engineering design with project based learning with focus on fundamental technical knowledge intertwined with the project environment suitable for development of skills and attitude for better engineering.

3.1.1 Implementation of CDIO and EESD

CDIO addresses SD as a contemporary theme and informs its design course module to form an important educational experience [28]. CDIO framework has been found useful to hitchhike in efforts to embed SD in curriculum [28] although, developmental efforts was required in terms of educating practitioners on good implementation of EESD based on recommendations [29].

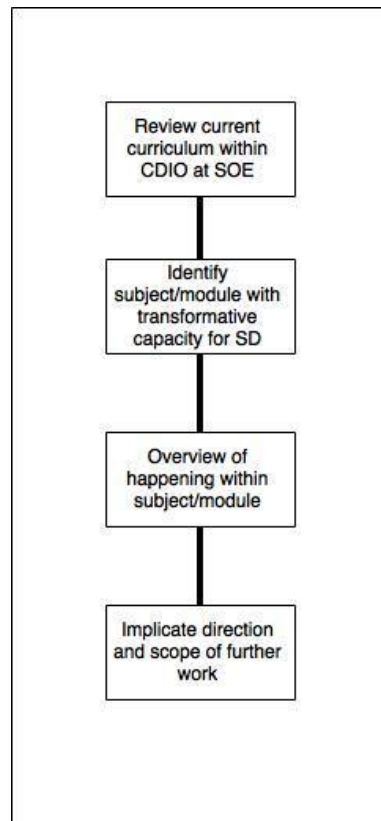
At the heart of CDIO initiative is education focused on integrated design experience for engineers and is a unique endeavor of active learning [28]. The possibility of situating learning in a design context resonates with the transformative outcome advocated for EESD. Transformative Sustainability Learning (TSL) has been identified an appropriate pathway in development of attitude and identity and is relevant towards the cause of developing better engineers for SD [9]. However, in what capacity is the transformation able to occur in terms of available resources and management of practice is of interest based on the concerns detailed in various issues discussed as part of the global agenda.

In the next section, the methodology to localize the agenda to the context of SOE will be discussed.

4.0 Methodology for localizing (contextualizing) agenda

The methodology is built based upon literature on action research and how baseline of a situation is to be explored. The first step was undertaking the review of current curriculum setting at SOE to identify courses with transformative outcome for SD, as shown in the flowchart in Figure 4.0. The focus was on engineering design course modules within the CDIO initiative. The Multidisciplinary Engineering Design (MED) module was the only subject explicitly identifying sustainable development as its outcome.

Figure 4.0 Flowchart depicting the steps required to approach localizing of the agenda to integrate SD into the current curriculum at SOE



Introspective work into what was happening within the identified courses was needed before looking into what else could be done. This required a systemic approach rather than searching for symptoms of a poor practice as this is an example of a functional practice and much consideration is required to disrupt an organized process that is already systematically connected.

A systemic approach would allow better understanding on the transformative capacity, even for a social system. Soft Systems Methodology's approach of CATWOE identifies elements that encapsulate the essence of a system which makes it a useful tool to provide overviews for the study [23]. Approaching MED with a soft systems approach would benefit understanding in terms of an overall view on people, issues or environment that contributes to a situation rather than, seeking answers from the narratives of the students alone [23].

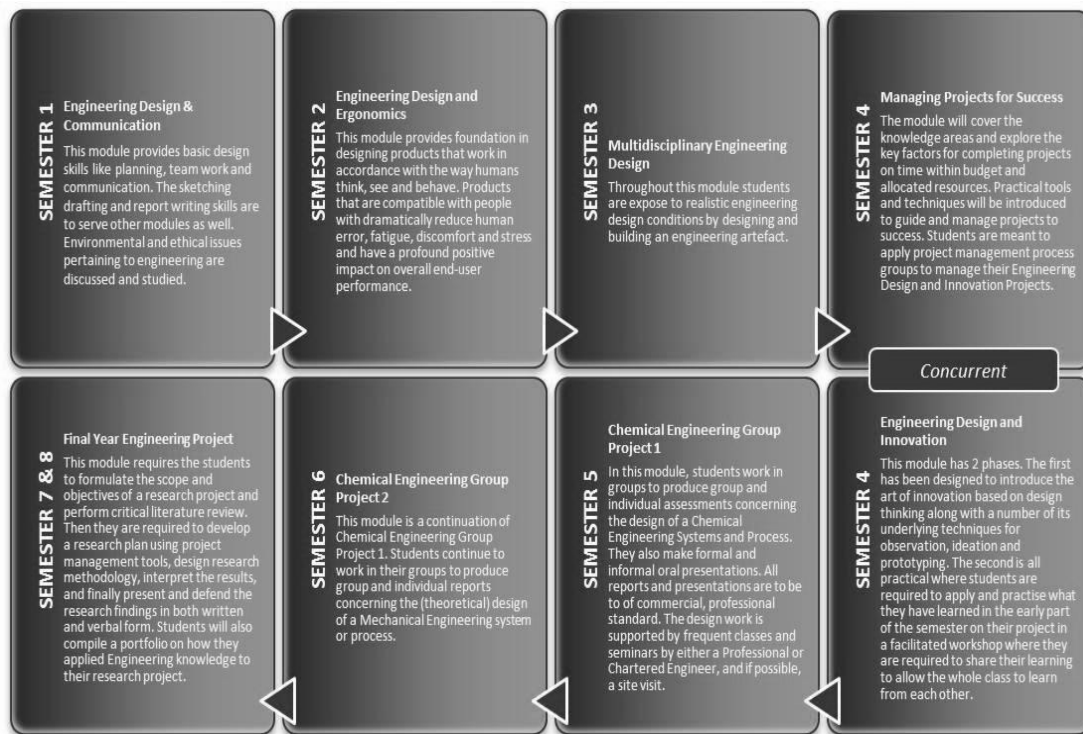
Immersion of context was possible with CATWOE as well as recognizing power distribution for research which is part of the dialectics required for the employment of action research methodology as bigger part of the agenda [23].

4.1 Description on context of study

The study is held as part of a PhD study in Engineering Education at Taylor's University's School of Engineering (SOE). The context of study is located within the practise of Multidisciplinary Engineering Design (MED) focusing on sustainable development held for the students of three disciplines namely, Mechanical Engineering, Chemical Engineering and Electrical Engineering as part of CDIO initiative.

The CDIO initiative at SOE is covered mainly around eight design modules that cover different themes with one theme explicitly on sustainable development covered in semester 3, as shown in Figure 4.1 with description of other design modules. The first 4 design modules are held within a multidisciplinary setting prior to them taking their disciplinary paths for engineering design from semester 5 onwards.

Figure 4.1 Multidisciplinary Engineering Design (MED) in Semester 3 as part of 8 engineering design modules with description of each module



The students within this study are undergraduate students acclimated with multidisciplinary setting through two other design modules prior to this. As the third design module, the content of the module explicitly identifies the bringing of the three disciplines for solving a common problem and further grounds the concept around sustainable manufacturing. The content and context is facilitated by a module coordinator with students involved in separately supervised projects for product design.

4.2 Consideration of actions for good sight of significant happenings in context

The CATWOE analysis features 6 aspects namely; Client, Actors, Transformation, Worldview, Owner and Environmental. It represents identification of the various contributors to the capture of essence of the 'system' and transformative capacity. Each aspect represents the respective description stated [25];

i.	client	-who are the system beneficiaries
ii.	actors	-who transform inputs to outputs
iii.	transformation	-from inputs to outputs
iv.	worldview	-the relevant world views
v.	owner	-the person with power of veto
vi.	environmental limitation	-that needs to be considered

Through an immersive exercise into context with observations and discussion, details of the context were retrieved during the period from 15 Feb 2015 until week 8 of the semester (i.e. sem 1/2015). The details collected were narratives from students and primary evidence and discussion between the module coordinator who facilitates and coordinates the module.

In terms of working with the module coordinator, a collaborative exercise was initiated through the development of a project for the module. The task of the module coordinator was numerous, and this collaborative effort was necessary to keep track, understand the concerns and reality of the module coordinator in facilitating this module. One project became the base of the collaboration which was the ‘Mini Aquarium Monitoring and Communication Project’.

Through this involvement at the initial stage, the processes that were necessary to be explored was evident through the established quality assurance procedure at SOE with regards to multidisciplinary engineering design. As the module coordinator, the lecturer is required coordinate the processes within this module to fit within the rest of the multidisciplinary design modules. A committee has been established to ensure the quality of the project, supervision and assessment is maintained for the 4 design module due to the nature of the multidisciplinary setting.

Evidences such as the classroom teaching and assessment materials that support the development of project for the students were provided with consent to provide more details of the processes. As for students, discussion was held with students with regards to the projects they were involved and their thoughts on the various projects. The discussions were held in groups and students were from a population of students in semester 3 of their studies from the three disciplines. Key informing group were chosen based on their progress and involvement with the respective projects. Students were familiar with the first author (i.e. author taught the students before), therefore were comfortable in providing inputs and were briefed and consent was retrieved from students, lecturer in-charge and academic management.

5.0 Findings and discussion

As part of the efforts to localize the agenda, the CATWOE analysis yielded the high level overview to understand what was happening within the context as well as implicating the direction of further works with regards to educational improvement and integrating SD.

Using the CATWOE analytical approach to capture the essence of the system, each aspects were given a deeper consideration based on the literature and was discussed between the module coordinator in a number of occasions. From the process above, these details were retrieved as compiled in Table 5.0.

Table 5.0 CATWOE Analysis for overview of MED system

CATWOE Aspects	Description
Client	The system beneficiaries are students and academicians directly or indirectly connected to the context of the Multidisciplinary Engineering Design

Actor	Module Coordinator, individual project supervisors, other relevant subject coordinators
Transformation	Transforming aspiring engineers using a systemic approach to produce change agents who works within the i. consideration of the three main operational aspect (i.e competitiveness, environmental sustainability and employment) ii. multidisciplinary setting and develops to be a transdisciplinary engineer
Weltanschauung (worldview)	For aspiring engineers to become transdisciplinary engineer for sustainable development
Owner	Owners are industrial stakeholders, community stakeholders, SOE and Taylor's University
Environmental constraints	Human, economic and environmental resources constraint

The description in the table is substantiated using evidences from the literature and from the current situation within the context. In sections below, the aspects are described in detail as per the substantiation starting with the aspect of transformation and the world view

5.1 Transformation

Gathered from the literature, the view on transforming aspiring engineers is through use a systemic approach [34] to produce change agents who works within the

- i. consideration of the three main operational aspect (i.e competitiveness , environmental sustainability and employment) [23], and
- ii. multidisciplinary setting and develops to be a transdisciplinary engineer [9 , 13 , 35].

The recognition of sustainable development as a multi-dimensional domain than that which concerns environment alone was emerging as more narratives of the students suggested skew of mindset towards economic growth and competitiveness of ideas in the market. The narratives provided below were by students from different project groups when asked about why they like a project.

“I don't like the aquarium project because if you look at the environment, right... like a lake.....you can't apply what you design to the lake...it's impossible “

“Student A : I chose the aquarium because such system is not available in the market.

Student B : I prefer the Chemicar project because petrol is expensive, so I am interested“

The students were given options to choose from available proposed projects or propose their own project challenge. The democratic environment that SOE promotes increases affective responses in students in terms of finding project challenges they are passionate about. SOE is also associated with the Grand Challenges of Engineering and having this initiative promotes the idea of connecting to the agenda of the world in terms of engineering challenges and finding better solutions. However, the types of projects do not reflect a distinct concern in reporting whether it addresses environmental or social concern. Majority of the projects are environmental concerns and developing social concern based projects are also not easy since it concerns subjectivity. A better context to address the social aspect is through case studies. Ethics studies for engineers remain the fertile domain for the discussion of such contextual elements as evidenced in literature [36, 37, 38, 39].

In proposing a project on their won, a group of students provided these narratives.

*“Student :We are interested in designing a hovercraft that works with chemicals
Researcher :Can you tell me why do you need a hovercraft...purpose....agenda ?
Student :It is multidisciplinary and we want to learn something...marine
design..and..environmental “*

The narratives suggests the importance on addressing the affective domain of learning where students can differentiate between a good and bad purpose for design, rather than true and untrue or it could also be said it is rather a crowd’s answer; SD should mean environmental and therefore, altering fuel with chemical makes it a good design problem. The narrative is also evidence that suggests the need for creating opportunities to learn to design pro-active solution based on integrative efforts rather than reactive solutions based on coordinated efforts [15].

5.2 Weltanschauung (Worldview)

In the worldview, it fits within the call for the development of transdisciplinary engineer. Mollinga [13] describes the necessity to bring the dimension of equity, ecology and justice within the dimensions of education for engineers. Incorporation of sustainability and ethics as decision making dimensions have been explored by , however, there has been failure in terms of increasing the cognitive outcome in relation to design [20].

In order to contemplate further on how shifting the responsibility, it was important to validate the suggestion against the tenets of sustainable education addressed earlier. Based on discussion, it was arguable that continuing to increase responsibilities on one module would unhealthy when opportunity to shift is viable within the curriculum. This suggestion also implies the research to be potentially directed towards introducing a transformative approach for another module for learning as well integrating with a relevant module to support each other in the transformative action.

5.3 Client

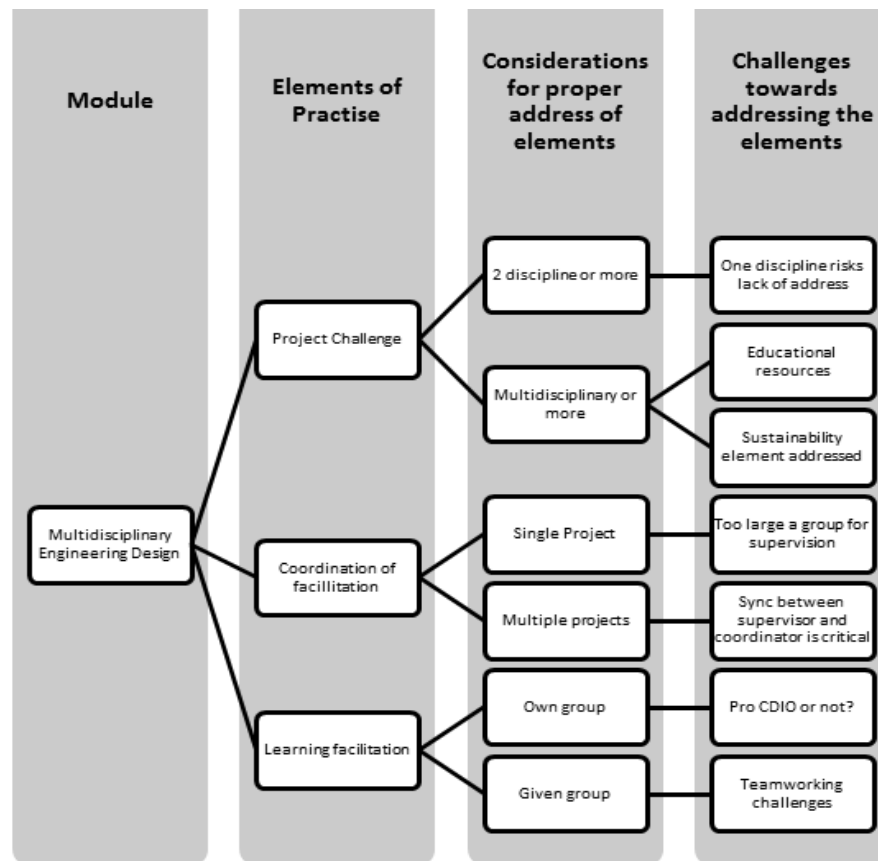
The beneficiaries of the system is determined based on the reality of this system is for everyone directly within context or indirectly around the context. This means it involves the entire academic community at SOE. Embedding SD within curriculum together with CDIO at Chalmers University [39] provided a similar perspective which was implemented in academics identifying ways how their subject is connected to sustainable development

outcomes of the curriculum. Through this exercise, they were able to engage almost the entire community and enable transformative action to take place holistically. If the focus is on the students, there are chances for exploitation of other members of the community such as over-tasked facilitators and supervisors. It is with this thought that the authors decided not to use students' feedback from students as a representative of the current happenings in the module.

5.4 Actors

The actors identified through the discussion, as stated in Table 5.0 are the module coordinator and the individual supervisors. The nature of project based learning and use of CDIO approach guides the actors in implementing the transformative action as claimed in the literature as well [39 , 40]. However, although it is expected for both the module coordinator and the supervisors to be in sync with the system requirement, the responsibility which lies mainly on the module coordinator to facilitate the content makes coordination a challenging task.

Figure 5.4 showing the elements of Multidisciplinary Engineering Design Project for with corresponding challenges for respective areas



In the diagram shown above, the 16 areas to be considered per operational module suggests the task relies heavily on the module coordinator to facilitate the content and learning outcomes and ensuring supervisors are in sync with the practise. The coordination based context requires all actors within the context to be informed of CDIO approach. The situation is shared by all the module coordinators of multidisciplinary based design module at SOE. From the discussion and overview of quality documents, it is evident that further allocation of task is not sustainable.

Possible challenges would also arise in collaborative work with other non-scientific areas where CDIO needs to be introduced. CDIO is educational framework that comes with its set protocol and document trail for quality assurance. It is most appropriate if the scope for collaboration is sectorial integration that works on identification of agenda setting. This kind of collaboration is conceptual and allows for development of planning as learning concept

In examples on initiatives within education setting, literature also show inability to engage affected the expected outcome of the learning experience especially when they are involved but not in charge. In an ethnographic study [41], the project which involves students engaging with theatre experts with whom they were not able to learn much although the engineering product was completed. The author describes the challenges in coordinating between experts who are stationed away from the institution were challenging in getting everyone together. However, in terms of capability of CDIO in bringing other fields to work along, it has potential to be implemented in both concrete and abstract application and a possibility has been addressed in literature [42]

The outcomes of [41] should not be taken with complacency as social experts express deep concern and find their position abused in the context of problem solving and their respective roles along with engineers must be identified from the problem definition stage [43]. With current development in transdisciplinary engineering education even at undergraduate level, the initial suggestion is to explore the boundaries of work through education. A multidisciplinary approach to social subjects such as safety is a useful way to include other in the picture as safety surpass individual to culture of an organization [44].

5.5 Owners or Stakeholders

The owners or stakeholders identified were industrial, community and academic stakeholders. Of this, engaging community stakeholders was a possible area to look at since many NGO's are appearing to be in need of such intervention in Malaysia as well. The importance of this intervention could be seen in terms what are the possibilities in terms of transformation that engagement of this kind could provide to students. In an article on efforts under EPICS program at Purdue University [45] which focused on engaging with the community which allowed the development of the perspective of care as an image that engineers would be interested in developing.

5.6 Environmental Constraints

Environmental constraints identified are in terms of human and economic resources. Projects involving product design incurs a lot of cost especially for prototyping and laboratory testing. Apart from that, human and educational resources are limitations that affect student learning process. In a discussion with a group of student working on a fuel-cell related project, on the initiative of the supervisor, they were brought to another university where it was possible to show the opportunities that lie in the field of fuel cell development. The simple act of being in the context has inspired student and provided these narratives to support their view

“I was inspired to see a real-life golf cart running on fuel cell at the university. We told the researchers we would like to work on something new with this technology. But the researchers said it will take many years “

However, these arrangements are usually done on own initiatives of lecturers and supervisors which would affect student learning experience and the transformation itself. A platform to experience socio-technological context with design is an opportunistic area to be brought into to also explore ethical dimension in its responsive dynamics [45]

6.0 Conclusion - Moving multidisciplinary and beyond for sustainable development at SOE

This paper was intended to provide readers with better understanding on what it means localizing a global agenda for EESD implementation. Information on what forms the concerns in the global agenda for integrating SD into the curriculum were detailed. Using a soft system approach as a methodology, the localizing exercise was undertaken with the specific use of CATWOE as the analytical tool.

The overview development as well as case building exercise was covered collaboratively with identification and discussion on actions considered to provide good sight into the happenings of the context. The different aspects that form the CATWOE analysis was discussed in what could be the potential in progressing and how does it fit in with the other aspects.

Each aspect was discussed extensively what it meant to bring in changes when compared with practices across the literature. The narratives of students and transformative capability of the subject suggests a direction in shifting the transformative aspect particularly in the affective towards another subject that could provide the platform for context building. In exploring the extent of implication through examples in practice in other institution, the direction and scope of further work emerged based on the implication of these findings

a. Transformative opportunities for learning through introduction of projects concerning social aspects were difficult and case based studies remain the better pedagogy to capture the details of a social dimension. A number of articles with content in light of this have been substantiated although remarks have been made on the sterility of the condition which decontextualizes issues that may arise [20, 36, 37, 38, 39].

b. The worldview with regards to the development of a transdisciplinary engineer is best worked through two kinds of synergies using the TSL approach [31]. MED works on creating synergy between the “head: and the “hand” in EESD mainly due to the rooting in the cognitive domain [10]. This approach affirms the view of engineers in terms providing effective disciplinary contribution but not on the broadening of perspective to understand the human environment. Education for Sustainable Development (ESD) requires rooting of educational experience in the affective domain [34]. This also provides possibility to understand fairness in decision making and why liberal and utilitarian approaches have to be considered by engineers [6].

Based on these findings, the following are suggested as further actions to progress

a. Transformation of *Professional Engineers and Society* module to reflect transformative approach for EESD

As stated above, the shift of responsibility for transformation in terms of SD could also be taken by other subjects. In the context of SOE, a further review into available subjects showed ‘Professional Engineers and Society’ (PES) module was viable as it was not currently approached using any transformative objectives. Literature shows that the nature of the

subject rooted in the affective domain and is anticipated to benefit the MED module in terms of

- i. developing the perspective of ethics as building blocks for the 3 pillars of SD for justifying good design [33,35,37]
- ii. situating engineers as professionals who are engineering designers and action competent citizens who are both emancipative and instrumentalist in their approach to SD [20,46]

b. *Integrative framework for infusing SD across the curriculum*

Approaching a new module is both an opportunity as well as a challenge as further study is required to identify how it will bear the transformative capability in hand with MED to contribute to better infusion of SD across both the subjects. [47,48,49,50] Bringing these subjects together suggests a need to understand integrative efforts as a systematic activity that allow transition from the isolated condition it prescribes to currently in the setting of the curriculum to becoming infused with SD [47,48,49,50]. Transformative approaches can then be part of curriculum design itself through engagement and developmental efforts of the group of practitioners and teachers rather than being bold initiatives of individual educators or organizations happening in isolation [47,48,49,50].

The gold standards to be achieved for sustainable development through engineering education are yet to be established. Kastanhofer et.al [9] states how it is far away from expectations although a significant number of institutions has embraced the call for sustainable development in their curriculum. Nevertheless, it is important to note the various efforts of actors in coming together for quality education of engineers through initiatives like CDIO and adheres to the tenets of sustainable education [26]. The articles provides a detailed introspect into what is required for integrative efforts of SD for a local context is required to accommodate the aspirations in global agenda for EESD. In these details, the considered actions for initiating efforts for immersion into context and provide good sight of the happenings within context were included for the purpose of raising consciousness on what the avenues of educational research provide for the engineering education community in a local context.

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Cryogenic Liquefaction of Air as an Energy Storage: Numerical Study of Liquefaction and Power Recovery Process

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Abstract

The use of energy storage is necessary as the world moves towards renewable sources of energy. Energy storage allows for the storage of off-peak and off-location renewable energy and moving them to areas where and when required. Liquid air has been studied for its potential in storing energy. This paper describes the preliminary study on the implementation of a small-scale liquefaction and power recovery system. Process modelling was used to study the effect of pressure ratio on the liquefaction and expansion cycles. It is found that higher pressures gave a higher efficiency in both the liquefaction and expansion cycles, however, the use of high pressures would incur more challenges in safety and cost. Hence a balance has to be struck between efficiency and cost to make the system feasible.

Keywords: Liquid air energy storage, liquefaction cycle, power recovery cycle, process modelling.

1. INTRODUCTION

Renewable energy use worldwide has been increasing due to the demands of an industrialized and globalized country. However, renewable energy use is often limited to time and place. Renewable energy generated at locations away from where the electricity demand is and often at off-peak hours. In 2013, 72% of wind energy in Northern Ireland is curtailed due to wrong time, wrong place generations [1]. Energy storage systems are necessary to curb this waste of energy. Current energy storage systems include pumped hydro, compressed air energy storage, batteries, supercapacitors and thermal energy storage systems. These energy storage systems have certain constraints restricting their use. Pumped hydro and compressed air energy storage systems are geographically constraint. Batteries and supercapacitors have relatively short lifespan. There has been a recent increase in interest towards liquid air as an energy storage system. Liquid air energy storage system is a type of cold thermal energy storage [2]–[4].

This research focuses on achieving an optimal design for a small-scale liquefaction and expansion system which is able to achieve exergy efficiency of over 30%. By using process modelling software, UniSim, the first step towards a small-scale liquefaction plant was conceived and designed. This paper describes the background of the study, the thermodynamic background, and the analysis of a Linde-Hampson cycle and direct expansion cycle to achieve small-scale liquefaction.

2. BACKGROUND

Air can be liquefied using renewable energy when the renewable energy produced is greater than the demand, this allows for energy to be stored in the form of liquid air instead of being wasted. Energy demand throughout the day fluctuates and various energy sources are used to supply the demand as seen in Fig. 1. Air can also be liquefied using grid energy during off-peak local electricity demand, this utilises the lower electricity tariff, in addition to levelling the electricity demand. The liquefied air can then be expanded or the cold energy used indirectly in power recovery cycles to run turbines which in turn generate electricity when required.

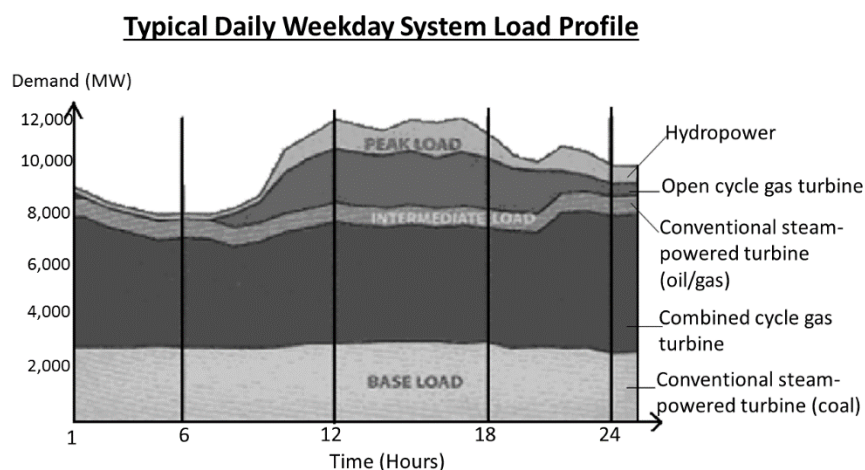


Figure 1. Daily energy demand curve in Malaysia [5]

Since liquid air vaporises at minus 196°C, the heat required to expand air can be wholly attainable from the environment or using low grade waste heat from the

industry. Furthermore, liquefied air is stored at low pressures in insulated vessels, thus making the storage safe and easy [4]. An example of a liquid air energy storage plant is the Highview Power Storage facility in the UK [6].

The scaling-up of systems is generally easier and allows higher efficiencies. However, for localised use of liquefaction plants, small-scale systems, which are able to liquefy air at a rate of 10 tonnes/day, for use with renewable energy sources are more convenient as the amount of energy harnessed from renewable energy may not be sufficient for large-scale liquefaction systems. Thus, there is a need to develop small-scale liquefaction systems for that purpose. This also addresses two of the 14 Grand Challenges for Engineering, making solar energy affordable, and improving and restoring urban infrastructure. By designing and implementing a small-scale liquefaction cycle, solar energy can be used to generate electricity to produce liquid air, this can be stored and used when required in both rural and urban areas. In urban areas, this allows the reduction in the dependence on fossil fuels, allowing for greener and more sustainable infrastructure.

However, due to conventional negative scaling effect, as a system is scaled-down, the capital cost to liquefy a gallon a day increases as the efficiency decreases, therefore, small-scale liquefaction systems with high efficiencies are hard to achieve [10]. Small-scale liquefaction processes have been designed for liquefying natural gas on floating liquefied natural gas, FLNG platforms, as well as to recover vapourised LNG in storage tanks [7]–[9].

3. PROCESS CYCLES

The process cycles used in the study are the Linde-Hampson cycle and the direct expansion cycle. The Linde-Hampson cycle and direct expansion cycles are used because of their simplicity. In small-scale systems, keeping the design simple and easily maintained is important, especially for use in less developed areas. This section describes the Linde-Hampson cycle and the direct expansion cycle.

Air in the simulation was specified as 79% of nitrogen and 21% of oxygen. The simulation was carried out using UniSim Design Suite under steady-state conditions.

Air enters the cycle and is mixed with uncondensed air. The mixture is compressed by a compressor, increasing the pressure of the mixture. The high pressure gas then enters a condenser where the air is cooled back to inlet temperature before entering the heat exchanger. In the heat exchanger, the mixture of air is cooled by the stream uncondensed gas counter-currently. Exiting the heat exchanger, air is throttled through a throttle valve, air expands and the temperature of the gas decreases, liquefying the air. The resulting vapour-liquid mixture enters a phase separator where liquefied air is removed and un-liquefied air is recycled. The air which is still in gaseous form will be recycled back into the cycle, it also acts as a refrigerant to the incoming air in the heat exchanger. The recycled air mixes with a fresh air stream to make up 1 kg/hour of air at 300K and 1bar. The Linde-Hampson cycle used for simulation is shown in Figure 2.

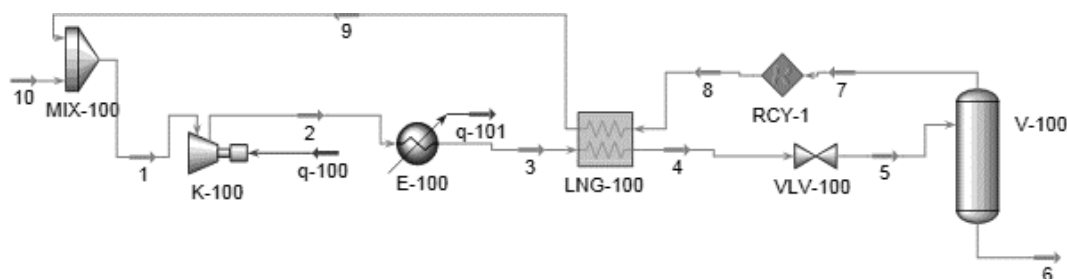


Figure 2. Linde-Hampson liquefaction cycle

The direct expansion cycle consists of a pump, a heater and an expander turbine. The pump is required to pump the liquid nitrogen through the system; the heater expands the liquid nitrogen; the expander turbine expands the air further, generating power and cold. Liquid air enters the system at stream 11 at atmospheric pressure and 77K. It is then pumped to the desired pressure ratio by the pump and then heated to 263K before entering the turbine.

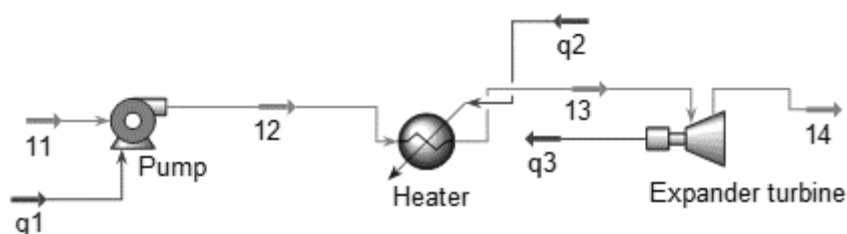


Figure 3. Direct expansion cycle

This paper studies the effect of pressure ratio on the efficiency of the systems and the cost of the cycles.

4. Thermodynamic Background

The efficiency of the system will be measured using exergy. Exergy efficiency is chosen over the overall energy efficiency because it reveals a more complete picture of the energy used in the system.

To measure exergy, the energy balances on the system have to be calculated [10],[11].

4.1 Energy balance on liquefaction system

To measure the fraction of air liquefied:

$$h_3 - h_4 = x(h_9 - h_8) \quad (1)$$

Where h is the enthalpy of the numbered stream, and x is the fraction of not liquefied. Eq (1) can be used to measure the fraction of air in vapour phase.

Hence, the fraction of liquefied air is calculated by:

$$y = 1 - x \quad (2)$$

Where y is the fraction of liquefied air.

The actual work done per unit mass of gas by the compressor is calculated using Eq (3). This is yielded from the energy balance on the compressor.

$$W_{compressor} = h_2 - h_1 - T_1(s_2 - s_1) \quad (3)$$

Where T_1 is the temperature of the stream at point 1, before entering the compressor; s_1 and s_2 are the specific entropy of the stream 1 and stream 2.

Thus, the actual theoretical work done per unit mass of gas liquefaction is given by:

$$W_{compressor} = \frac{h_2 - h_1 - T_1(s_2 - s_1)}{y} \quad (4)$$

4.2 Energy balance on the direct expansion cycle

Energy balance on the pump as well as the expander is required. Work required for the pump to increase the pressure of the liquid cryogen to the desired pressure ratio. The energy required to heat the cryogen is assumed to be obtained from solar energy and hence not included.

Work required by the pump is calculated by Eq (1):

$$W_{Pump} = h_{12} - h_{11} - T_{11}(s_{12} - s_{11}) \quad (5)$$

Work generated by the expander:

$$W_{Turbine} = h_{13} - h_{14} - T_{13}(s_{14} - s_{15}) \quad (6)$$

Net work generated by the direct expansion cycle:

$$W_{Net} = W_{Turbine} - W_{Pump} \quad (7)$$

4.3 Calculating Exergy Efficiency

To evaluate the system, the ratio of compressor work to reversible work is calculated. This ratio is the exergy efficiency. Exergy efficiency is the efficiency of the second law of thermodynamics. It is the work that can be obtained from the energy input into the liquefaction cycle and the liquid air input into the direct expansion cycle; under ideal conditions which is to apply reversible processes, using heat from the environment only. In this case the heat is the environment is the surrounding temperature.

Reversible work, w_{rev} is the minimum work input requirement per unit mass of liquefaction for the liquefaction cycle:

$$w_{rev} = h_6 - h_1 - T_o(s_6 - s_1) \quad (8)$$

Where T_o is the surrounding temperature which is set at 27°C or 300 K;

s and s_6 are the specific entropy of the stream 1 and stream 6.

Reversible work for the expansion cycle:

$$W_{rev} = h_{14} - h_{11} - T_o(s_{14} - s_{11}) \quad (9)$$

Therefore, exergy efficiency of liquefaction and expansion is calculated by:

$$\eta_{ex} = \frac{W_{Theoretical}}{W_{rev}} \quad (10)$$

4.4 Cost Analysis

The cost analysis takes into the account electrical energy required and the cost of the electricity generated from the expansion of liquid air. It is a simple analysis and does not take into account the cost of equipment as both cycles used remain the same for all pressure ratios.

This was done by using the industrial grid-electricity tariff for medium-sized industries for off-peak electricity. The cost of electricity is RM0.291 per kWh [12].

For liquefaction using the Linde cycle, the cost of liquefaction per hour is calculated using the work done by the liquefaction cycle.

$$\text{Cost}_{\text{liquefaction}} = W_{\text{theoretical}} \times \text{Cost of electricity} \quad (11)$$

For power recovery, the cost of energy produced per hour is calculated using the net work generated by the power recovery cycle.

$$\text{Cost}_{\text{Power recovery}} = W_{\text{net}} \times \text{Cost of electricity} \quad (12)$$

5. Results and Analysis

The effect of pressure ratio on the liquefaction cycle is summarized in Table 1.

Table 1. Effect of pressure ratio on liquefaction cycle

Pressure ratio	Efficiency (%)		$W_{\text{Theoretical}}$ (kWh)	Cost of liquefaction (RM/kg)
	Liquefaction	Exergy		
10	0.89	2.00	11.65	2.551
20	13.00	37.78	0.55	0.121
30	15.00	38.39	0.54	0.119
40	16.25	38.35	0.54	0.119
50	17.73	39.46	0.53	0.115
55	18.02	40.05	0.52	0.114
60	18.80	39.95	0.52	0.114
70	19.45	39.83	0.52	0.114
80	20.60	40.92	0.51	0.111
90	21.11	40.85	0.51	0.111
100	22.08	41.71	0.50	0.109

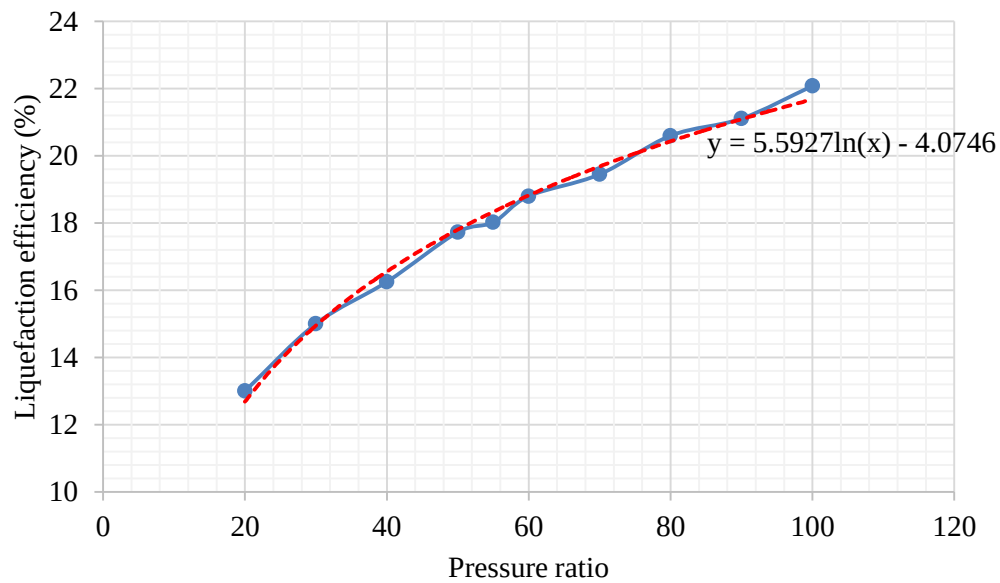


Figure 4. Effect of pressure ratio on liquefaction efficiency

It is seen that as the pressure ratio of the liquefaction cycle increases, the liquefaction efficiency of the cycle increases. The effect of pressure ratio of liquefaction efficiency approximates a logarithmic trend line following the equation $y = 5.5927\ln(x) - 4.0746$. The gradient of the increase of liquefaction efficiency as the pressure ratio reduces until a certain point where the pressure ratio no longer effects the liquefaction efficiency. The highest liquefaction efficiency achieved is 22% from this data set.

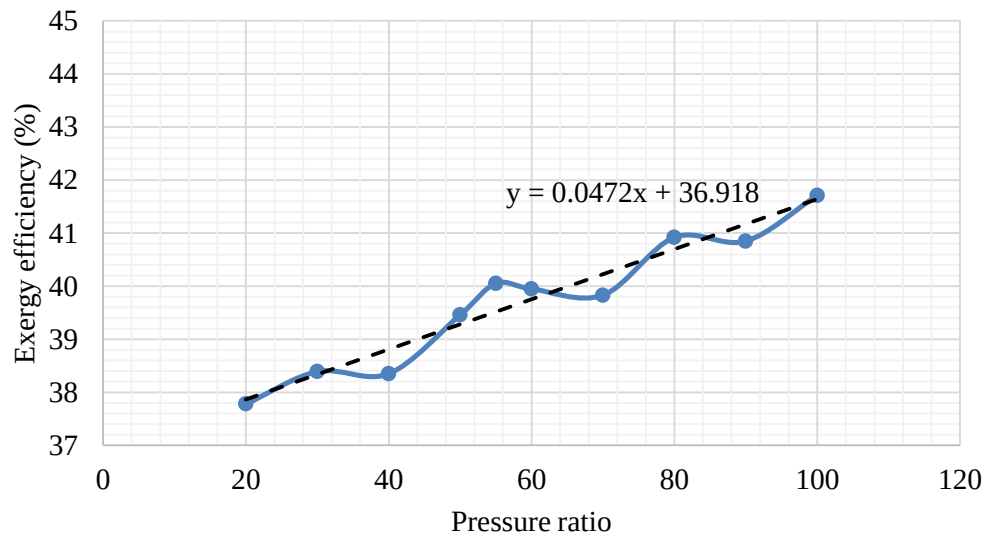


Figure 5. Effect of pressure ratio on exergy efficiency of liquefaction cycle

The effect of pressure ratio on the exergy efficiency approximates a straight line. As the pressure ratio increases, the exergy efficiency increases according to the

straight line $y = 0.0472x + 36.918$. The highest exergy efficiency achieved is 41.8% from the dataset.

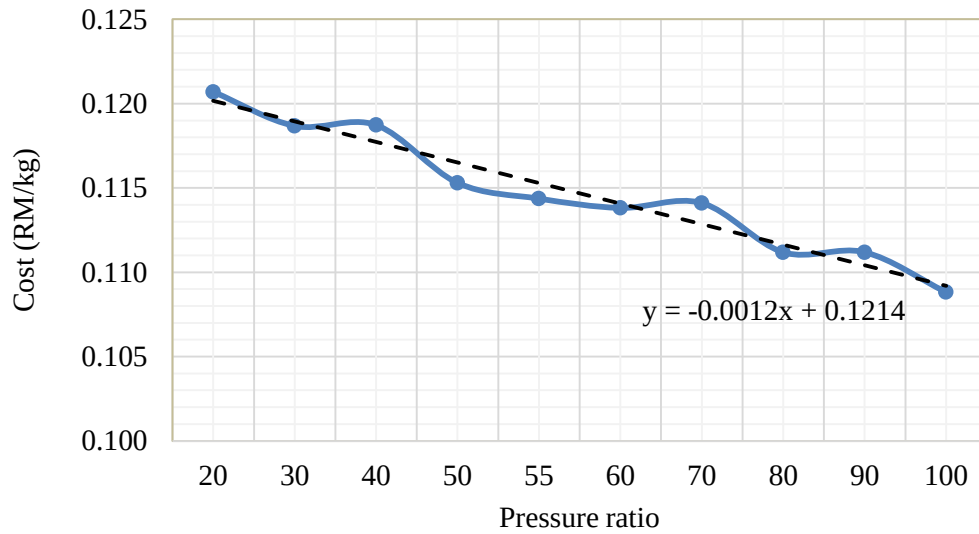


Figure 6. Effect of pressure ratio of cost of liquefaction per kg of liquid air produced

As the pressure ratio increase, the cost to liquefy one kg of air reduces. This follows the trendline $y = -0.012x + 0.1214$.

The effect of the pressure ratio on the direct expansion cycle was also tested. Table 2 shows the effect of pressure ratio on the exergy efficiency, the net work generated per unit mass of air and the earnings generated by the generation of electricity from the expansion cycle.

Table 2. Effect of pressure ratio on direct expansion cycle

Pressure Ratio	Exergy efficiency (%)	Wnet per kg of air (kWh)	Earnings (RM/kg)
10	21.51	0.0270	0.0059
20	27.73	0.0317	0.0069
30	31.40	0.0338	0.0074
40	33.96	0.0350	0.0077
50	35.98	0.0356	0.0078
60	37.60	0.0361	0.0079
70	38.99	0.0364	0.0080
80	40.15	0.0366	0.0080
90	41.16	0.0367	0.0080
100	42.10	0.0369	0.0081

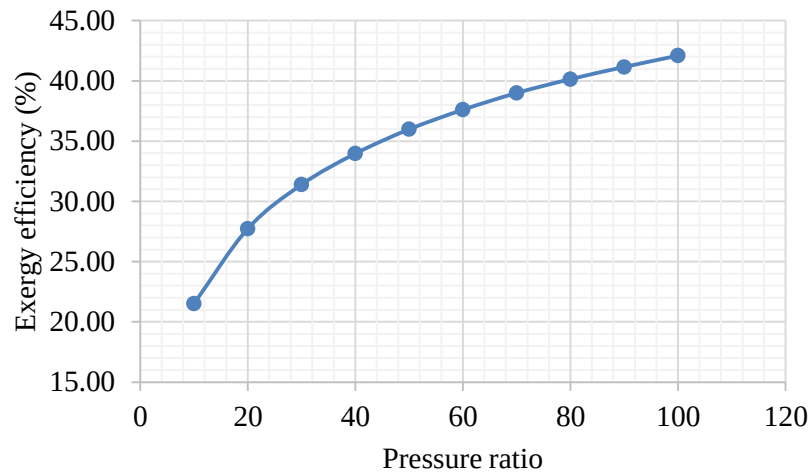


Figure 7. Effect of pressure on the exergy efficiency of expansion cycle

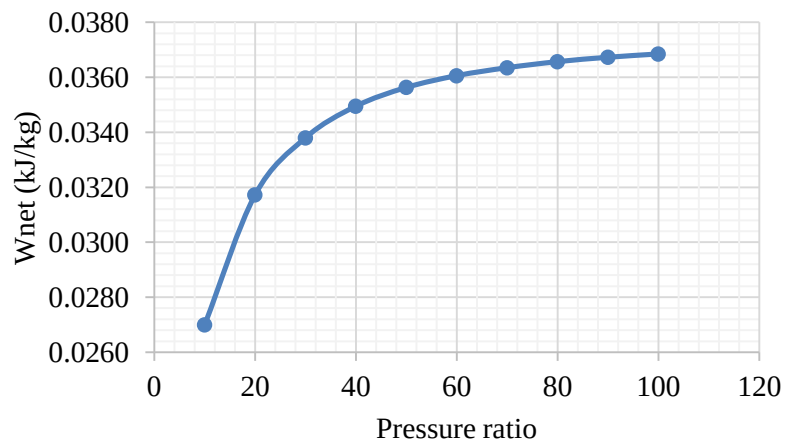


Figure 8. Effect of pressure ratio of net work output of expansion cycle

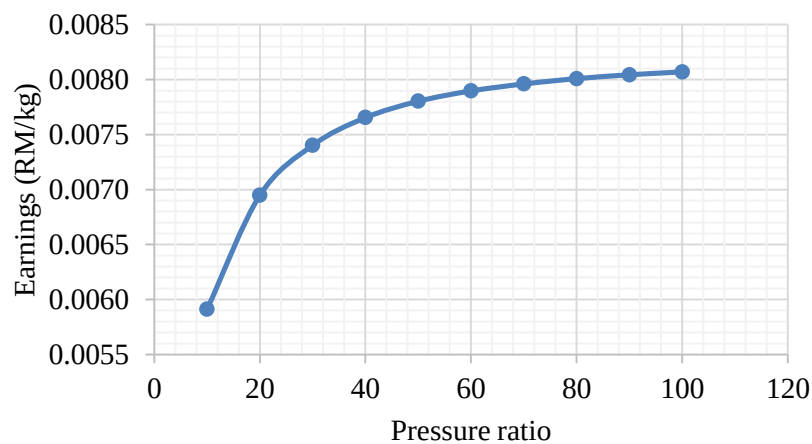


Figure 9. Effect of pressure ratio on the earnings generated from the expansion of liquid air

The effect of pressure ratio on the exergy efficiency, net work generated and the earnings per unit mass of liquid air increases until a certain point before it starts plateauing. The point is at the pressure ratio of approximately 60. After which the increase in pressure ratio reduces to a negligible increase in all 3 parameters. The highest exergy efficiency achieved is at the pressure ratio of 100 with an exergy efficiency of 42%.

Table 3. Cost of liquefaction and expansion

Pressure Ratio	Cost (RM/kg)		
	Required for liquefaction	Generated from expansion	Total cost of system
10	2.551	0.0059	2.5446
20	0.121	0.0069	0.1138
30	0.119	0.0074	0.1113
40	0.119	0.0077	0.1111
50	0.115	0.0078	0.1075
60	0.114	0.0079	0.1059
70	0.114	0.0080	0.1061
80	0.111	0.0080	0.1032
90	0.111	0.0080	0.1031
100	0.109	0.0081	0.1008

The cost required for the system reduces as the pressure ratio increases. However, the cost of electricity generated from the expansion cycle is not sufficient to offset the cost of liquefaction.

The expansion and liquefaction cycles are simulated separately and hence the integration of pitch technology into the system is not studied. The simulation of a coupled liquefaction-expansion cycle would provide a better combined efficiency.

When choosing conditions for small-scale liquefaction, it is important to consider all the parameters stated above, as well as the cost incurred to achieve the required conditions. The trade-off between liquefaction efficiency for the liquefaction cycle and the exergy efficiency of the liquefaction and direct expansion cycle, as well as cost should be taken consideration during the design stage. It should also worth mentioning that although simulation may allow a fast and cheap alternative to time-consuming building of real life plants, simulations are not 100% perfect, there are many assumptions that are required for simulation. Process simulation softwares such as UniSim only acts as “black boxes”, the results obtained are only as good as the combination of knowledge, experience, and the close-to-real-life assumptions applied to the simulation.

The realization of a small-scale liquefaction plant would assist in addressing two of the 14 Grand Challenges for engineering, making solar energy affordable and to improve and restore urban infrastructure. The integration of the system into

existing infrastructure would reduce the dependence upon grid energy of which majority comes from fossil fuels. The use of solar energy for liquefaction would help make solar energy economical.

6. Conclusion and Further Work

The use of energy storage system is important for renewable energy application due to the inconsistent supply of energy according to demand. Liquid air energy storage systems can be used to address this need for energy storage.

This paper shows the preliminary steps in conceiving and designing a small-scale liquefaction cycle and expansion cycle using the UniSim Design Suite. The sole effect of pressure ratio on the Linde-Hampson cycle and the direct expansion cycle was studied. The cycles were chosen due to their simplicity.

The increase in liquefaction efficiency and exergy efficiency for the Linde-Hampson cycle can be achieved by increasing the pressure ratio of the system. And as the efficiencies of the cycle increase, the cost to produce one kg of liquid air would decrease to. The increase in exergy efficiency as well the net power output of the direct expansion cycle can be achieved by increasing the pressure ratio. However, the cost of electricity generated from the expansion of liquid air using the direct expansion cycle was very small. It was not sufficient to offset the cost of electricity required to generate liquid air. Currently, the study shows potential, however, optimization of more parameters are required to realize a small-scale liquefaction plant that is efficient. The realization of a small-scale liquefaction plant would assist in addressing two of the 14 Grand Challenges for engineering, making solar energy affordable and to improve and restore urban infrastructure.

Further work in this area can be carried out by coupling the liquefaction and expansion cycles to integrate the heat flow in the system as well as capturing the cold energy generated after the liquid air is expanded in the turbine. The integration of heat flows and cold energy capture is able to reduce the amount of power required for liquefaction. Furthermore pinch technology can be incorporated to maximise the utilisation of heat flow in the system, hence reducing waste.

Acknowledgment

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Influence of Manganese Dioxide Dopants on the Microstructure and Mechanical Properties of Yttria Stabilized Zirconia

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Abstract

8mol% yttria stabilized zirconia (8YSZ) is a popular material used in the fabrication of solid oxide fuel cell. Poor mechanical properties of 8YZ electrolyte layer can cause failure to the fuel cell. Besides, 8YSZ ceramic with low mechanical strength is not suitable to be used as the anode supporting structure in the fuel cell. The addition of manganese dopant is hypothesized to be beneficial to the mechanical properties of 8YSZ ceramic. In this study, the influence of the manganese dioxide (MnO_2) on the relative density, apparent porosity, microstructure, Vickers hardness and fracture toughness of 8YSZ were systematically investigated. 0.5wt%, 5wt% and 8wt% of MnO_2 were doped into 8YSZ commercial powder and sintered at temperature ranging from 1300°C to 1550°C . At sintering temperature of 1300°C , 8wt% MnO_2 showed the greatest enhancement in densification (from 64% to 93% relative density as compared to undoped sample) of 8YSZ specimens. The apparent porosity of the specimens became negligible when more than 5wt% of MnO_2 was doped into 8YSZ powder. Among all the sintered samples, 0.5wt% Mn-8YSZ specimen exhibited the highest Vickers hardness (12.5MPa) at 1550°C and achieved the highest fracture toughness ($3.6\text{Mpa}\cdot\text{m}^{1/2}$) at 1500°C . Both relative density and Vickers hardness of 8wt% Mn-8YSZ decreased when heated at higher temperature (above 1300°C). The reduction of Vickers hardness and relative density could be associated with the abnormal grain growth observed in the SEM micrograph. In conclusion, MnO_2 enhanced densification, eliminated apparent porosity and improved Vickers hardness and fracture toughness of 8YSZ ceramic.

Keywords: Manganese, Mechanical properties, Microstructure, YSZ, Zirconia.

1. Introduction

Yttria stabilized zirconia (YSZ) is a zirconia based ceramic. Pure zirconia is unstable at high temperature. Phase transformation of pure zirconia will involve large volume changes. Hence, yttria additive is used to stabilize zirconia cubic structure to prevent destructive cubic(c)→tetragonal(t)→monoclinic(m) phase changes [1, 2]. Under proper sintering condition, 2-3mol% of yttria stabilizer is used to produce tetragonal zirconia polycrystals (TZP). At room temperature, 3Y-TZP exhibits high mechanical strength (~ 1GPa) [3]. Due to its high mechanical strength, 3Y-TZP is widely used in clinical applications [4, 5].

Fully stabilized zirconia with 8mol% yttria exhibits high ionic conductivity [6]. Cubic zirconia lattice structure in the 8YSZ has oxygen vacancies that ease ions transportation [2]. At elevated temperature, 8YSZ shows high ionic conductivity but low electronic conductivity. Due to these reasons, 8YSZ material is widely applied in ionic conductor industry. One of the important applications of 8YSZ ceramic is in the fabrication of solid oxide fuel cell (SOFC) [7-9]. Unlike some fuel cells, all the parts of SOFC are made up of solid material. SOFC shows high performance at moderate temperature (~1000°C). 8YSZ ceramic exhibits high ionic conductivity and phase stability at SOFC operating temperature, hence it is always served as the electrolyte layer in the fuel cell. In SOFC, 8YSZ electrolyte layer allows oxygen ions to travel from the cathode to the anode for electrochemical reaction [10].

Thickness of the electrolyte will affect the ionic conductivity of the SOFC [6, 11, 12]. Thin layer of electrolyte has low internal cell resistance which enhances ionic conduction. Hence, 8YSZ layer needs to be as thin as possible to increase the performance of the fuel cell. However, 8YSZ is claimed to have poor mechanical strength which limits the electrolyte design in achieving low thickness layer [13]. Besides, electrolyte in the SOFC acts as the blocking layer to avoid the fuel gas at the anode side from mixing with the oxygen gas at the cathode side. In order to prevent burning resulted from the mixing of fuel gaseous and oxygen, the layer of the electrolyte must be free from crack [10]. In this case, dense layer of 8YSZ is preferred to serve as the electrolyte [14].

Several authors have reported that the addition of dopants will improve the mechanical properties of YSZ. An investigation on the influence of alumina addition to the YSZ was carried out by A.A.E.Hassan and his team [15]. Alumina was found to produce crack-free layers and improve the performance of the fuel cell [15, 16]. In addition, R.M. Batista and E.N.S. Muccillo had noted that nickel oxide enhanced densification of 8YSZ up to its solubility limit [9]. Recently, a comparative study on the effect of transition metal additives on the physical properties of cubic YSZ was done by a group of researchers in the Michigan State University [17]. It was concluded that different dopants will produce varying effect on the grain growth, densification and sintering temperature of 8YSZ.

Manganese dopant had shown positive results in densification, Vickers hardness and fracture toughness of 3Y-TZP [18]. It was hypothesized that manganese dioxide will improve mechanical properties of the 8YSZ. For these reasons, the effect of manganese dioxide doping in 8YSZ seems to be important for the improvement in the physical properties of 8YSZ. Strengthened 8YSZ ceramic can be used to compensate the usage of 3Y-TZP as the supporting structure at the anode side of SOFC. This helps to widen its applications in ionic conducting products [8, 19-21]. Using the same material in the fabrication of anode and electrolyte is able to reduce the manufacturing cost of the fuel cell.

In current work, a wide range (0.5-8wt%) of manganese dioxide dopant was added into 8YSZ powder. The samples were then sintered at temperature ranging from 1300°C to 1550°C. The relationship between the sintering temperature, manganese additive contents, densification, apparent porosity, microstructure and mechanical strength were investigated which has not been studied extensively before. The main purpose of the research is to determine the effect of the manganese additive contents on the microstructure, Vickers hardness and fracture toughness of the 8YSZ ceramic.

2. Experiment Methods

2.1 Sample Preparation

The commercial 8YSZ powder (Daichii, Japan) and high purity manganese (VI) oxide (MnO_2) powder (Essex, United Kingdom) were used as the raw materials. 0.5wt%, 5wt% and 8wt% of MnO_2 were ultrasonically mixed in ethanol solution for 30min to obtain homogeneous mixture. Then, the mixture was ball milled for 60min at 500rpm and oven dried at 70°C. The dried powders were then sieved to obtain soft, ready-to-press powder.

The resultant powder was uniaxially pressed at 6MPa to form 20mm diameter pellets (each weighing 3.0g) and 13mm x 32 mm rectangular bars (each weighing 3.5g) followed by cold isostatic pressing at 200MPa. The specimens were then pressureless sintered in air using a standard rapid heating furnace, at various temperatures from the range of 1300°C to 1550°C. For all specimens, the heating rate were kept constant at 10°C/min and maintained at holding temperature for 120min before cooling to room temperature. All sintered pellets were grinded on one surface by SiC papers and polished by 1 μm diamond paste to produce a mirror finishing surface.

2.2 Characterization

The bulk densities of the sintered pellet were determined by the water immersion technique based on the Archimedes principle. This was done by using distilled water as the measuring medium according to the ISO18754 standard. Relative density was calculated using theoretical density of 5.96g/cm³ [22]. Apparent porosity of the sintered pellets was estimated referring to ASTM C830-93 [9]. Prior to scanning electron microscope (SEM) (Phenom proX) examination, all disc specimens were thermal etched at 50°C lower than its corresponding sintering temperatures for 30minutes.

Vickers Hardness (Hv) was calculated using the Vickers indentation method (Shimadzu HMV microhardness tester) on polished surface of the sintered pellets. For each pellet, 5 indents were made with load of 2kgf and a loading time of 5s was employed. The indentation diagonal lengths and crack lengths were measured using light microscope (Olympus BX61). The resonant frequency of the sintered rectangular bars was measured by sonic resonance instrument (Grindosonic; MK5, Belgium). Young's modulus (E) was calculated using experimentally determined resonant frequencies, according to standard test method [23]. Nihara's formula was used to calculate fracture toughness, K_{IC} values [24].

3. Results and Discussions

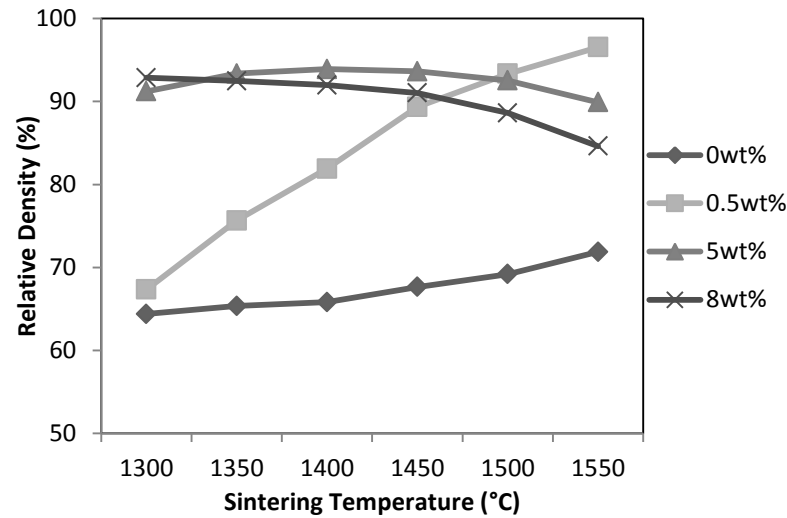


Figure 10. Relative density of 0-8wt% Mn-8YSZ at various temperatures

Fig. 1 showed the bulk densities of 8YSZ sintered at temperature from 1300°C to 1550°C. At all sintering temperature, the relative densities of Mn-8YSZ specimens were found to be higher than that of undoped 8YSZ specimens regardless of the amount of dopant added. With increasing sintering temperature, the relative densities of both the undoped and 0.5wt% Mn-8YSZ increased. The increment in relative density suggested that MnO₂ enhanced the densification of 8YSZ. However, increasing sintering temperature reduced the relative density of both 5wt% and 8wt% Mn-8YSZ. This could be due to the secondary recrystallization grain growth at high temperature.

The comparison of 8YSZ microstructures with different MnO₂ contents, sintered at 1300°C and 1450°C were shown in Fig. 2. Examination from SEM had revealed that the undoped 8YSZ specimen remained in crystallite forms after the pellets were sintered at 1450°C (Fig. (2b)) while the sample with 0.5wt% MnO₂ had achieved fully dense grains (Fig. (2d)). Similar finding has been reported by T. S. Zhang et al. [25], who claimed that manganese dopant reduced sintering activation energy of 8YSZ and promoted grain growth. A few very large grains were observed in the SEM micrograph of 8wt% Mn-8YSZ sintered at 1450°C (Fig. (2f)). The abnormal grain growth observed was in agreement with the fall of relative density in 8wt% Mn-8YSZ.

Addition of MnO₂ greatly reduced the apparent porosity of 8YSZ specimens (Fig. 3). The apparent porosity of 0.5wt% Mn-8YSZ became negligible after heated above 1500°C. There was no significant changes in weight observed after 5wt% and 8wt% Mn-8YSZ were removed from immersing in distilled water. In another words, there was no liquid trapped within the specimens. Therefore, it was hypothesized that large water molecules was unable to enter the micro-pores of the dense specimens, which results in negligible apparent porosity. The apparent porosity of the 8YSZ specimens were correlated with the relative density results.

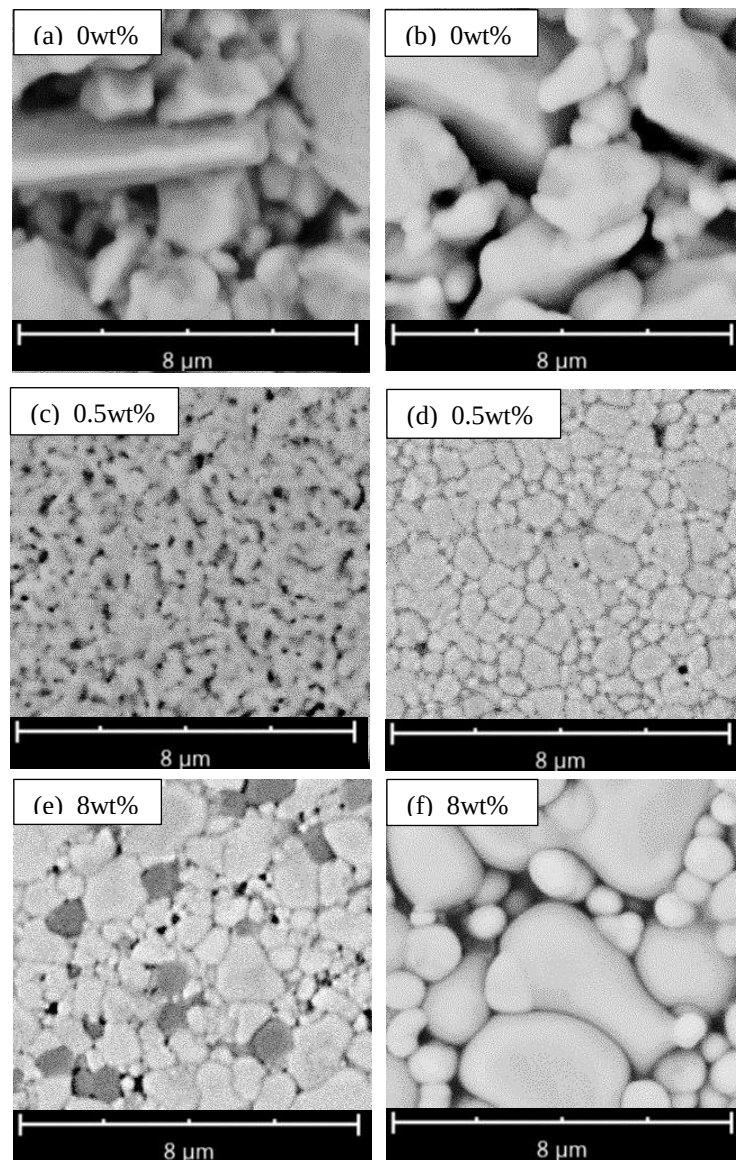


Figure 11. SEM micrograph of (a) the undoped 8YSZ at 1300°C, (b) the undoped 8YSZ at 1450°C, (c) 0.5wt% Mn-8YSZ at 1300°C, (d) 0.5wt% Mn-8YSZ at 1450°C, (e) 0.5wt% of Mn-8YSZ sintered at 1300°C and (f) 0.5wt% of Mn-8YSZ sintered at 1450°C.

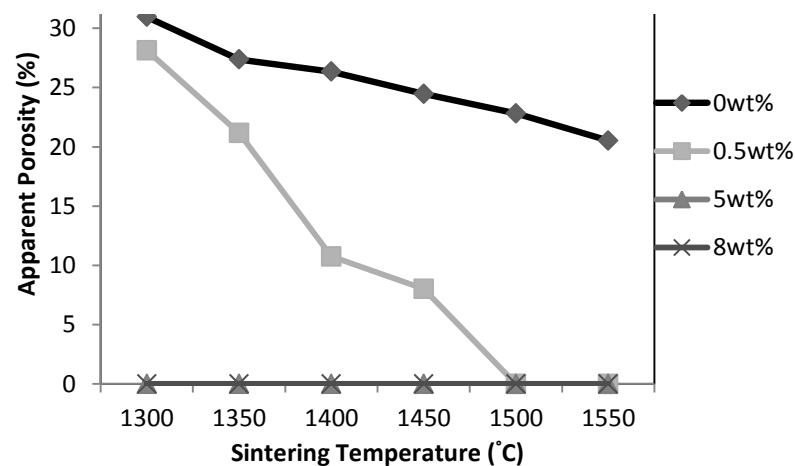


Figure 12. Apparent porosity of 0-8wt% Mn-8YSZ at various temperatures

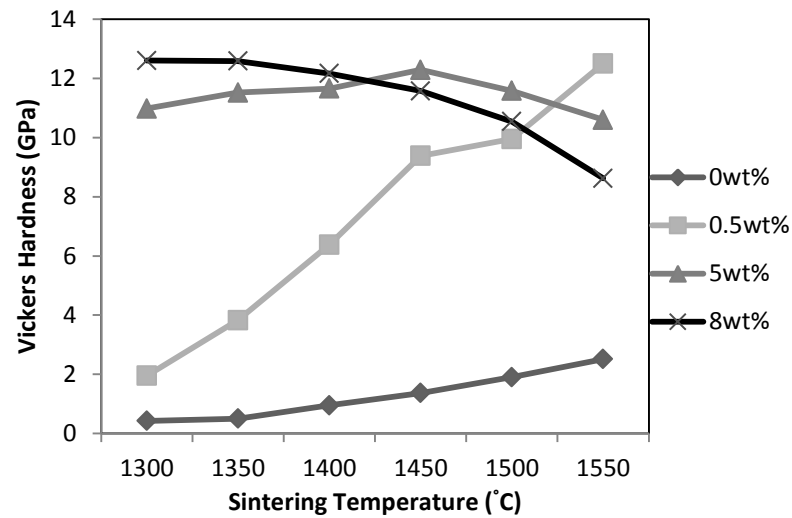


Figure 13. Vickers hardness of 0-8wt% Mn-8YSZ at various temperatures

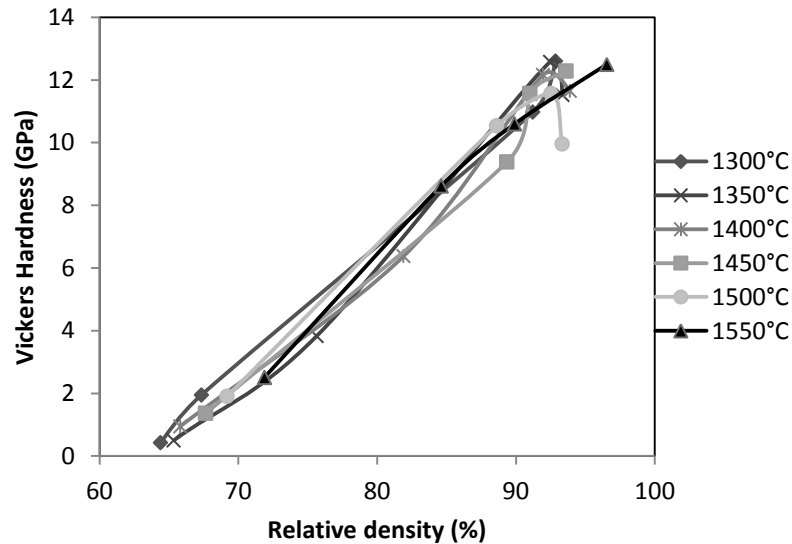


Figure 14. Relationship of Vickers hardness, relative density and sintering temperature

The doped specimens showed higher Vickers hardness than the undoped specimens at random sintering temperature indicated that MnO_2 improved Vickers hardness of 8YSZ. Both relative density (Fig. 1) and Vickers hardness (Fig. 4) of the specimens increased with the increasing of sintering temperature. Hence, the relationship between Vickers hardness, relative density and sintering temperature was illustrated in Fig. 5. A linear relationship was observed between Vickers hardness and relative density regardless of the sintering temperature. This is in agreement with the work of Hongming Zhou et al. [26], who reported that densification of 8YSZ specimens attributed to the increasing of Vickers hardness. However, in this study, the Vickers hardness value reached its maximum at about 13GPa with the relative density close to 92%. Beyond that point, further increase of relative density did not improve the Vickers hardness. Secondary recrystallization induced large grains growth that could lead to the reduction in Vickers hardness of 8YSZ ceramics.

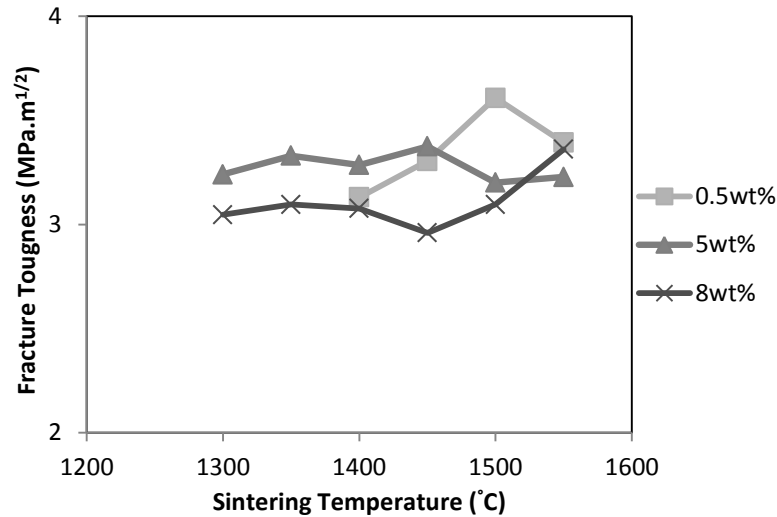


Figure 15. Fracture toughness of 0-8wt% Mn-8YSZ at various temperatures

Fracture toughness of the undoped 8YSZ specimens was not measurable because Vickers indentation on the undoped 8YSZ pellets did not induce any cracking lines. Similar to the undoped specimens, cracks were not able to be detected after Vickers indentation on the surface of 0.5wt% Mn-8YSZ pellets which were sintered at low sintering temperature of 1300°C and 1350°C. The undetectable cracking lines were due to the incomplete fusion of powder particles. As a result, the microstructure of the pellets was still remained as scattered crystallite hence unable to resist fracture (Fig. 2 (a-c)).

From the results shown in Fig. 6, the addition of MnO₂ had improved the fracture toughness of 8YSZ ceramic. Unlike the Vickers hardness results, abnormal grain growth found in the 8wt% Mn-8YSZ specimens (Fig. 2(f)) did not show significant effect on the fracture toughness value. Once the grains were formed in the pellets, the Mn-8YSZ specimens maintained its fracture toughness value above 3MPa.m^{1/2} regardless of the sintering temperature and additives contents.

7. Conclusions

In this research, the microstructure and the mechanical properties of the undoped, 0.5wt%, 5wt% and 8wt% Mn-8YSZ specimens were studied. The results are summarized as below:

- (i) Addition of MnO₂ improved the Vickers hardness and fracture toughness of 8YSZ ceramic.
- (ii) MnO₂ promoted grain growth, reduced percentage of apparent porosity and enhanced densification of 8YSZ specimens.
- (ii) Relative density was proportional to the Vickers hardness of 8YSZ specimens regardless of the sintering temperature.
- (iii) When the MnO₂ additives exceeds 5wt%, the relative density and Vickers hardness of 8YSZ specimens reduced with increasing temperatures. However no significant effect was observed in fracture toughness.

Addition of MnO₂ showed enhancement in the mechanical properties of 8YSZ. This suggests that MnO₂ can act as a promising dopant of 8YSZ in the SOFC application. Further research will be carried out to investigate the effect of MnO₂ on the crystallographic and conductivity of 8mol% yttria stabilized zirconia.

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Review of Regenerator for Stirling Engine

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Abstract

Stirling engine is an external combustion engine that can be fueled by various types of thermal energy sources such as fossil fuel, biogas and solar heat energy, unlike the internal combustion engine that can only be powered by combustion reaction of burning fuels which compromise environmental security. The Stirling engine has been proven as the most suitable engine for waste heat recovery, such as being the co-regenerator in power plant stations and has been commercialized in well-developed countries. It is a high thermal efficiency low noise operation engine. The three main components in a Stirling engine are the expansion piston, compression piston and regenerator. The increasing temperature difference between hot and cold portions of the engine will increase the output power, but the properties of material used to construct the engine limits the engine power output. One of the ways to improve the efficiency of the Stirling engine is to enhance the regenerator effectiveness.

The regenerator is one of the vital parts in a Stirling engine where it functions as a heat exchanger to maintain the temperature difference of the working fluid. The regenerator effectiveness directly influences the overall efficiency of the engine. There are 4 main methods to improve the regenerator effectiveness, which are to increase the surface contact area, reduction of flow frictional losses, different types of material selection for the regenerator and changing the geometrical configuration of the regenerator. This paper reviews the development of regenerator effectiveness enhancement from 2013 to 2015.

Keywords: Stirling engine, Regenerator, review, heat exchanger, renewable energy

1. Introduction

The Stirling engine is an external combustion engine and was invented by Robert Stirling in 1816. It can be powered by various types of fuel [1] such as solar thermal, fossil fuels, natural gas, biogas or even waste heat from wood pellets [2]. This has allowed the Stirling engine to generate energy from renewable energy such as solar energy as well as the co-generator in a power plant station to harvest the waste heat that is generated from the combustion chamber. On top of that, the Stirling engine has low noise, and with combustion process in the engine, it has low emissions [3] and is environmental friendly [4]. The Gamma type Stirling engine is considered the most efficient waste heat recovery device [5]. It has two cylinders which are separated by heat exchangers and it is mechanically simple where it only the pistons are needed to sealed[5]. The output power of the Stirling engine can be improved by:

1. Increasing the regenerator effectiveness
2. Increase the input power
3. Changing the configuration of the engine such as beta type, alpha type and gamma type
4. Improving the driving mechanism such as using the rhombic drive mechanism [1], yoke ross [6] and etc.
5. Minimize leakage of working fluid
6. Reduction of gap between piston and cylinder

2. Development of Stirling Engine for cogeneration plant

The three latest commercial Stirling engines are the 5kW A600-V3 Stirling engine by Frauscher Thermal Motors GmbH [7], 1kW WhisperGen Stirling engine by WhisperTech [8], [9] and 1kW Ecogen free piston Stirling engine by Baxi [10]. Stirling engines have also been used to harvest waste energy from the cogeneration plant for generation of electricity. The maximum achieved power output from the alternator powered by the Stirling engine is 1.5kW which translates into 30% saving in fuel consumption as suggested from the simulation with TRNSYS and GenOpt [11]. This cogeneration plant uses the Alpha type Stirling engine (PPS16-24MD) where Anton[11] suggested the output power of the Stirling engine can be improved by changing the heat exchanger arrangement. The modification of the arrangement of the exhaust heat exchanger has contributed to an achievement of 0.26 electric to thermal ratio (ETTR) as compared to 0.15 ETTR with the existing design. In Sweden, the Stirling engine is integrated with the wood pellet boilers to produce power and heat energy for residential applications i.e. the Stirling engine generates electricity from the excess energy generated from the residential burners for space and water heating purposes. With the integration of Stirling engine to the commercial boiler, the overall efficiency of the whole system has improved to 72% [12]. Micro-cogeneration Stirling engines are introduced for residential applications in Italy where their commercial Stirling units are able to achieve up to 8kW of hot water heat capacity and 1kW of electricity [13]. Meybodi et.al [14] claimed that the introduction of a Stirling engine in coal mine CHP system is able to help improve the economics as well as reducing the burden of the carbon tax scheme. Furthermore, the Stirling engine is suggested to be the prime movers for coal mine CHP systems which help to reduce the emission of methane which is a greenhouse gas.

Multi-objective Particle Swarm Optimization (PSO) algorithm was found able to provide 15% to 20% more accurate output power predictions of Stirling engine compared to

the traditional genetic algorithms [15]. Araoz [16] built a simulation model to estimate the output power of Stirling engine to predict the performance of the engine when integrated with other systems. The parameters included in the simulation model are the adiabatic working space, dead volume heat transfer in isothermal heat exchangers, mechanical losses such as friction, and imperfect regeneration and thermal losses.

In short, the output power range of commercial Stirling engine is between 1kW to 5kW. It is potentially to be used in power plant stations to enhance the efficiency of the power generation and help to solve the challenges of high energy demand due to the growth of population.

3.0 Stirling Cycle

The Stirling Cycle has 4 stages and involves two isothermal and two isobaric process, as shown in Figure 1 below:

State 1 to state 2 is an isothermal compression process where the compression piston move toward to the regenerator and the expansion piston remain in its position. State 2 to state 3 is an isobaric process where the both of the pistons move together. The compression piston will continue to move toward to regenerator whereas the expansion piston will move away from thee regenerator. State 3 to state 4 is an isothermal expansion process where the expansion piston continues to move away from the regenerator while the compression piston remains in the same position that holds the minimum volume of working fluid at this state. State 4 to state 1 is an isobaric process where the both pistons move together. The compression piston will move away from the regenerator whereas the expansion piston moves toward the regenerator.

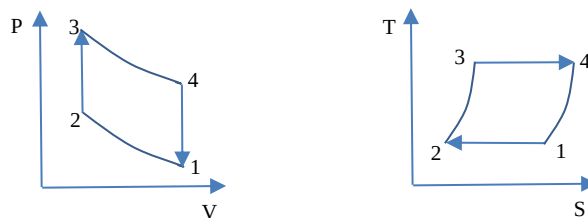


Figure 1. Diagram of pressure vs volume and temperature vs entropy

4.0 Regenerator for Stirling Engine

The regenerator is one of the main components which affects the output power of the Stirling engine. It couples the hot and cold pistons and at the same time maintain a temperature difference between the pistons[17]. The main function of the regenerator in the Stirling engine is to heat and to cool the working fluid when it passes through the flow channels at different stages. Higher temperature difference between the hot and cold regions increase the thermal efficiency and output power from the Stirling engine. Energy is harvested from the expansion and compression forces acting on the working fluid inside the Stirling engine. Without an effective regenerator in the Stirling engine[13-14], thermal equilibrium will occur which reduces the temperature difference and leads to poor efficiency and low power performance.

This work presented in this paper is the outcome of a review on 30 papers from which four methods have been recommended to improve the regenerator effectiveness. The four areas for improvement are:

- Surface contact area
- Flow frictional loss
- Material properties
- Orientation or position of regenerator

4.1 Increase of surface contact area

There are four main parameters, identified from the prior research work, which are of significance to increase the surface contact area between the working fluid and the regenerator, which are

- surface to volume ratio
- size of the regenerator
- porosity of the regenerator
- contact angle between the flow direction of the working fluid and mesh wires

The surface to volume ratio can be increased by introducing fins-like design in the regenerator as suggested by Opubo [20]. The challenge of having the fins-like structure in the regenerator is manufacturability. The fin-like structure in the regenerator leads to higher complexity of manufacturing. This has also implication to increase the dead volume for Stirling engine, which reduces the efficiency of the Stirling engine. Typical porosity of the regenerator is in the range from 75% to 90%. Carolina [23] has tested the effect of porosity in the range from 52% to 72%, where 72% porosity has the highest friction factor, C_f . Ramla Gheith [21] has tested in the porosity range from 75% to 95% and suggested to use 85% porosity stainless steel as the regenerator for maximizing Stirling engine efficiency. Also, the increase of porosity percentage leads to reduction of pressure drop and friction coefficient. The simplest and most popular method to implement this porosity is to insert wire mesh inside the regenerator[22]. Zhigang claimed that the wire mesh has large heat transfer surface area, low axial thermal conductance as well as high convective heat transfer coefficient due to the structure and the shape of the wire mesh[22]. The challenges of using the wire mesh are flow separation due to cross flow of the non-uniform porosity that leads to eddies in the flow, high flow friction and potential breakage of the fibers in the wire mesh after long term operation. Wire mesh regenerator is designed to be perpendicular to the working fluid flow direction. This leads to the working fluid flow having more resistance and creating undesired turbulence that causes friction inside the regenerator. The orientation of wire mesh or porous sheets influence the Stirling engine power output. Wen Lih [24] observed the output power of the Stirling engine performance is 2.3 to 2.5 times more when it is in perpendicular orientation as compared to the parallel orientation. However, for the porous sheets, it is suggested to design the sheets parallel to the flow of working fluid. Zhigang and Yoshihiko [22] suggested to use compact porous sheets that have multiple parallel flow channels which enable thermal efficiency up to 43.9% able to be achieved. This design has significantly reduced the flow friction losses as compared to the wire mesh design and it also fulfills the heat transfer characteristic as well as reducing the dead volume.

4.2 Reduction of flow frictional loss

The velocity of the working fluid flow affects the heat transfer performance of the regenerator[25]. The oscillating frequency and the pressure of the working fluid are related to the time-average heat transfer coefficient. Gang Xiao [26] suggested an empirical oscillating heat transfer correlation where the empirical formula is derived from the kinetic Reynolds number which is based on the oscillation amplitude, as shown in Eq. (1) below:

$$Nu = 0.0162Re_w^{0.40}A_0^{0.85} \quad (1)$$

The kinetic Reynolds number, Re_w , is in the range from 12 to 71, A_0 is the dimensionless fluid displacement.

Reduction of flow frictional loss is achieved by reducing the hydrodynamic entrance length and the time needed for fully developed reciprocating laminar flow. Laminar flow of working fluid in the micro-channel tubes minimizes the eddy current and hence the friction losses. However, increasing the surface contact area of the regenerator, increases the flow friction in the working fluid. For example, the wire mesh used for fabricating the regenerator has high heat transfer area to increase the heat transfer rate, but it will create high flow friction losses due to the larger physical surface contact area. The loss of energy in the wire mesh is caused by flow separation, turbulent eddies, stagnation zones and wakes [27]. Zhigang and Yoshihiko [22, 28] recommended the micro-channel type porous sheets are capable increasing the heat transfer rate, and at the same time reduces the flow frictional losses. Micro-channel porous sheets consists of large number of micro-channel tubes, which increases both the surface area and heat transfer between the regenerator and working fluid. Due to the low hydrodynamics entrance length of the hexagonal shape porous sheets, the time needed to develop the full reciprocating laminar flow is shorter, hence the flow frictional losses reduces. Figure 2 shows the porous sheets from of hundreds of hexagonal shape stainless steel micro-channels.

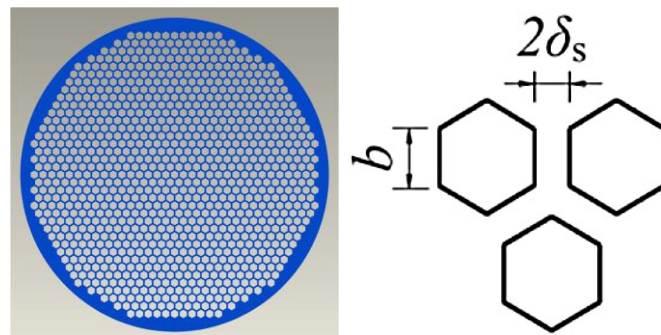


Figure 2. Micro channel porous sheet for Stirling engine regenerator.

4.3 Different type of material used for construction of regenerator

Several types of materials have been considered to be used as regenerator in order to improve the effectiveness of a Stirling engine. This includes wire mesh, plates, finned pipes, stacked screen and steel wool, woven wire [19–21], stainless steel mesh [17], etc. The material which has high thermal conductivity are favorable for construction of the regenerator to give high heat transfer with the working fluid. The available time for heat transfer is short in each cycle when the Stirling engine is working at high speeds. Hence a regenerator with

high heat capacity material may have inadequate performance at high engine speeds due to the low heat transfer rate. Wen-lih [24] has suggested high heat capacity materials with large heat transfer surface areas are favorable at low engine speeds whereas low pressure drops in the regenerator is critical at high engine speeds. A regenerator with high thermal conductivity has high heat transfer rates which assists in separating temperature difference between both components. It reduces thermal equilibrium between high temperature and low temperature working fluid inside the Stirling engine. The regenerator assists in reheating the working fluid when it flow from the low temperature to the high temperature.

Other material properties, such as melting point of the material, lifespan [9] and the cost of the material are taken into consideration when designing commercial Stirling engines. Copper metal is used to construct the regenerator for Stirling engines with high output power due to the high thermal conductivity[24] which gives higher heat transfer rates, but when the working fluid temperature reaches the melting point of the copper, it will cause the copper regenerator to deform and a replacement is required. Deformation of the copper mesh regenerator will cause changes to the optimum porosity and increases the resistance of air flow which lead to reduction in the effectiveness of the regeneration. Degradation of copper material with the present of oxygen in the working fluid also causes rapid oxidation and reduction in effectiveness after long hours of operation. Stainless steel has lower thermal conductivity as compared to copper, but it has high durability and resistance to heat.

Maintenance cost is another crucial criterion to consider for the operation of the Stirling engine. The replacement of the regenerator is highly challenging because it is inside the sealed engine. Ramla Gheith [21] suggested to use stainless steel over copper, Monel 400 and aluminum especially for construction of gamma type Stirling engine. Although copper has the highest thermal efficiency and output power, but due to limitation of the working temperature range and the degradation of material under the presence of oxygen, the author claimed that copper is not the best choice for day-to-day applications. Also aluminum has the same limitation of melting point as copper, although it does not degrade with oxygen in the working fluid.

4.4 Configuration of regenerator

There are three possible locations for the regenerator to be integrated into the Stirling engine, i.e. in between the expansion and compression parts of the Stirling engine[32], inside the displacer of the engine and outside the hot cylinder of the engine[28–30]. These are illustrated in Figure 3 below:

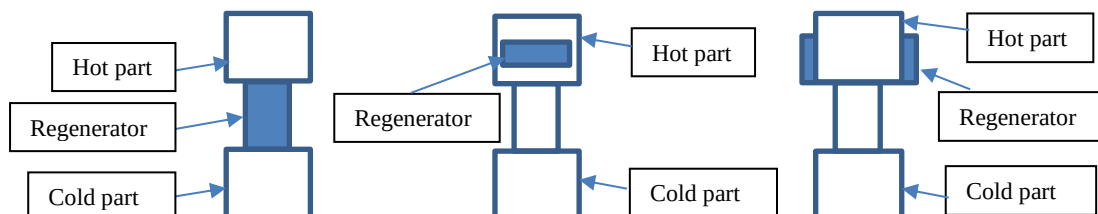


Figure 3. Three possible locations for regenerator

Of the three, the configuration of the regenerator in between the hot and cold parts of the engine seems to have higher potential to give higher effectiveness, but it requires more

space for the regenerator and more dead volume is introduced into the Stirling engine indirectly. Micro-channel porous tube is one of examples for such regenerators. The main challenges for this design are the potentially higher flow friction for the working fluid and difficulty for replacement if there is any defect or damage.

When the regenerator is designed inside of the displacer, it is called as a moving regenerator [24]. The main advantage with of this type of regenerator is the saving in space where it is inside the displacer. This design also has potential to have lower pressure drop but it needs to compromise with the effectiveness of the regeneration. This design utilizes the Stirling engine part to perform multiple functions and potentially has a more compact design for the Stirling engine. The challenge of this design is that the regenerator inside the displacer will increase the weight of the piston and more energy to push the displacer. This is done at the expense of the energy to rotate the flywheel. The displacer of the Stirling engine should be light weight to enhance the efficiency of the system.

The regenerator that is placed outside the displacer might not be as effective as the previous two designs, but this design allows researchers to easily test the effectiveness of different materials in the regenerator. This is because the material can be easily replaced as compared to the previous two designs. This type of regenerator design is usually cooled by water whereby the water is channeled to the outer cylinder wall in between the hot and cold parts of the engine to reduce the temperature of the working fluid from the hot part before entering the cold part of the Stirling engine.

Besides the water cooling method, fins structure are also introduced on to the regenerator for the Stirling engine. The fins increases the contact surface areas and improved the heat removal of the working fluid before entering the cold part of the engine. Hence it helps to maintain the temperature difference between the hot and cold pistons. The only drawback of the cooling water method and the finned-regenerator is the low effectiveness on reheating the working fluid when it flows from the hot part to the cold part of the due engine.

These two methods have positive impact on the Stirling engine to help maintain the temperature difference between both parts of the engine, even though there is some energy loss during the process.

5 Conclusions

In conclusion, the regenerator is a critical part to enhance the overall efficiency of Stirling engines. The research works concluded that the effectiveness of regenerator can be improved by:

- Increasing the heat transfer between the working fluid and regenerator,
- Reducing the flow frictional losses
- Selecting the optimum regenerator materials, and
- Increasing the temperature difference between the hot and cold pistons.

Large number of research works have focused on the design of micro channels in the regenerators. Several research shows that the stainless steel micro-channel porous tubes with the hexagonal flow channels has able to maintain high temperature difference between the hot and cold parts of the engine, while at the same time improving the heat transfer between

the regenerator and the working fluid in the engine. The flow friction in the stainless steel hexagonal flow channels has also been reduced.

The solar thermal stirling engines have been suffering from poor efficiency and low power output. One of the potential solution to improve the performance of solar thermal stirling engine is by integrating the new design micro channels in the stirling regenerator. The similar design can also be used in other applications like power generation, micro-CHP unit and etc.

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A Preliminary Assessment of Malaysian Wood as Potential Material for Future Soundboards of Classical Guitars

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Abstract

The trend in research on Classical guitars is to increase their sound level as the maximum volume is still considered soft. Research into the use of a variety of materials and different types of bracing patterns have not yet been successful in solving this problem. The tradition is to use spruce for the soundboard of Classical guitars as this is considered the best material. This choice is not surprising as spruce is the preferred choice of luthiers for good quality Classical guitars made in Europe. Since Malaysia has an abundance of tropical forest, it would be natural to tap into this resource to find better materials for future soundboards. The frequency range of investigation should not extend beyond 4 kHz as this is the maximum audible range of human hearing. Researchers have shown that the soundboard plays an increasingly important role as a radiating element of acoustic power at frequencies beyond 250 Hz of the sound spectrum as compared to the sound hole and the bridge. This paper focuses on the soundboard as the most important acoustic radiating element of the Classical guitar. CAD files of the soundboard are designed in CATIA and imported into ANSYS for analysis. Dimensions of the soundboard are those of the Torre model. Results of modal analysis up to frequencies of approximately 600 Hz are presented for European white spruce and Malaysian woods. These results are compared to published work on the correlation between plate frequencies and the physical and mechanical properties of other materials. Initial results show that the Malaysian woods are viable alternatives to European white spruce for future soundboards of Classical guitars. Malaysian woods investigated are podo-carpus, sempilor and damar-minyak (agatha-borneensis).

Keywords: Classical guitars, Materials, Frequencies, Audible range, Soundboards.

1 Introduction

Classical guitars are unique musical instruments as each piece of a particular model responds differently from another although they are all made by the same luthier. Characteristics of sounds sought after by musicians are tone, loudness, softness, coolness, warmth, brightness and mellowness. From the evolution of the Classical guitar since 1500 AD, it is a consensus among luthiers that the type of wood used and the design and arrangement of bracing on the soundboard and the reinforcement of the back plate also play important roles in the assembly of a good quality instrument. The most suitable woods for the soundboards are cedar for Flamenco guitars and spruce for Classical guitars.

The design of modern Classical guitars has traditionally followed that of the Spaniard, Antonio de Torres Jurado (1817-1892). It was his conviction that the soundboard plays the key role in good quality Classical guitars. Up to the present time, his arrangement of bracings of the soundboard is among the best as no other better designs have emerged. Design of bracings refers to the role of bracings in enhancing good vibrational and acoustical characteristics. However, even with this best design, the volume of sound projected from this instrument is considered insufficient. The focus of research in this paper is centered on the role of new designs of the soundboard of this instrument in providing greater volume using Malaysian wood as the country of Malaysia has an abundance of tropical wood. Success of this research will no doubt increase the commercial value of this commodity and provide better instruments to all musicians.

The frequency spectrum to be considered in investigating frequency response of Classical guitars should not exceed 4 kHz as this is approximately the frequency at a minimum audible loudness of 10 phons corresponding to a minimum sound pressure level of approximately 3 decibels. This is the recommendation of ISO 226:1987 [1].

Bader [2] has shown that from 300 Hz to around 5 kHz, the surface of the soundboard is the most important frequency dependent radiation area of the Classical guitar whereas from around 70 Hz to 300 Hz the sound hole is the most important radiation area. This is illustrated graphically in Fig.1. In the investigations of Hill *et al.* [3], there is a lack of data on radiation beyond 500 Hz.

The soundboard of the Classical guitar can be considered as a thin plate as the ratio of its thickness (varying from approximately 2 mm at the sound hole to approximately 1 mm at its outermost contour) to the width of the upper bout (approximately 2667 mm) is less than 0.05. This satisfies the criterion of thin plates according to Rao [4]. The theory for thin plates can be applied to the shape of the soundboard. One such application is as detailed in Chaigne [5]. An appropriate numerical method of analyzing thin plates is the finite element method.

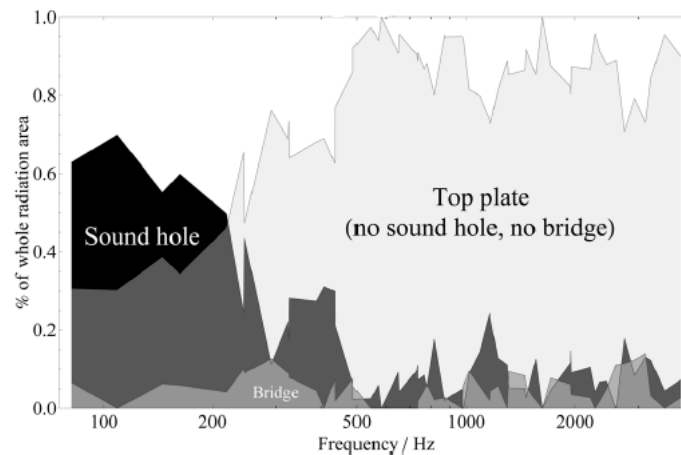


Figure 1. Frequency dependent areas (normalized absolute radiation amplitudes) for an LK model Classical guitar. The graph shows the radiation areas of the sound hole, the bridge and the top plate (soundboard) [2]

2 Methodology

The potential of Malaysian wood as future material for soundboards of Classical guitars can be evaluated either by using discrete models made up of mass, spring and dampers or by considering the soundboard alone as a continuous thin plate in flexure.

Mass-spring-damper models of Classical guitars are the 2-, 3-, and 4-degrees of freedom models by Christensen and Vistisen [6], Christensen [7] and Popp [8] respectively. The range of frequencies investigated with these models is from 80 Hz to 250 Hz. The 2- and 3-degrees of freedom models correctly predicted two and three eigenvalues respectively in this frequency range. A more realistic model consisting of 4-degrees of freedom was proposed by Popp [8]. In his investigation, only three eigenvalues were obtained and the fourth eigenvalue was missing. The possible reasons for this anomaly are explained in Section 2.1. This model is therefore inadequate for further investigation into modal analysis of the guitar. Moreover, inclusion of more degrees of freedom would make this approach cumbersome.

An alternative approach in this paper is to consider finite element modeling. Instead of analyzing the complete guitar over a wide range of frequencies it is sufficient to analyze the soundboard alone as this is the most important component of the guitar compared to the sound hole, back-plate and the bridge in terms of sound radiation at frequencies extending beyond 250 Hz as explained in Section 1.0. ANSYS is used to obtain results of modal analysis of soundboards. The results of the first 6 modes for soundboards of white spruce are compared with three Malaysian woods, podo-carpus, sempilor and damar-minyak. The soundboards are designed using CATIA and imported into ANSYS for modal analysis. The shape and dimensions of the soundboards are based on that of the Torre model.

The objective of this paper is to provide a preliminary assessment of Malaysian woods as alternative materials to spruce for future soundboards of Classical guitars.

2.0 Anomalies of 4-degrees of freedom model

To gauge the relative importance of low-order modes in relation to mid-frequency response, Popp [8] added a fourth oscillator represented by the “ribs. This model is shown in Fig. 2 where x_a , x_t , x_b and x_r are the displacements of the air-piston, top plate, back plate and ribs respectively.

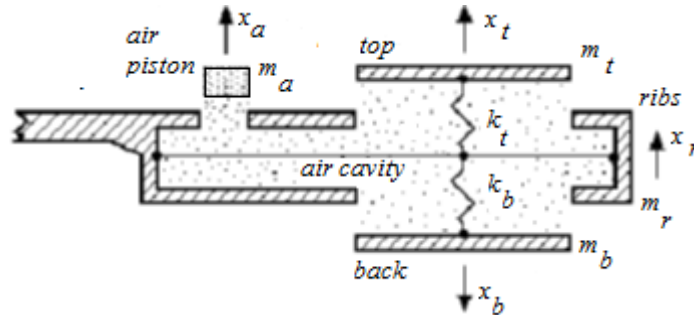


Figure 2. 4-degrees of freedom model [8]

Stiffnesses k_t and k_b of the top and back plates respectively were measured directly and their effective areas and equivalent masses m_a , m_t , m_b and m_r of the air-piston, top plate, back plate and ribs respectively were used to calculate the frequency response, and resonances. The calculated and measured resonances agree reasonably well as shown in Fig. 3 where the frequency response is represented by velocity per unit force.

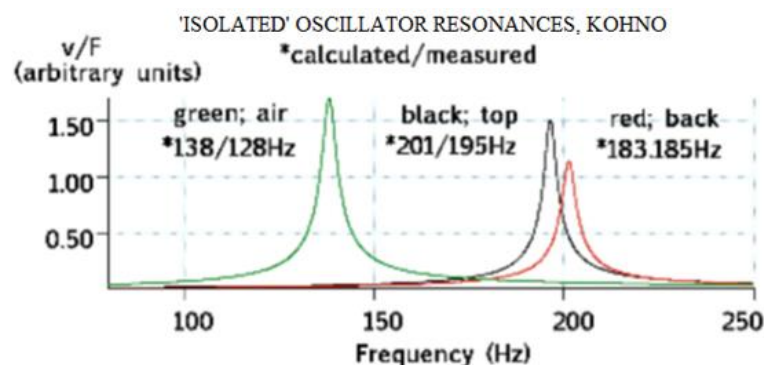


Figure 3. Input admittance for individual oscillators of 4-degree of freedom model of a Kohno Classical guitar [8].

The 4-degrees of freedom model also predicted three eigenvalues in the frequency range of 80 to 250 Hz but a fourth eigenvalue was missing. Popp [8] reasoned that assigning a fourth-degree-of-freedom in the form of a finite mass to the ribs only changes the boundary conditions and does not introduce a new elastic restoring force and hence there is no fourth eigenvalue.

However, it must be stated here that for the Kohno Classical guitar and the stiffness introduced between top plate and the ribs ($k_t = 4.08\text{E}+04$ N/m) and between the back plate and the ribs ($k_b = 5.30\text{E}+04$ N/m) by Popp [8], a simple calculation for springs in series show that the stiffness between the top plate and the back plate to be $2.31\text{E}+04$ N/m

A similar deduction for the D28 folk guitar for $k_t = 1.39\text{E}+05$ N/m and $k_b = 0.59\text{E}+05$ N/m, shows that the stiffness between the top plate and the back plate to be $0.414\text{E}+05$ N/m. Thus the ribs are relatively stiff in comparison with the stiffness between the top plate and the back plate.

The fourth degree of freedom was simulated by suspending the guitars on rubber bands. As no information was provided on the stiffness of the rubber bands, it is reasonable to conclude that this arrangement could make the ribs even stiffer than if the instrument was placed on the player's laps. The addition of a fourth-degree-of-freedom therefore does not introduce any additional frequency in this model.

Moreover, in two (D28 and Penade models) of the six (D28, Kohno, Krempel, Framus, Kingston and Penade models) guitars tested, three resonances of the three-degree-of-freedom model were reduced to two. That is, one resonance frequency was missing from each of the two guitars in this 4-degree-of-freedom model. This model has introduced anomalies that need further investigation.

3 Results/Discussion

ANSYS was used to obtain results of modal analysis of soundboards of constant thickness of 1 mm but without bracings. Six resonance modes were considered for each type of soft wood. The six modes for each type of wood are as shown in Appendix A. Modes are described using the convention suggested by Wright [9]. Thus in mode T(1,2), for example, the letter T indicates top plate (soundboard). The two numbers in parenthesis indicate the number of anti-nodal regions horizontally (in line with the bridge) and vertically (in line with the strings) respectively. When similar patterns are encountered, subscripts are used to indicate phase relationships. For example: T(1,2)₁ and T(1,2)₂ would indicate two similar modes with opposite phases.

Resonant frequencies of soundboards from Malaysian woods “agathis borneensis” also known as “damar minyak”, “sempilor” and “podo carpus” were compared to those from “white spruce.” Computed results are shown in Table 1.

Table 1: Comparison of resonant frequencies between “white spruce”, “sempilor”, “damar minyak” and “podo carpus”

Mode	White Spruce $\rho = 430 \text{ kgm}^{-3}$ $E = 7.0 \text{ E}+09$ Pa $\nu = 0.42$	Sempilor $\rho = 445 \text{ kgm}^{-3}$ $E = 11.6 \text{ E}+09$ Pa $\nu = 0.42$	Damar Minyak $\rho = 580 \text{ kgm}^{-3}$ $E = 12.0 \text{ E}+09$ Pa $\nu = 0.42$	Podo Carpus $\rho = 735 \text{ kgm}^{-3}$ $E = 10.5 \text{ E}+09$ Pa $\nu = 0.42$
	Frequency (Hz)			
1 T(1,1)	179.60	190.68	172.12	140.70
2 T(1,2)	265.56	279.90	254.50	208.03
3 T(1,3)	355.08	375.55	340.28	278.16
4 T(2,1)	379.93	405.97	364.09	297.62
5 T(2,2)	542.73	571.27	520.12	425.16
6 T(1,4)	575.07	606.93	551.11	450.49

Results from Table 1 show that two Malaysian woods “damar minyak” and “podo carpus” yielded lower resonant frequencies than “white spruce” but this was not the case with “sempilor” which showed an increase in resonant frequencies. Among the Malaysian woods, resonant frequencies from “podo carpus” were lower than those from “damar minyak” although the former had a higher density but a lower Young’s modulus than the latter. The trend in this finding concurs with that obtained by Stanciu *et al.* [10] that wooden materials with higher density have lower natural frequencies.

The difference in the modal frequencies between the findings in this paper and that of Stanciu *et al.* [10] is due to the difference in thickness of the soundboard and the presence of bracings in the latter case. The absence of bracings and the thinner soundboard of this investigation results in a more flexible plate in flexure compared to that used in [10] thus resulting the lower modal frequencies obtained.

Fig. 4 shows the variation of frequencies with mode numbers. An example of similar investigation on the correlation between plate frequencies and the physical property (thickness) and mechanical properties of wooden materials by I. Curtu *et al.* [11] is as shown in Fig. 5. The trend at the lower end of the frequency spectrum shown in Fig. 4 indicates that damar minyak and podo carpus have lower first mode frequencies compared to white spruce. Even in the case of sempilor, the first mode frequency approaches that of white spruce. Thus, lower frequencies of the first mode for damar minyak and podo carpus and the convergence of the first mode of sempilor towards that of white spruce indicate that these woods are excellent candidates for future soundboards of Classical guitars.

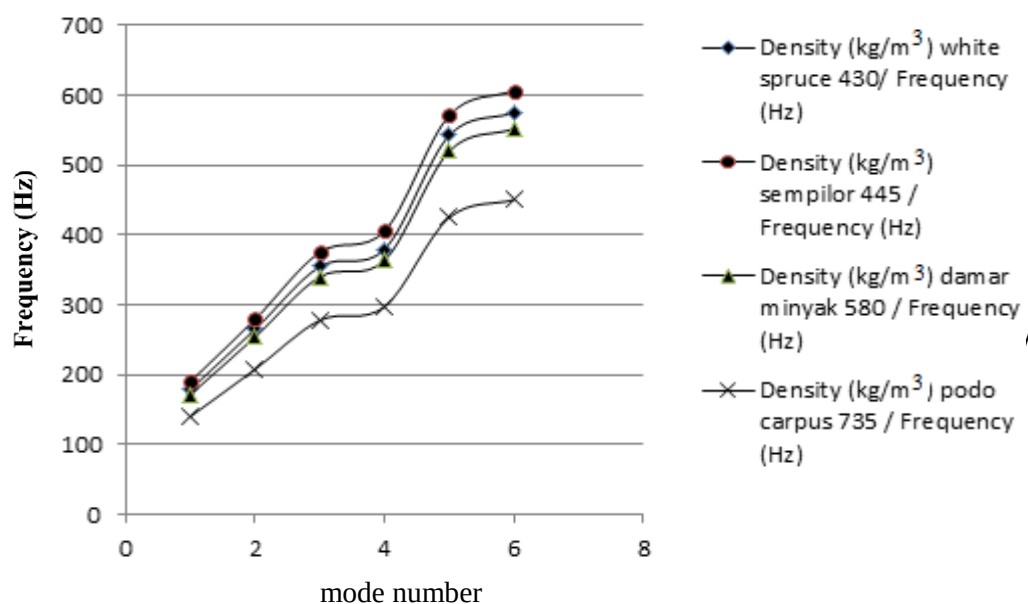


Figure 4. Relationship between frequency and mode number of four soundboards without bracing and with constant thickness of 1 mm.

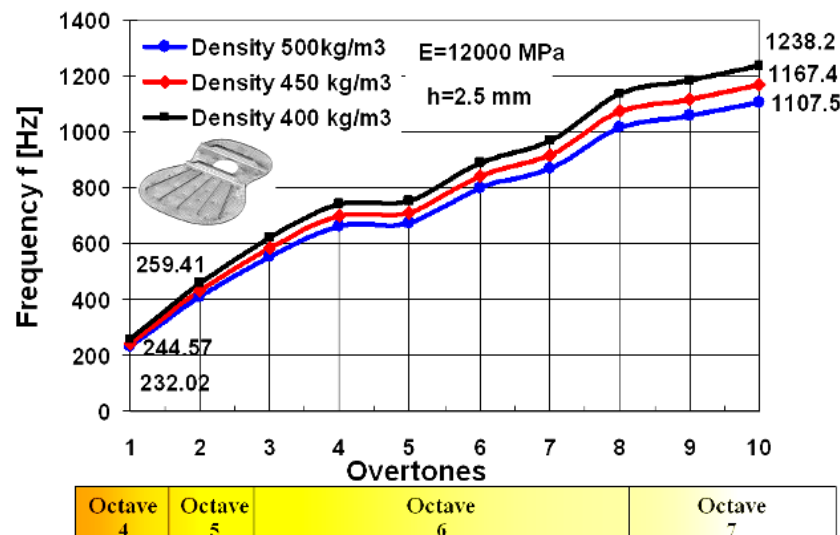


Figure 5. Variation of the fundamental frequency with the harmonics for a plate with 5 top braces [11].

The characteristic of lower resonant frequencies is important as monopole radiation dominates dipole radiation at the lower frequency spectrum from 220 Hz to 500 Hz. This is a desirable feature for soundboards from results of investigation on three different quality Classical guitars by Perry and Richardson [12]. Dipole radiation tends to reduce the radiation efficiency due to the dipoles working in opposition to each other. This conclusion was based on radiation efficiency studies where radiation efficiency was defined as the ratio of acoustical power output to mechanical power input [12]. More detailed study included frequency response analysis where mobility is plotted against frequency. This parameter is a measure of how a stringed instrument reacts to an excitation force and could be used in comparison with studies in radiation efficiency [12]. It was also noted that radiation efficiency could be an indicator of good quality soundboards as it differentiated good quality guitars from inferior ones as results from 200 Hz to 500 Hz seemed to indicate [12].

4 Conclusion

As stated in Section 3.0, monopole radiation dominates dipole radiation in the frequency range from 220 Hz to 500 Hz. This is important as monopole radiation reinforces acoustic radiation and enhances acoustic power while dipole radiation tends to reduce acoustic power due to dipoles working in opposition to each other. Lower resonant frequencies of Malaysian woods “damar minyak” and “podo carpus” compared to those of “white spruce” suggest that these materials could be suitable substitutes for “white spruce” for future soundboards of Classical guitars. At the lower end of the frequency spectrum, results for “sempilor” tend towards those of “white spruce” thus indicating that “sempilor” is also a good potential material for future soundboards of Classical guitars.

At frequencies from around 70 Hz to 300 Hz the sound hole is the most important radiation area of sound compared to the soundboard. Thus there should be negligible difference between the choice of “white spruce”, “damar minyak”,

“sempilor” or “podo-carpus”. The preliminary assessments of Malaysian woods seem to confirm this fact.

5 Recommendation

The above are results of preliminary assessments of the possibility of replacing spruce with Malaysian soft wood for future soundboards of Classical guitars. Further results using various bracing patterns, different thickness and increasing the frequency bandwidth will be carried out to determine conclusively the viability of using Malaysian wood for future soundboards of Classical guitars.

Appendix A

(a) No bracing/constant thickness: 1mm

Material: White Spruce.

According to Oliver [13], the density and Young's modulus are:

Density = 430 kg/m^3 and Young's modulus = $1.0 \text{ E}+10 \text{ Nm}^{-2}$

Poisson ratio = 0.42 (typical value)

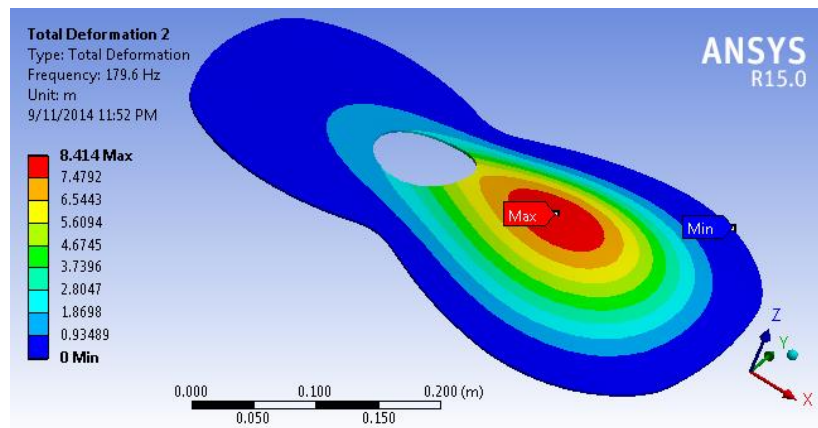


Figure A1 - 1st resonance T(1,1)

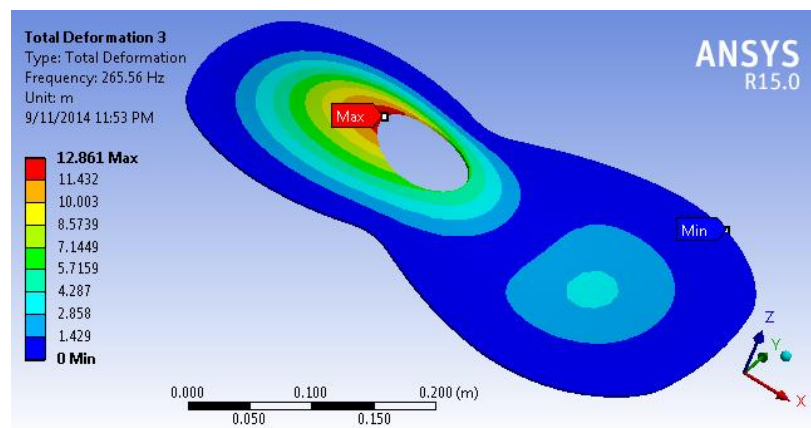


Figure A2 – 2nd resonance T(1,2)

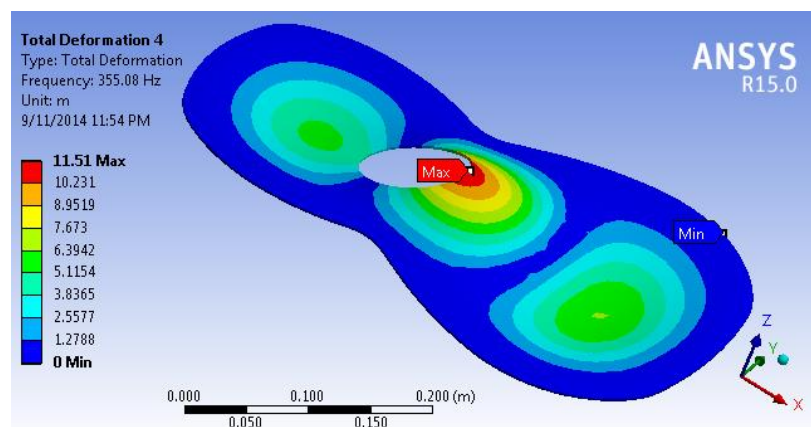


Figure A3 – 3rd resonance T(1,3)

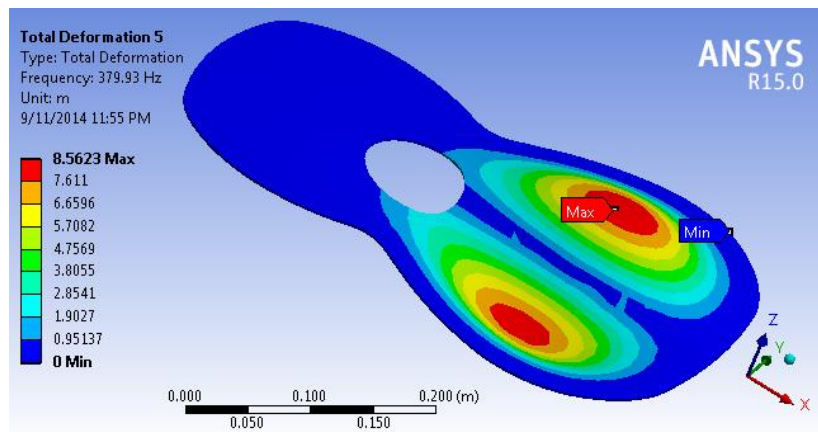


Figure A4 – 4th resonance T(2,1)

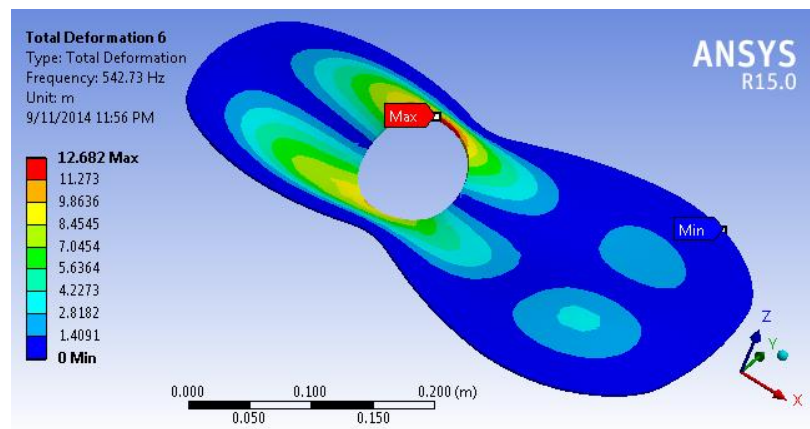


Figure A5 – 5th resonance T(2,2)

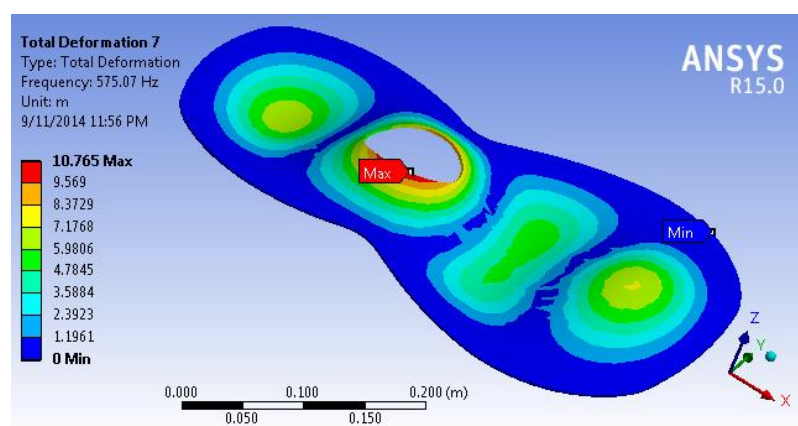


Figure A6 – 6th resonance T(1,4)

(b) No bracing/constant thickness: 1mm

Material: Damar Minyak – Malaysian wood.

According to Mohammad [14], density = 580 kg/m^3 and according to Yeangdonal [15], Young's modulus = $1.20 \text{ E}+10 \text{ Nm}^{-2}$
Poisson ratio = 0.42 (typical)

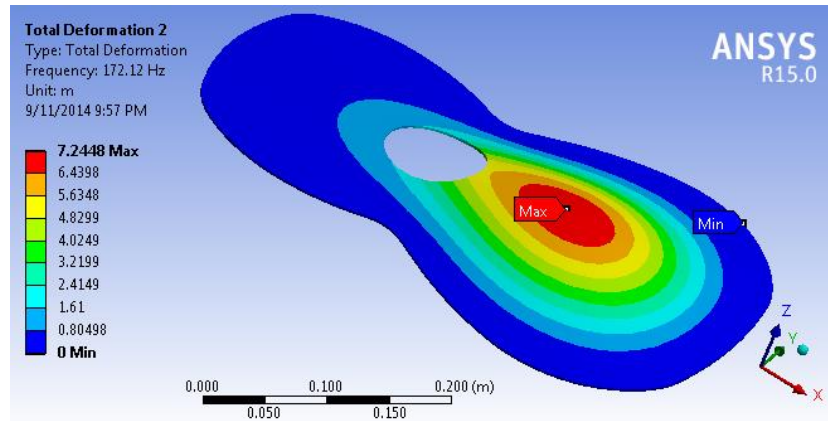


Figure A7 – 1st resonance T(1,1)

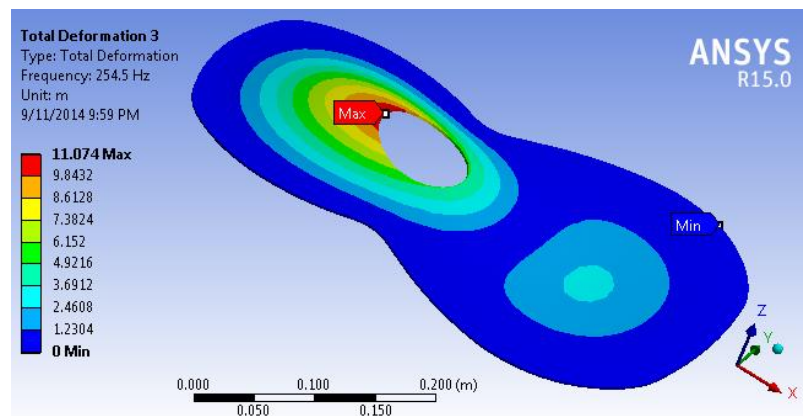


Figure A8 – 2nd resonance T(1,2)

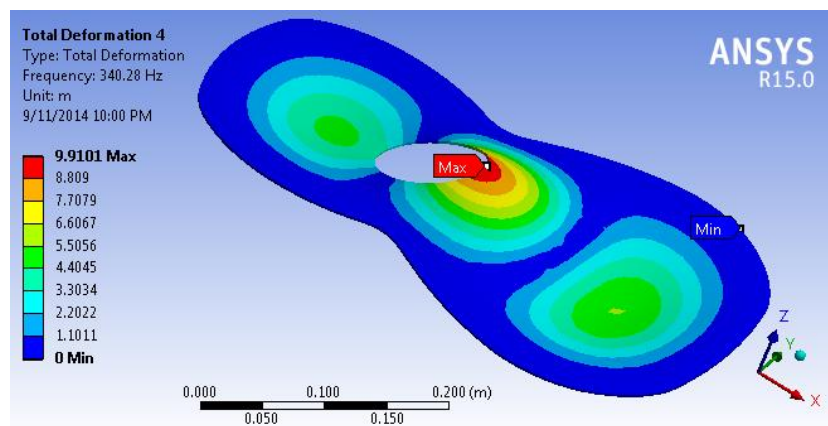


Figure A9 – 3rd resonance T(1,3)

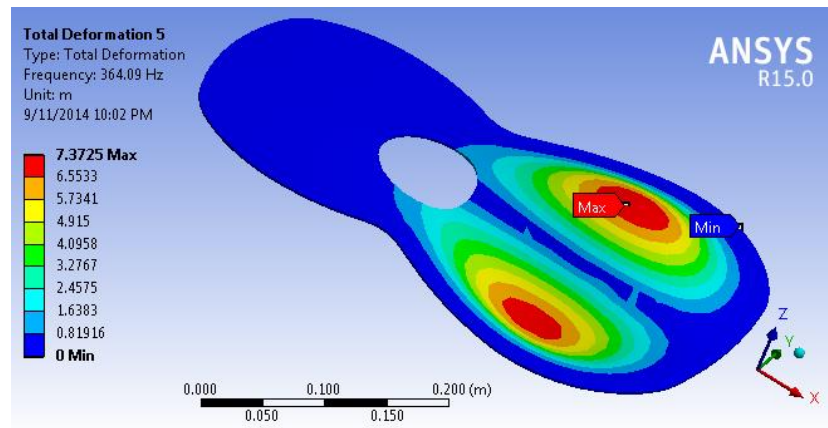


Figure A10 – 4th resonance T(2,1)

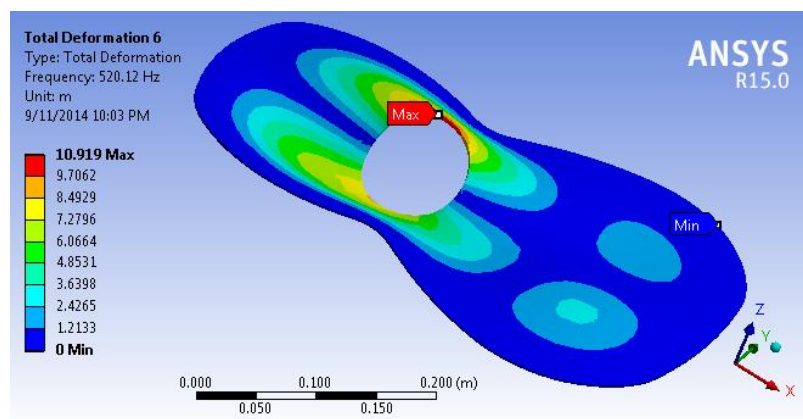


Figure A11 – 5th resonance T(2,2)

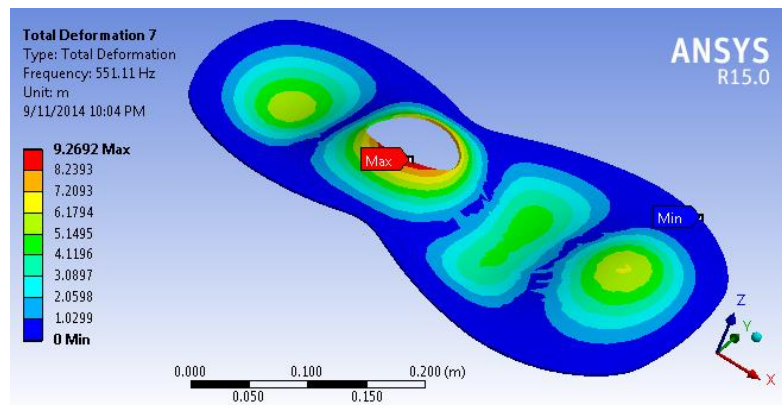


Figure A12 – 6th resonance T(1,4)

- (c) **No bracing/constant thickness: 1mm**
Material: Podo – Malaysian wood

According to Mohammad [14], density = 580 kg/m^3 and according to Yeangdonal [15], Young's modulus = $1.20 \text{ E}+10 \text{ Nm}^{-2}$
Poisson ratio = 0.42 (typical)

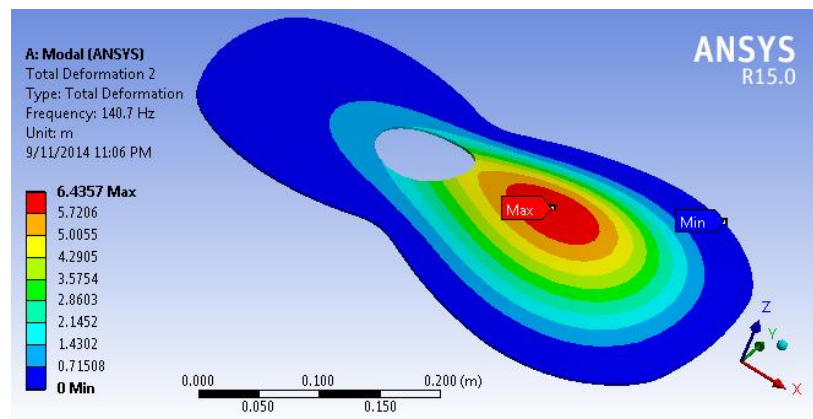


Figure A13 – 1st resonance T(1,1)

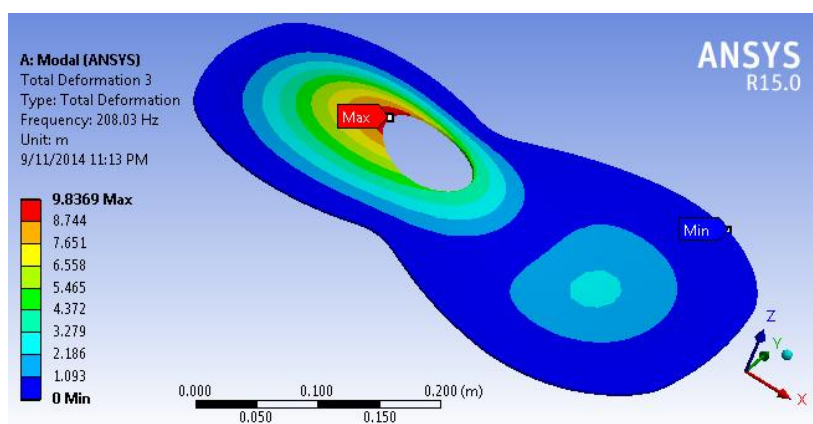


Figure A14 – 2nd resonance T(1,2)

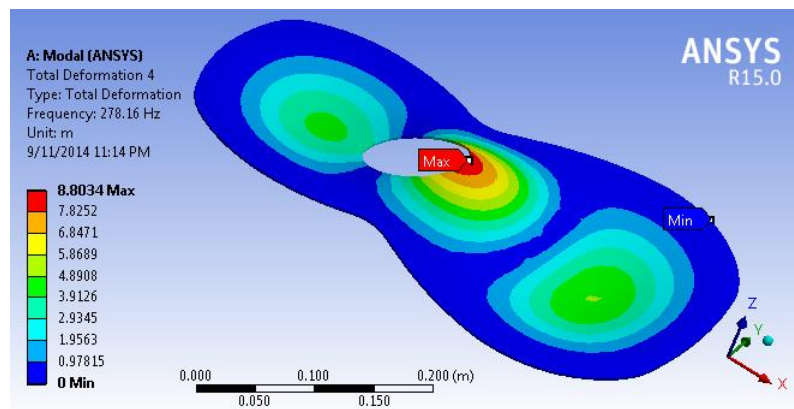


Figure A15 – 3rd resonance T(1,3)

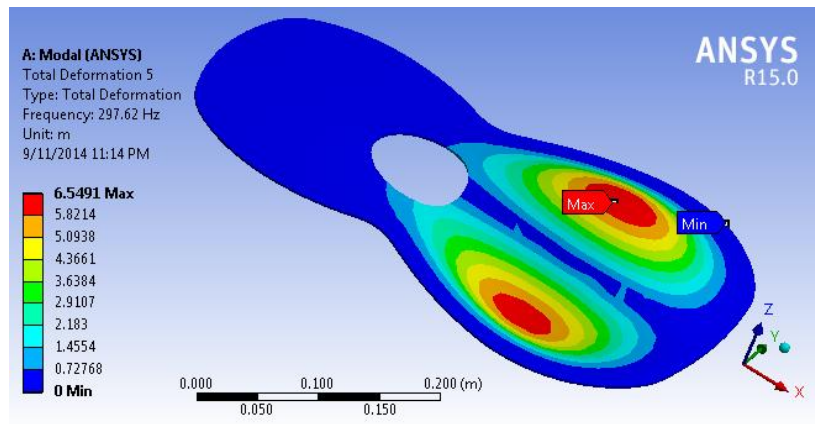


Figure A16 – 4th resonance T(2,1)

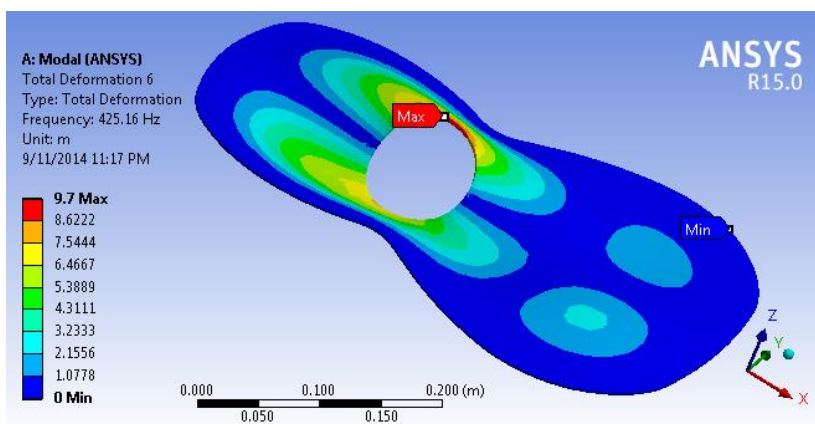


Figure A17 – 5th resonance T(2,2)

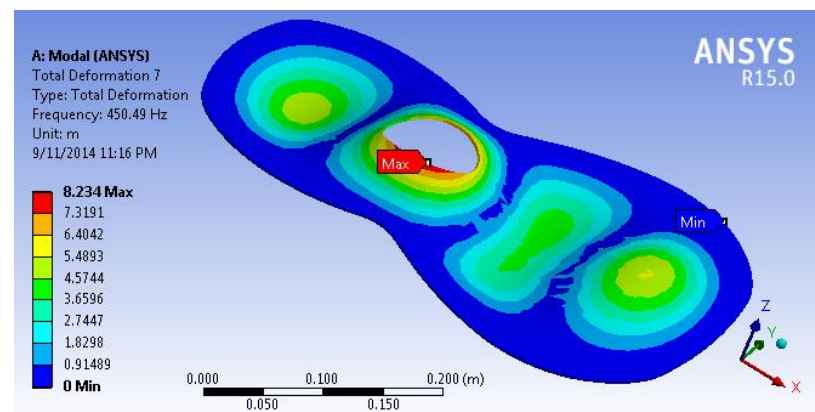


Figure A18 – 6th resonance T(1,4)

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Pretreatment of Rice Husk for Application as a Fuel Source in Direct Carbon Fuel

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Abstract

Direct Carbon Fuel Cells (DCFC) is well known for its efficiency and environmental friendly power source compared to traditional method of burning coal. It has twice the efficiency of the traditional method (>70%) and it does not produce as much CO₂ as to burning coal. Biochar are used as fuel in DCFC and they are made from natural waste. Rice husk was brought in to attention because it can be easily obtain in Malaysia. To increase the value of rice husk biochar, pretreatment using the chemical treatment and heat treatment was analyse to determine the optimum condition. Rice husk biomass will be treated with 0.1 mol, 0.5 mol and 1.0 mol of KOH at 12 hours and 24 hours respectively before heading for pyrolysis. The pretreated rice husk was carbonised at 650°C in a tube furnace with nitrogen flow of 10 l/min for two hour. The samples were tested for char yield, moisture content and ash content. Moisture content and ash content was carried out using the standard ASTM E 190-87 and ASTM E 897-88 methods. From the char yield analysis, mass reduced was due to the removal of volatile content during carbonisation and 1.0mol of potassium hydroxide has the lowest char yield at 33% while the highest is only at 38% for 0.1mol. The moisture content was increasing due to the ability of moisture vaporising when duration and concentration increases. However the ash content result was poor, ash content increased when concentration of the pretreatment increase. The chemical treatment is used to remove the impurities especially silica to prevent formation of SiO₂ which is not desired in a DCFC. Furthermore the amount of pores increases on the surface so do the size of pore. On the other hand, heat treatment will increases carbon form as temperature increase. The longer carbon chain will increase the capability of biochar to react when used in DCFC.

Keywords: Rice Husk, Biochar, Pretreatment, DCFC

1. INTRODUCTION

Direct Carbon Fuel Cell (DCFC) have been the interest of worldwide and it could be the key to a better renewable source [1]. It has a theoretical efficiency close to 100%, which is the best among other types of fuel cell. DCFC undergoes electrochemical reaction and it can be converted to electricity. This fuel cell is environmental friendly and safe to use because solid carbon were used as fuel and produce CO_2 which has high purity and reduce the cost of separating the output gas. Many work has been done to improve the performance of the DCFC, which include using different type of anode to enhance electrochemical performance of DCFC [2], choosing the best fuel used in DCFC, pre-treatments on biomass [3] and finding different types of carbon source. For example, Yu et al. have tried using corncobs as carbon fuel to improve the performance of DCFC [4] Besides that Choi et al. used wood char to power the DCFC system [5], [6]. Li et al also did research on the carbon black fuel which has added metal elements on catalytic gasification process [7]. Furthermore, Kulkarni et al. compared the electrochemical performance of DCFC with titanate anodes [2]. However, as for now there are not much research on the best pre-treatment and its optimum temperature for best yield on RH biochar.

To have a good DCFC performance it requires high surface area and porosity characteristics in a biochar to allow oxygen to be adsorbed and react on the surface of the biochar. The porosity of the biochar can be increased through chemical pretreatment and allow more reaction between carbon and oxygen to occur [8]. The crystalline structure of the biochar is closely related to the porosity of the biochar, disorganised structure will allow more oxygen to enter and react. A high amount of carbon content is required in a biochar as high carbon content will enable more reaction to occur when used as fuel in DCFC. The working principle of a DCFC is the biochar will be oxidised by oxygen and form carbon dioxide. It will generate electricity as the ions move. The reactions can be seen on the equation below.

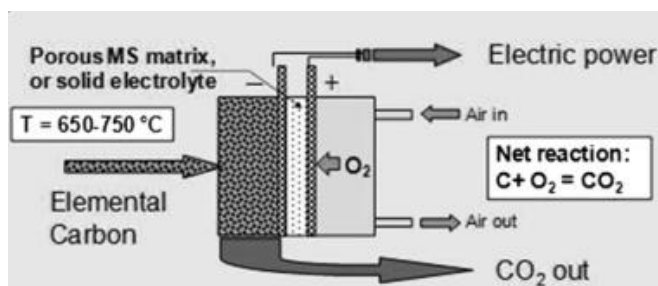


Figure 1. Schematic Diagram of DCFC



Other than the porosity and the carbon yield of the biochar, the physical structure of the carbon in the biochar is one of the factors that affect the performance of DCFC [9]. Table 1 shows the power density and voltage density yield when different types of carbon fuel used in DCFC. The performance of the DCFC is getting higher when the biochar has less graphitized carbon and higher edges of biochar which can causes good electrochemical reaction because more disorder carbon atom in the biochar [10]. Smaller size biochar will produce higher power density than larger size in a same fuel capacity of DCFC because more surface area available for contact [11]. The rate of diffusion of oxygen will be intensified provided the biochar is occupied with high carbon content [12]. However if it is too small oxygen will not able diffuse through the pores [11]. Nevertheless, the presence of smaller particle size of activated carbon possessed the drawback of refraining the uniform diffusion process of oxygen through the structure and thus affects the performance of the fuel cell [11]. Based on research done by Wang et.al. Alkaline is more suitable for pretreatment of biomass used as fuel for DCFC compared to acid. Biochar treated with alkaline produce higher power density than those treated by acid solution. Alkaline solution increase the surface area of when there is formation of H^+ . However it is the opposite for acid pretreatment, it will reduce the pore surface of the biochar hence lower power density [13]

Rice husk has high percentage of lignin which is an advantage over other biomasses [14]. Cellulose, hemicellulose and lignin are commonly found in most plant biomass. Lignin will decompose and convert in to biochar under pyrolysis and hemicellulose and cellulose will turn in to volatile components [15]. However it contains impurities such as silica and has to be removed through chemical treatment in order to obtain high purity of carbon content [16]. Rice husk has

The experiment involves two different types of pre-treatment on RH, chemical treatment or heat treatment. Potassium hydroxide (KOH) is chosen to use under alkaline treatment. From these pre-treatment on RH, effectiveness of these pre-treatment method are based on the crystalline structure form, carbon contents and impurities in the RH because these properties will affect their adsorption ability. Sustainability of the chemical use for pre-treatment is also important due to the cost of treatment. The chemical should be effective yet cheap and environmental

friendly. After pre-treatment, the RH will be burn at different temperatures to investigate the optimum temperature to produces the highest amount carbon content of biochar.

However, there is a research gap as there are no comparisons with RH which is pretreated with different concentrations of chemical and the duration of the chemical pretreatment process. Hence the objective of this study is to produce a biochar that has the best adsorption properties. By doing so, the research focuses on two objectives in order to achieve the desired outcome.

- I. To determine the optimum parameters for alkaline pretreatment of rice husk.
- II. To investigate the optimum residence time yielding the best quality and quantity of biochar from rice husk.

2. METHODOLOGY

2.1 Sample Preparation

There is an abundance of paddy fields in Malaysia. The rice husk will be chosen locally and serves as the main experimental subject. The raw material (RH) obtained from Sekinchan is rinsed with distilled water to remove dirt and other adhering materials on the surface of the husk [63]. This is an important step as the pretreatment would be ineffective if impurities are present on the surface of the rice husk. Subsequently, the RH is dried at 105°C for 24 hours to remove the moisture content which was given by ASTM D2867-09 standard [71]. The dried sample is then grinded using an equipment names. The size of rice husk milled was sieved to range 2mm to 500 µm using sieving Machine (RX-812-1, W.S Tyler USA) [72].

2.2 Chemical Treatment

The dried rice husks are placed into six conical flasks, each containing 20 g of rice husk. Then, the flasks would be filled with different concentrations of KOH, ranging from 0.1mol to 0.5mol and 1.0mol at room temperature for 12hours and 24 hours on an orbital shaker to ensure even and proper mixing. The selected range was discussed in section 2.3.2. 0.561g of KOH pellet (R&M Chemical, Evergreen Engineering & Resources) was dissolved in 100ml of distilled water to form 0.1mol of solution and different mass of KOH pellet was diluted with distilled water to obtain 0.5mol and 1.0mol. After the reaction took place, the samples were washed with distilled water

until pH reaches 7 with pH meter (pH211-M446321, Taylor's University) to remove the potassium silicates formed as seen in equation 6. During this treatment, impurities would be removed while micropores and mesopores will be formed through the generation of H_2 in that reaction. The main reason for doing so is to increase the yield of biochar as lower temperatures would be required to remove impurities such as silica and prevent biochar burn off. Potassium hydroxide was selected as the chemical for alkaline treatment on the rice husk due to its renewability and economical sustainability.

2.3 Heat Treatment

Before being thermally treated, the samples were dried again at 105 °C for 24 hours [64]. Horizontal split tube furnace (Carbolite, UK) was utilised to carry out the pyrolysis at 650°C with 10°C/min heating rate for 1 hour residence as discussed on section 2.3.3 for the production of the rice husk biochar. Nitrogen gas was also purged into the furnace at a rate of 1 l/min to eliminate oxygen from the furnace while pyrolysis was ongoing.

Table 1. Experimental Table

Concentration of KOH (M)	Duration (hr)	
	12	24
0.1	A1	B1
0.5	A2	B2
1.0	A3	B3

2.4 Physicochemical Characterisation of Biochars

Through pyrolysis the carbon yield can be obtain by measuring the weight differences of dried samples before and after carbonisation. To extend the analysis further, proximate analysis for moisture content and ash content of the biochar was carried out under the following standard ASTM E 190-87 and ASTM E 897-88. Biochar with the lowest amount of ash was selected for ultimate using Vario MACRO Cube CHNS, Germany. The rice husk biochar sample with the highest carbon content with its deciding factor based on previous analysis was test for the following analysis. Specific surface area and the porosity was measured using Brunauer–Emmett–Teller (BET) analysis (Quantachrome Autosorb 1C). Thermal gravimetric analysis (TGA) was performed to analyse the thermal stability under instrument Seiko Exstar 6300. Crystalline structure of the biochar was one of the factor affecting performance of DCFC therefore it is

nessary to perform X-ray diffraction analysis (XRD) using Bruker Advanced D8. A set of analysis was done for non-chemical treated rice huck biochar as well for comparison.

Table 2. Type of Analysis Performed and Purposes

Analysis	Results
Proximate analysis	Moisture content Ash content
Ultimate analysis	CHNS
Brunauer–Emmett–Teller	Surface area Mesopore size
Thermal gravimetric analysis	Thermal stability

3. RESULT AND DISCUSSION

3.1 Visual Result

The colour of the sample changes when different concentration of KOH and duration of pretreatment is tested on the rice husk. The darkest sample would be B3 which is 1.0mol of KOH at 24 hours. Rice husk sample show an increase of darkness as concentration increase form 0.1mol to 1.0mol. Furthermore the colour becomes darker as the duration of impregnation increases from 12 hours to 24 hours. Due to the decomposition of hemicellulose and partial decomposition of cellulose cause by the alkaline treatment, fractions of carbon had develop and hence rice husk sample appearance has become darker [21].

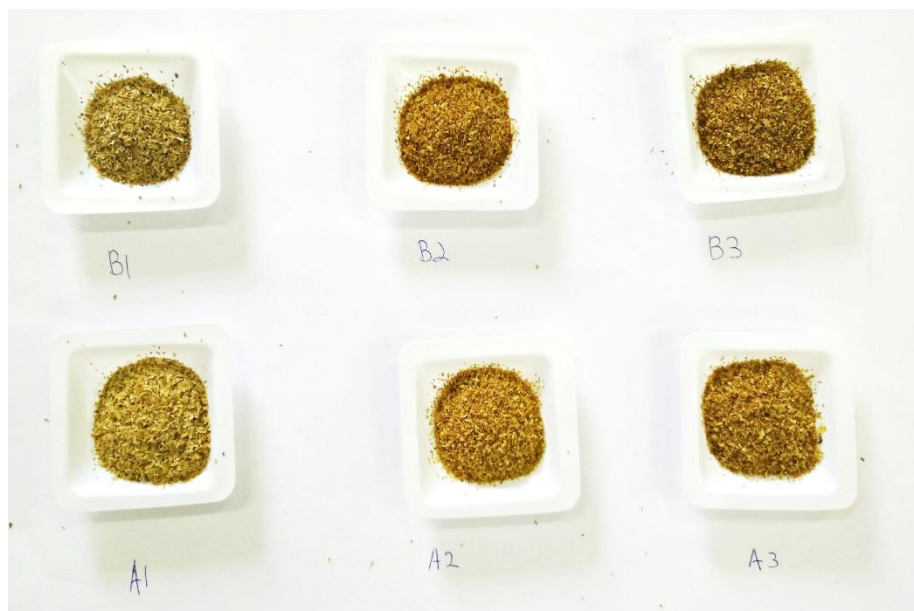


Figure 2. Visual of the rice husk sample after impregnated with KOH

3.2 Biochar Yield

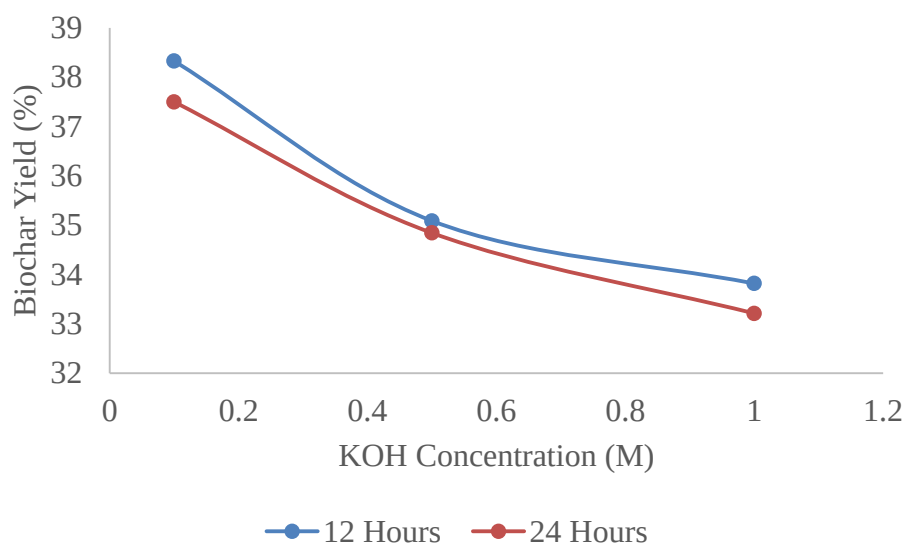


Figure 3. Biochar Yield of Biochar at Different KOH Concentration and Pretreatment Duration

Based on Figure 2, there is a decreasing trend of carbon yield as the concentration of potassium hydroxide used increases. Biochar with the concentration of 1mol possess the lowest char yield at (33%) The duration of the pretreatment also affects the carbon yield of the biochar. Rice husk

which went through a longer period of pretreatment with KOH has lower char yield. Longer duration means more reaction happening between the rice husks. There was a study done by Taha et al. (2012) that the cause of the mass reduced was due to the decomposition of hemicellulose and later on partial decomposition of cellulose followed by lignin [17]. According to Chen et al. (2014) and Phuong et al. (2010) hemicellulose has ability to absorb moisture and it is soluble in an alkaline solution hence volatile vaporised as byproduct as it undergoes pyrolysis [21, 22]. The carbonisation process will remove the volatile content leaving the remain which are the non-volatile component in the rice husk biochar [24]. While higher KOH concentration will decrease its required thermal activation [24, 25]. Since temperature was maintained at 650°C for all 3 set of biochar with different concentration. Biochar with 1.0mol concentration would have experience higher thermal activation than 0.1mol hence more volatile is loss [25]. It is ideal when the char yield is held constant, this shows that the remaining product contains minimal volatile content and more solids.

3.3 Moisture Content

From the Figure 4, moisture content in the rice husk biochar is increasing as the concentration increases. Rice husk impregnate with 0.1mol and 0.5mol for 12 hours has biochar lowest moisture content at 9%. Meanwhile biochar treated with 1.0mol at 24 hours has highest percentage at 18%. There is an increase of moisture being vaporised as the chemical pretreatment duration change from 12 hours to 24 hours. Duration of the pretreatment has an effect on the moisture content because it allow more reaction on the rice husk [16]. When rice husk has reacted longer with KOH, the thermal activation decreases. Therefore higher concentration and longer impregnation duration will increase moisture content. However it is best to select the condition which produce a constant moisture content to make sure all moisture are removed and remain solid. But other factors such as porosity, surface area, carbon yield and impurities remain need to be taken into consideration when producing the desired biochar for DCFC use.

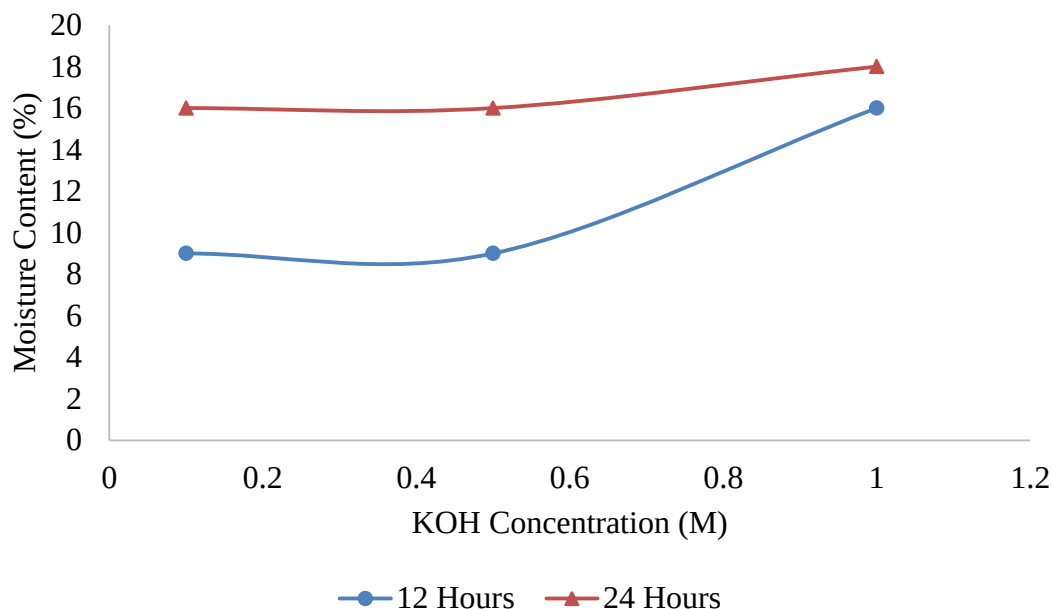


Figure 0 Moisture Content in Rice Husk Biochar at Different KOH Concentration Pretreatment

3.4 Ash Content

Ash content of the biochar is important as is affiliated to the DCFC performance. Rice husk has abundance of inorganic element, mainly being silica which will convert in to ash after pyrolysis. Researchers have found that the ashes in the biochar affects the performance of the DCFC due to accumulation of dissolved SiO_2 on the electrodes surface in long term [75]. Not much research on impurities on performance on DCFC however Also biochar with low ash content biochar has less amount of organic and inorganic substance in it and is more suitable for DCFC [79]. It was found that the rice husk treated by 0.5mol of KOH for 24 hours has the highest ash at 35% and the lowest ash produce is 0.1mol of KOH at 12 hours with only 7% formed. There is a significant change in ash formed as duration is concerned. The higher duration will form more ash on the biochar base on result found because more reaction happening between the rice husk and potassium hydroxide to form potassium silicate (K_2SiO_3) when duration is extended.

According to Du et al. and Chen et al there is an increase of ash in there result when treating rice husk at a higher temperature. Due to the fact that higher KOH concentration will decrease the thermal activation needed, 0.5mol experience ash content higher than 0.1mol for 24 hours when temperature is remained. However, there was a decrease of ash content in the biochar for 1.0mol KOH for 24 hours, the reason for it is that at this concentration it starts to have effect on the silica. High concentration will lead to partial dissolution of some components that could be

found in rice husk [11]. Furthermore, more ash are formed as concentration increases because potassium carbonate undergoes oxidation in the middle of pyrolysis process. The remains of decomposed potassium carbonate will act as impurities in the biochar [80]. Aside from that, there is another possibility that the increase of ash as concentration increase is due to the increase of mesopore formation. Mesopore are form through the micropore wall structure breakage, this allows more potassium to be trapped in the rice husk. The common trend show increase of ash as concentration increase. However the sudden increase of ash content for 0.5mol KOH for 24 hours could be a possibility that the samples was not rinsed properly as there are left over residue with the rice husk.

The nontreated biochar has as 49 wt% when tested using ASTM E 897-88 method. While the 0.1 mol/l KOH for 12 hours manage to reduce the as to 7 wt%. This is relevant to the research found by others as discussed in section 2.3.2, when silica is reacted with KOH and form K_2SiO_3 which was removed during rinsing.

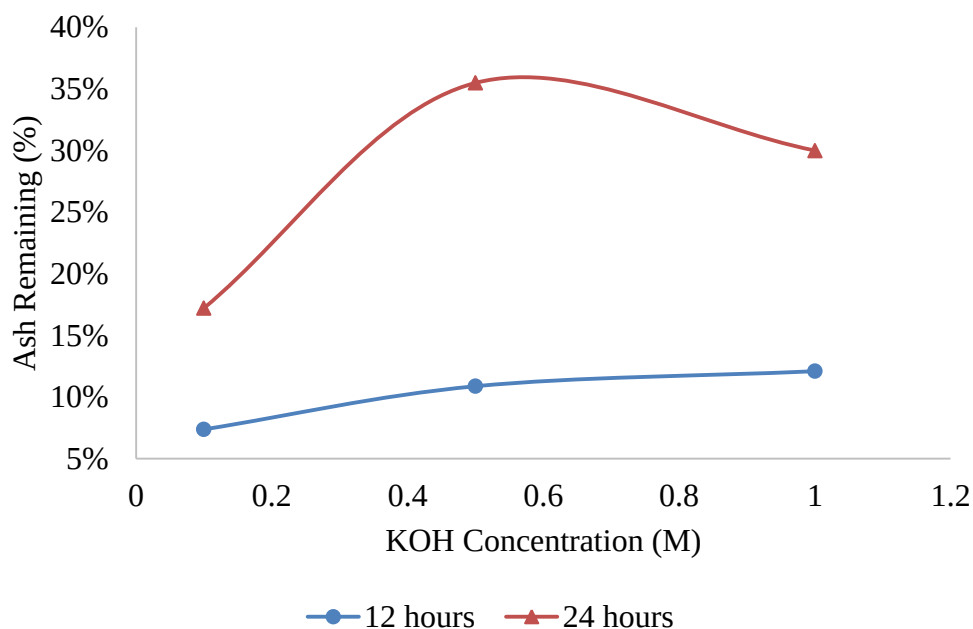


Figure 5. The Percentage of Ash Remaining at Different Concentration of KOH

3.5 Ultimate Analysis

An improved biochar is desired for producing high power density and has potential to be carbon rich fuel in DCFC. According to literature done, the treatment should be headed to the right direction where carbon content is increased and increase of porosity where impurities are removed

through KOH impregnation and thermal degradation of hemicellulose and cellulose to increase the weightage of carbon yield but that was not the case after experiment was carried out. Ultimate analysis was performed to obtain the elemental analysis of C, H, N and S. The most noticeable changes found is the carbon content in the biochar. Table 3 shows a decrease of carbon content from 54.07% to 39.43% when compared with non-chemically treated sample over chemical treated biochar which indicates that there are less carbon to be reacted in DCFC which will decrease performance. Cellulose and hemicellulose present in the non-treated biochar still remained intact hence carbon content remained high. The reason being that is it did not go through the KOH pre-treatment process and remained as long chain of carbon compound which will turn to volatile matter during the pyrolysis process [81]. This shows that the pre-treatment successfully lower the activation energy required to remove the volatile component, therefore at temperature 650°C more of carbon chain was removed in treated biochar. Moreover, the loss of carbon yield is compensated with higher porosity on the biochar. Silica removal might have affected the carbon content by breaking down the carbon and removed together with potassium silicate during washing.

According to the ultimate analysis, percentage of hydrogen, nitrogen and sulphur display low fractions in the biochar. Pyrolysis has little effect on sulphur content hence S in treated rice husk biochar is higher because the carbon content decrease however composition of sulphur remains the same therefore the weight percentage is increase [57]. There is no obvious changes in the H, only hydrocarbon CH₄ or higher is released at high temperature [82].

So according to the ultimate analysis, it present that the rice husk biochar being treated with chemical treatment of 0.1mol for 12 hours is a weaker carbon fuel for DCFC. But the sample will be analysed for TGA and BET for further understand before it can be concluded that it is not suitable.

Table 3. Ultimate Analysis of Treated Biochar and Untreated Biochar

Sample	C (%)	H (%)	N (%)	S (%)
No KOH pre-treatment	54.069	1.273	6.344	0.100
0.1mol of KOH for 12 hours	39.427	3.398	7.271	0.05

Table 0. Actual Carbon Yield for Treated and Untreated Biochar

Sample	Biochar yield (%)	Carbon content (%)	Actual carbon yield (%)
No KOH pre-treatment	54.95	54.07	29.71
0.1mol of KOH for 12 hours	38.33	39.43	15.11

3.6 Thermo Gravimetric Analysis

Thermo Gravimetric Analysis (TGA) is a preferred choice at analysing weight loss of the biochar using thermal method. It analyse the mass change which include mass loss of moisture, volatile matter and also ash of a sample as temperature changes to understand the physical and chemical properties of material. Figure 4.5 shows the weight loss curve (TG) of and untreated biochar and treated biochar of 0.1mol at 12 hours respectively. Blue curve shows treated rice husk biochar while pink curve shows non-chemical treated biochar.

For TG graph, there is a sign of weight loss for both sample below 100°C as seen in Figure 6 Weight loss observed in the first slope is the vaporisation of moisture. The big drop of weight loss which starts from approximately 300°C to 450°C is the volatile matter and the remains will be ash. The TG graph for treated biochar has an earlier head start of volatile matter being removed at approximately 320°C while non-treated biochar vaporises at 360°C. It shows that the chemical treatment has reduce the thermal activation required to decompose hemicellulose and cellulose. That being said, heat required for producing biochar is lowered as well. Moreover, the result also show lower oxidation temperature for biochar treated with KOH compared to untreated biochar. The low oxidation temperature will give higher electrochemical reaction rate as biochar will be much susceptible to oxidation when used in DCFC [32]. In terms of ash content, the biochar weight remains constant after 450°C, which means all volatile matter has removed and only ash reminding. The treated biochar of produce significantly less ash compared to non-treated biochar which is similar to the result found through ASTM E 897-88 method discussed in section 4.4. This is a good sign as carbon fuel with less ash is desired in DCFC.

Figure 7 illustrate the differential weight loss between the non-treated and treated biochar. The DTG curve represent the ease of oxidation occurring on the biochar in DCFC. From the figure below, it was clearly shown that the oxidation of biochar for treated biochar was significantly lower than non-treated. Degradation point for treated biochar was 320°C while non-treated is 360°C which is a 40°C difference. A lower oxidation temperature of biochar is desired in DCFC,

the results are similar to literature found where by chemical treatment lowers temperature for biochar to be burn into CO_2 [32]. This indicates the operating temperature of DCFC can be lowered and cost can be reduced.

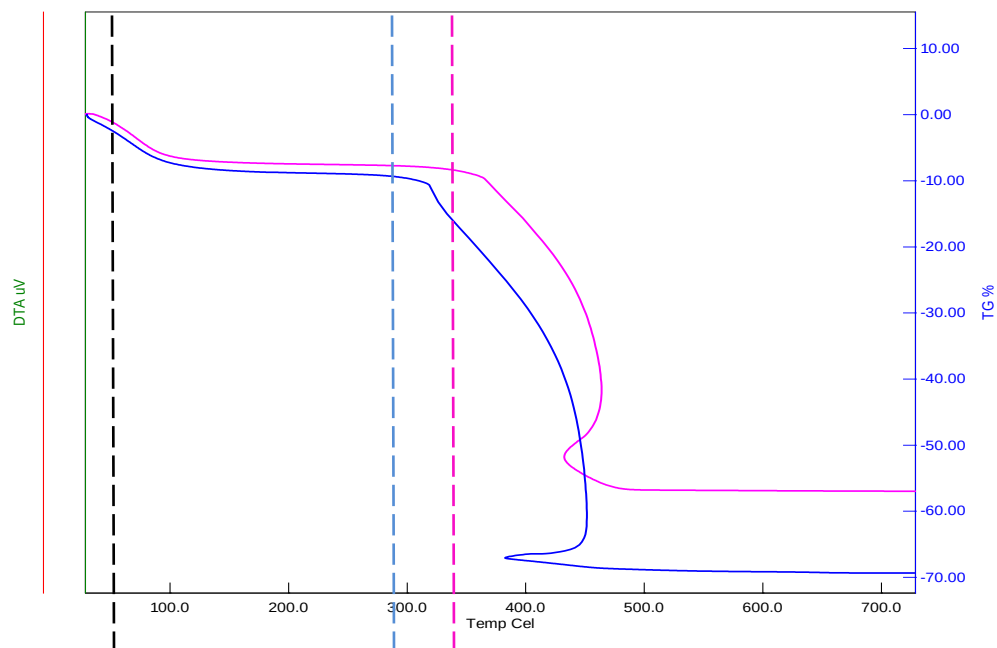


Figure 6 Weight Loss against Temperature in TG Analysis for Control Sample and Treated Biochar (0.1mol, 12hr)

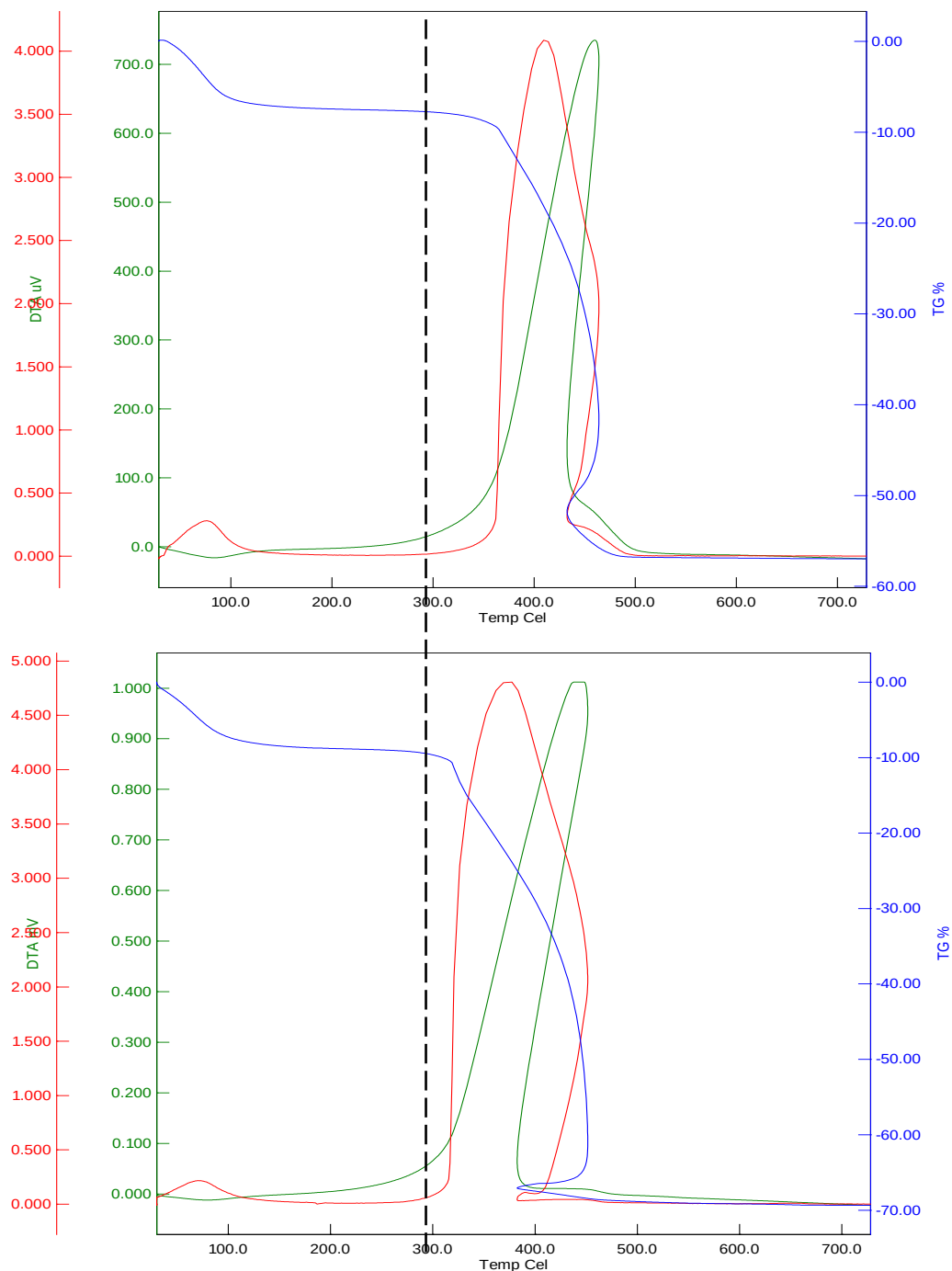


Figure 7 Differential Weight Loss in DTG analysis for Control Sample and Treated Biochar (0.1mol, 12hr)

3.7 Porosity and Surface Area

Porosity and surface area of a biochar is equally important as carbon content yield in biochar to be used as fuel in DCFC. As reviewed from literature, biochar with high surface area is desired as a fuel source due to the availability of active site ready for electrochemical reactions [24]. Table 5 shows BET surface area, mesopore area, total pore volume, mesopore volume, and pore size of rice husk biochar treated with 0.1mol of KOH for 12 hours and non-treated biochar. There was no improvement in porosity as well as surface area as seen over the non-treated biochar. Chemical treatment and pyrolysis has the ability to enhance the rice husk porosity and surface area proven by many researchers however one particular researcher has found that too high concentration will decrease the porosity due to breakage of biochar as discussed in section 2.3.2. The result in table 5 show lower BET surface area which can be explained due to high concentration and the duration of impregnation for 12 hours was too long. Formation of porosity through chemical treatment occurs during the removal of silica content in rice husk might have aggravate the loss in surface area as well. Pores are open while silica is removed during rinsing as it reacts with KOH to form K_2SiO_3 . When vaporising volatile components, the decrease of surface area as shown in table below can be attributed due to the vaporisation of volatile component after pyrolysis [62]. As discussed in literature review, mesopore volume in biochar will provide good diffusion rate for oxygen ion in DCFC application therefore the treated biochar is not suitable.

Table 5. BET Result for Control Biochar Sample and Pre-treated Biochar Sample

Sample	Non-treated Biochar	0.1mol KOH, 12 hours
BET (m^2/g)	213.9	116.1
Mesopore area (m^2/g)	17.9	19.76
Total pore volume (cm^3/g)	1.357×10^{-1}	8.553×10^{-2}
Mesopore volume (cm^3/g)	0.03605	0.0385
Average pore diameter (nm)	25	29
Micropore diameter (nm)	1.334	1.939

4.0 CONCLUSION

4.1 Summary and Conclusions

Through this research, the results showed that the alkaline concentration and pretreatment duration have an impact on the properties of biochar produced. The research objective was to investigate the concentration and duration of KOH pretreatment on rice husk. After the pretreatment, moisture and ash content analysis was carried out for all six samples of rice husk biochar. First of all samples treated by KOH for 24 hours contains more moisture content, this was due to the decrease in activation energy. The concentration of chemical treatment has little effect on moisture content only a small increase was observed. The improvement through this chemical treatment process shows a massive decrease in ash formation. The non-chemical treated biochar contains 49 wt% of ash where else the treated biochar with 0.1mol/l of KOH at 12hr has 7 wt%. The results are valid as ASTM E 897-88 method and TGA results obtain shows the same trend where ash is decrease when treated with KOH. Silicate reacted with KOH will form potassium silicate K_2SiO_3 and will be removed during rinsing hence lower ash.

From the analysis done above, the biochar with the lowest ash and have fairly high amount of biochar yield was selected for further analysis which includes BET, TGA and CHNS. The result of the selected biochar was compared with commercial carbon used as fuel source in DCFC. TGA analysis also contributed and support the claim of treated biochar has decrease the ash content which will help improve properties rice husk activated carbon used for DCFC. The TGA shows improvement on oxidative reaction temperature as well with the help KOH pretreatment, which decrease from 360°C to 320°C. However there was a tradeoff for lower ash content has decrease the carbon content and BET surface area on KOH treated biochar.

The carbon content of fuel used in DCFC is generally >90 wt%. The ultimate analysis done for treated biochar only manage to yield carbon content 39.43 wt% through the pretreatment, as compared with nontreated biochar which yield 54.07 wt% of carbon. Similar effects of high concentration and duration on treated biochar was seen on BET surface area and porosity. It has BET surface area of 116.1m²/g for treated biochar and it is lower than non-treated biochar of 213.9

m²/g which went through KOH pretreatment. The decreases of surface area and porosity is not desired by the DCFC. The high concentration and long impregnation period is the cause of the low carbon content because of lignin was decomposed as well where in normal condition only cellulose and hemicellulose was vaporized hence low carbon content and low BET surface area.

Based on all the analysis, the rice husk biochar had shown improvement in reducing ash content, where else there was no improvement in BET nor carbon content in the biochar. Therefore it still need further improvement before it can be used as an alternative fuel source in DCFC.

4.2 Future Work

Based on the analysis found on the pretreatment of biochar, the concentration and duration plays a big role in reducing ash, improving BET surface area and porosity and responsible for carbon content yield as well. For future work, the duration for of chemical treatment can be lowered more as biochar treated for 12 hours not suitable for DCFC use. Thus there can be further understanding on duration of impregnation and broaden the range. The impregnation period can test with a new set of range from 6 hours, 2 hours and 1 hour to see the improvement of biochar as fuel in DCFC. Secondly, the study of KOH concentration can be widen and send out more samples for in-depth analysis such as BET, TGA, CHNS and XRD.

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Palm Oil Methyl Ester as Phase Change Material

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The extraction of thermal energy is an alternative route to reduce the energy consumption. Latent heat storage (LHS) is the best thermal energy storage (TES) medium when compared to sensible or thermochemical heat storage. Phase change material (PCM) is the best representative for TES. PCM has the advantages of high energy storage efficiency and less temperature fluctuations during phase change process. PCM can be implemented on building materials, textile, heating and cooling applications. In this study, the hydrogenated fatty acid methyl ester (W.HFAME) which converted from waste palm cooking oil (WPCO) is potential to become a new participant in PCM from the investigation of different characteristics such as thermal, physical and economic. The WCO is first trans-esterified into W.FAME via two steps transesterification reaction and followed hydrogenation to further enhance its thermal property. From the DSC results, the latent heat of fusion for F.HFAME and W.HFAME is successfully increased from 66.73 to 107.81 J/g and 62.87 to 91.35 J/g respectively. Whereas the resulting melting temperature is also increased 14.82 to 20.27°C and 14.79 to 21.05°C. The simultaneous thermal analyzer (STA) showed the F.HFAME and W.HFAME are thermally stable at low temperature but reach 5 wt% loss when the temperature approximate to 190°C and 210°C. The density for both samples at 15 °C are 873 kg/m³ whereas the effect of volume expansion is minor when their temperature increases from 25 to 50°C. However, the F.HFAME and W.HFAME have relatively low thermal conductivity at low temperature and suffer little supercooling effect.

Keywords: Palm oil, phase change material, hydrogenation, fatty acid methyl ester

1.0 Introduction

Waste heat is a kind of thermal energy that is produced from household appliances like air-conditioner and refrigerator, combustion of car engine, and the largest contributor is from industrial process. The most known method to utilize the waste heat is throughout the heat exchange process which is so called the pinch analysis [1]. Since it is hardly to lower down the demand on energy, thermal energy storage (TES) is capable of reducing the wastage of energy and preserving for later use. Sensible heat storage (SHS), latent heat storage (LHS) and thermochemical storage (TCS) are the three main TES methods. Among of these methods, LHS is the most efficient energy storage method. Phase change material (PCM) is the main representative for the LHS method and it has the advantages of high energy storage density and less fluctuation during the phase change process.

PCMs are suitable for low temperature applications such as refrigeration system [2, 3], building materials [4, 5], textile applications [6–8], heating system [9–11], commercial freezers [12], [13], and domestic freezers [14]. PCMs are categorized into three different classes and they are organic, inorganic and eutectic. Figure 1 shows a clear classification of different PCMs [15]. For examples, paraffins and fatty acids are under the organic class due to the presence of carbon and hydrogen atom whilst metallic compounds and salt hydrates are under the inorganic class due to the absence of hydrocarbon compound. Eutectic compound is a combination of different PCMs from different classes including organic-organic, organic-inorganic and inorganic-inorganic.

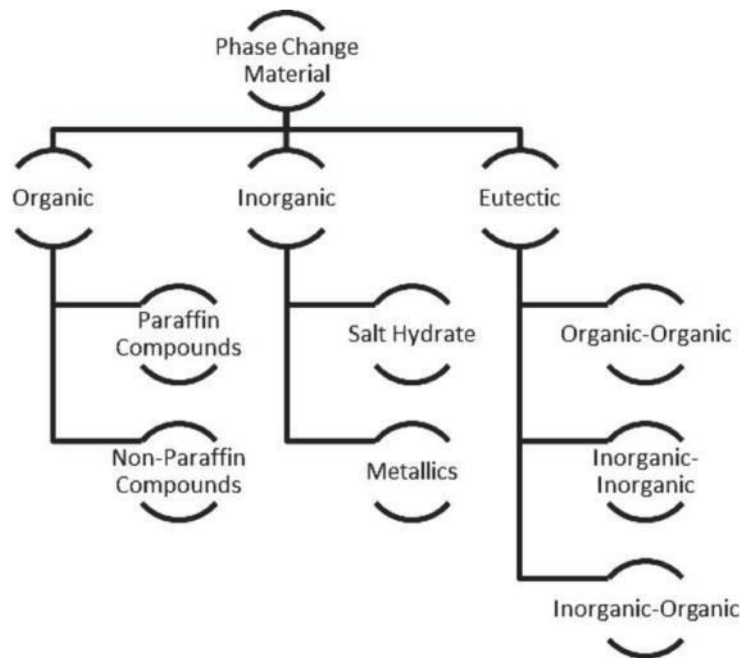


Figure 1: Classification of Phase Change Materials [15]

1.1 Phase Change Material

An organic PCM is known to have a wide range of melting (16 to 65°C) and freezing point (17 to 64°C). Palmitic acid, lauric acid, myristic acid, linoleic acid and fatty acid methyl ester are few examples of organic PCM. The main advantages of fatty acid PCMs are high heat of fusion at low temperature, small volume changes and do not undergo super-cooling effect but poor thermal conductivity is the major drawback of the fatty acid-based PCMs [16]. But, the thermal conductivity of the PCM can be improved by different microencapsulating methods [17]. Some fatty acids are mild-corrosive level therefore the selection of polymer during encapsulation process must be considered wisely.

Inorganic PCMs have high heat of fusion and thermal storage density (e.g. 240 kJ/kg), cheaper if compared to paraffin waxes, non-flammable, and showing good thermal conductivity [16]. The direct contact between inorganic PCMs and metals is not recommended due to its corrosion effects on metals. Thus, mostly the inorganic PCMs are encapsulated by interfacial polymerization, suspension polymerization and etc. The main defect of inorganic PCMs is super-cooling and phase decomposition which causes degradation on the thermal properties after recycle processes. Super-cooling is the liquid freezes at a point which is much lower than its freezing point [18].

Eutectic PCM is a combination of different classes of PCM for producing a mixture that has a manipulated property such as melting point and energy storage density. The combination of eutectic compound is divided into three groups: i) organic-organic ii) inorganic-inorganic and iii) organic-inorganic. The volumetric storage density of eutectics mixtures are slightly higher than that of organic compounds [19]. The thermal properties of eutectic mixture can be manipulated by mixing from two different basic PCMs. For example, new PCM can be fabricated in a combination of organic compound with high energy storage density compound and another inorganic compound with no phase segregation effect.

1.2 Selection of Phase Change Material

A proper PCM must have all the characteristics that listed in Table 1. For the thermal properties, high latent heat of transition and high thermal conductivity means the amount of heat energy that can be stored is high and it is easily heat transfer with surrounding. When it comes to physical properties, the PCM with high density allows more heat to be stored into a limited space whereas small volume changes and vapour pressure are important properties when the PCM is encapsulated. For the kinetic properties, the PCM with significant super-cooling effect must be avoided due to it will decrease the actual freezing temperature (properties degradation). The PCM must have sufficient crystallization rate to form crystals (liquid to solid phase) when the heat energy is released. Under the chemical properties, the PCM with long life time, easy compatible with building materials and shows no degradation after a numerous of cycle, no corrosion & toxicity and non-flammable is always preferable. For the economical concern, the cost of PCM must be reasonable and work well with the above discussed properties.

Table 1: Important Criteria for Thermal Energy Storage [15]

Characteristics	Requirements
Thermal properties	☐ High latent heat of transition ☐ High thermal conductivity
Physical properties	☐ High density ☐ Small volume change ☐ Low vapour pressure
Kinetic properties	☐ Low super-cooling ☐ Sufficient crystallization rate
Chemical properties	☐ Long-term stability ☐ Compatibility with materials of construction ☐ Reproducible crystallization without degradation ☐ No corrosiveness ☐ No toxicity ☐ No fire hazard
Economics	☐ Cost effective ☐ Availability

1.3 Fatty Acid Methyl Ester based Phase Change Material

In some early research works of PCM, most of the latent heat storage applications are dominated by paraffins and hydrate salt compounds. The performance of different methyl/ethyl based fatty acid as PCM was concluded to have a comparable latent heat value (~ 200 J/g) to paraffin PCM [20]. Another detail study on the thermal properties of palm fatty acids including lauric acid, oleic acid, palmitic acid and stearic showed that these acids have a latent heat of transition that vary from 153 to 182 kJ/kg [21] and this result is satisfied for the TES application.

A mixture of vegetable oils (i.e. coconut oil and its biodiesel (CCO, CCOB), palm oil and its biodiesel (PO, POB), jathropa curcas oil (JCO) and cook oil (CO)) and biodiesel as PCM is believed could replace the existing refrigerant that used in air-conditioner [22] in order to reduce the energy consumption. The results are summarized in Table 2. In addition, a study had also proven the melting enthalpy of an encapsulated fatty acid methyl ester-based PCM reached up to 52.3 kJ/kg and 53.5 kJ/kg in the presence of anionic and non-ionic surfactants [23]. In a recent study, a mixed ester based PCM experience no loss in weight when it's exposed to a temperature that is higher than its melting temperature whilst the paraffin mixture does [24].

Table 2: Melting and Crystallization Characteristics of the Oil Mixtures [22]

Vegetable oil	Mass ratio	T _m (°C)	H _m (kJ/kg)	T _c (°C)	H _c (kJ/kg)
CCO:PO	2:1	13.12	93.13	-7.39	81.27
CCO:CO	1:1	9.39	84.47	-2.43	61.07
CCO:JCO	1:1	9.12	70.10	-13.32	52.06
POB:CO	9:1	6.50	60.82	1.98	58.90
POB:CCOB	5:1	9.93	59.11	2.32	60.79
POB	100%	12.21	70.40	4.50	68.99

In summary, the feasibility of the conversion of biodiesels from waste cooking oils have been proven by a lot of researchers [25–33]. However, the produced biodiesel from waste cooking oils are never employed as PCM in any application even though the FAME-based PCM have been widely employed. The benefit of using waste cooking oils to produce FAME as PCM is due to its low cost if compared those conventional fatty acid ester-based PCMs which is 2-3 times more expensive. This FAME-based PCM is believed to have reasonable enthalpy value, optimal melting/freezing range during the phase change process.

The main objective of this research is to produce a new fatty acid methyl ester (FAME) as PCM from waste cooking oil was collected from restaurants. The waste cooking oil is first converted into biodiesel via a 2 steps transesterification process and followed hydrogenation to further increase its stability and properties. The characteristics of hydrogenated FAME including latent heat of energy, melting point, thermal durability, density and thermal conductivity will be investigated.

2.0 Experimental

2.1 Chemical

The waste palm cooking oils (brand: Sawit Emas, Sik Cheong Edible Oil Sdn Bhd) are collected from food restaurant. Also, a 2 liters bottle of the same brand fresh cooking oils is purchased from supermarket. Methanol (99%, ChemAR), hydrochloric acid (37%, R&M), potassium hydroxide (85%, R&M), n-hexane (99%, Bendosen), and pure hydrogen gas are provided by Process and Reaction Laboratory, SOE, Taylor's University. The 5wt% of palladium on carbon catalyst is purchased from Sigma-Aldrich.

2.2 Waste Cooking Oils Pretreatment Process

The waste cooking oils (WCOs) are allowed 2 weeks settlement for those heavy residues and particles. After that, the WCOs are filtered 2 times by a conventional filter bag and followed by dewatering process. The WCOs are transferred to a beaker and then immersed in Daniel Digital water bath at 70°C and under the presence of 500 rpm stirring speed for 10 hours.

2.3 2-steps Transesterification Reaction

2 steps transesterification reaction is proposed for the treated WCOs due to its higher acid content [26]. For fresh cooking oils, alkali transesterification reaction is proposed due to its relatively lower acid content (<1%) [34]. Even though two oils having different compositions, the alkali transesterification reaction condition for both oils will be the same.

Firstly, the WCOs react with methanol (CH_3OH) at a molar ratio of 1:10, 1 wt% of hydrochloric acid (HCl) as catalyst [35], 60°C temperature and 300 rpm stirring speed for one hour. After that, the WCOs are poured into separating funnel and gravity settling for 24 hours. Two separation layers formed after settling, top layer will be mainly WCOs and esterified oils (FAME) whereas the bottom layer is filled with water and unreacted catalyst. The separated WCOs and FAME are then placed in oven at 70°C for 2 hours to evaporate the remaining methanol [32].

For the alkali transesterification reaction, the oils to methanol molar ratio is 1:10, 1 wt% of potassium hydroxide (KOH) as catalyst [25], 60°C temperature and 300 rpm stirring speed for one hour. After that, the oil mixture is poured into separating funnel and gravity settling for 24 hours. Glycerol which is a heavy by-product that formed during the transesterification is settled at the bottom layer whereas the top layer will be FAME. However, the FAME is still very cloudy due to another by-product, soap. Set up a simple washing process by using hot distilled water at 80°C and volumetric flask. Repeat the washing until a clear FAME layer is formed. The FAME is then placed in oven at 70°C for 2 hours to evaporate the remaining methanol [32].

2.4 Hydrogenation Reaction

The purpose of hydrogenation reaction is to convert the unsaturated fatty acids into saturated fatty acids by breaking down the double bond and replace with hydrogen atom. FAME is mixed with 25wt% of n-hexane as solvent and 1wt% of palladium on carbon as catalyst [36]. The resulting mixture is transferred into a vacuum flask where the top is connected with a balloon and the hose barb is connecting to a vacuum pump. After the air is drawn off by the pump, the balloon is supplied with pure hydrogen gas. The reaction is carried out at a temperature of 60°C and 200 rpm for 4 hours. At the end of reaction, the catalyst is filtered out from FAME and the n-hexane is boiled out at 150°C.

2.5 Palm Fatty Acid Methyl Ester (FAME) Characterization

2.5.1 Latent heat of Energy, Melting and Freezing Temperature

The latent heat of energy, melting point and freezing point of the solidified FAME is analyzed by Differential Scanning Calorimetry (Perkin Elmer, DSC 8500). From the calibration result, the accuracy of the DSC is around $\pm 1.83\%$. The weight of sample is prepared at around 10 mg and sealed in an aluminium pan, an empty aluminium is prepared as reference. All samples are conducted at $10^{\circ}\text{C}/\text{min}$ for heating and cooling process and 20 ml/min of nitrogen flow where the maximum heating and minimum cooling temperature is set to 50°C and -10°C respectively. For each sample, the final result are calculated from the average of two readings for minimizing the uncertainties.

2.5.2 Thermal Durability

The thermal durability of the hydrogenated FAME is analyzed by simultaneous thermal analyzer (Perkin Elmer, STA 6000). The accuracy of STA 6000 is around $\pm 0.57\%$ between the measured value to the expected value. 10 mg of sample is prepared for each analysis and indium is used as reference. All the samples are conducted from 30°C to 700°C at a $10^{\circ}\text{C}/\text{min}$ heating temperature and 20 ml/min of nitrogen flow.

2.5.3 Density

The density of the hydrogenated FAME is analyzed by Anton Paar density Meter (DMA 4500 M). The density meter is calibrated by using a distilled water and the result showed a difference of $\pm 0.00003 \text{ g}/\text{cm}^3$ between the measured value to its theoretical value. After that, 10 ml of sample is prepared and tested at 3 different temperatures (i.e. 25°C , 50°C and 80°C). Three replicates for each temperature and its average temperature is recorded.

2.5.4 Thermal Conductivity

The thermal conductivity of the hydrogenated FAME is analyzed by KD2 Pro Thermal Properties Analyzer (Decagon Devices). The 6 cm single needle (KS-1) probe is selected for measuring the oil samples. The thermal conductivity meter is first calibrated in a pure glycerol solution. Whereas the measured value compared to the value in the manual, the accuracy of the instrument is around $\pm 5\%$ ($0.2 - 2.0 \text{ W}/\text{m.K}$). The next prepare 40 ml of the sample is measured from 25°C to 60°C at every 5°C interval. Each reading is repeated three times for improving the accuracy.

3.0 Result and Discussion

From the experiments, the fresh cooking oil (FCO) and waste cooking oil (WCO) has been successfully converted to fresh fatty acid methyl ester (F.FAME) and waste fatty acid methyl ester (W.FAME). After that, the fresh hydrogenated fatty acid methyl ester (F.HFAME) and waste hydrogenated fatty acid methyl ester (W.HFAME) are distributed into different samples and analyzed by DSC, STA, density meter, and thermal conductivity meter.

3.1 Latent heat of Fusion, Melting and Freezing Temperature

The results for four samples, fresh cooking oil made FAME with/without hydrogenation (F.FAME and F.HFAME) and waste cooking oil made FAME with or without hydrogenation (F.FAME and W.HFAME) are presented in separated DSC curve. After the hydrogenation reaction, the F.HFAME and W.HFAME sample show significant increases on the thermal properties including latent heat of energy, melting and freezing temperature compared to F.FAME and W.FAME sample. The latent heat of fusion of F.FAME and W.FAME is increased from 66.73 J/g and 62.87 J/g to 107.81 J/g and 91.35 J/g, whereas the melting temperature is increased from 14.82 °C and 12.79°C to 20.27°C and 21.05°C. The latent heat of crystallization of F.FAME and W.FAME is increased from -47.96 J/g and 32.02 J/g to -103.08 J/g and 87.80 J/g, whereas the freezing temperature is increased from 7.23°C and 6.03°C to 15.40°C and 17.62°C respectively.

From the Figure 4 and Figure 5, both F.HFAME and W.HFAME sample has two peaks during the melting and crystallization process. The two peaks are due to the eutectic impurities that present in the sample. The eutectic compound is a combination of FAME and hydrogenated FAME, where the first peak represent the melting point of the FAME that without hydrogenation and the second peak is the main melting point for the FAME with hydrogenation. This is due to the hydrogenation is only completed partially for both F.FAME and W.FAME sample. This means after the hardening process, the hydrogenated F/W.FAME is still containing some FAME component that without the hydrogenation reaction. However, all the DSC curves show that this PCM has a significant temperature fluctuation during the phase change process which varying from 10°C - 20°C between the onset and endset temperature. But the peak/melting temperature for both F.HFAME and W.HFAME sample is satisfied within the range of human comfort temperature (16°C to 26°C) if they are used in building applications [5].

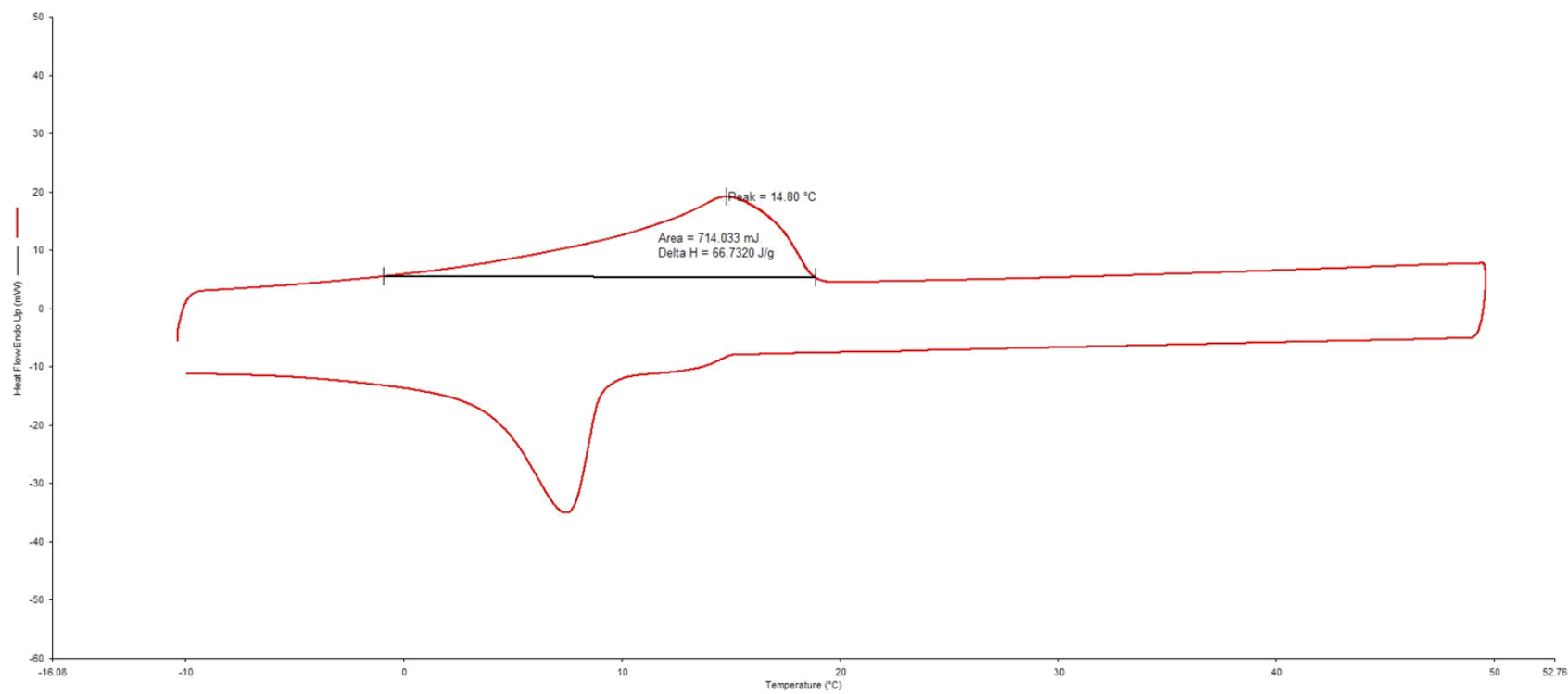


Figure 2: DSC Curve for F.FAME

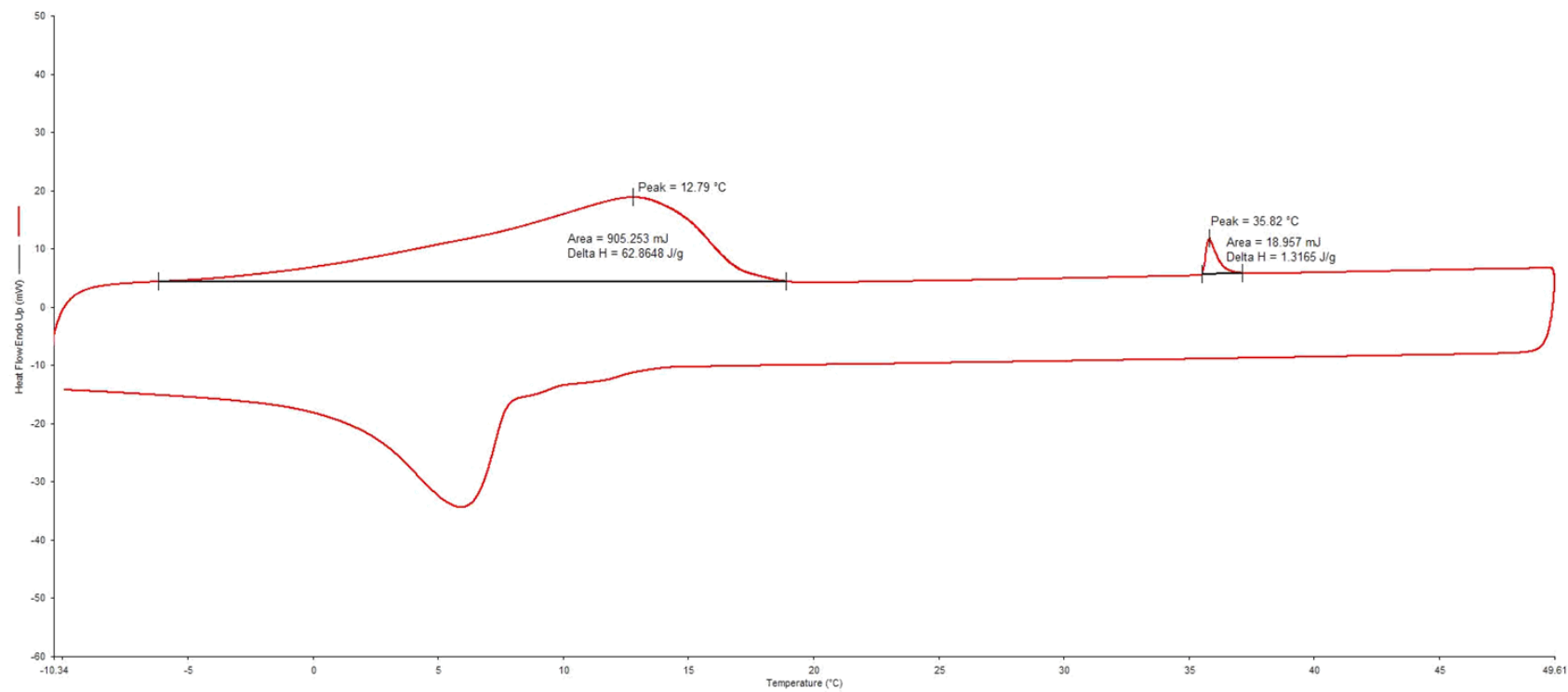


Figure 3: DSC Curve for W.FAME

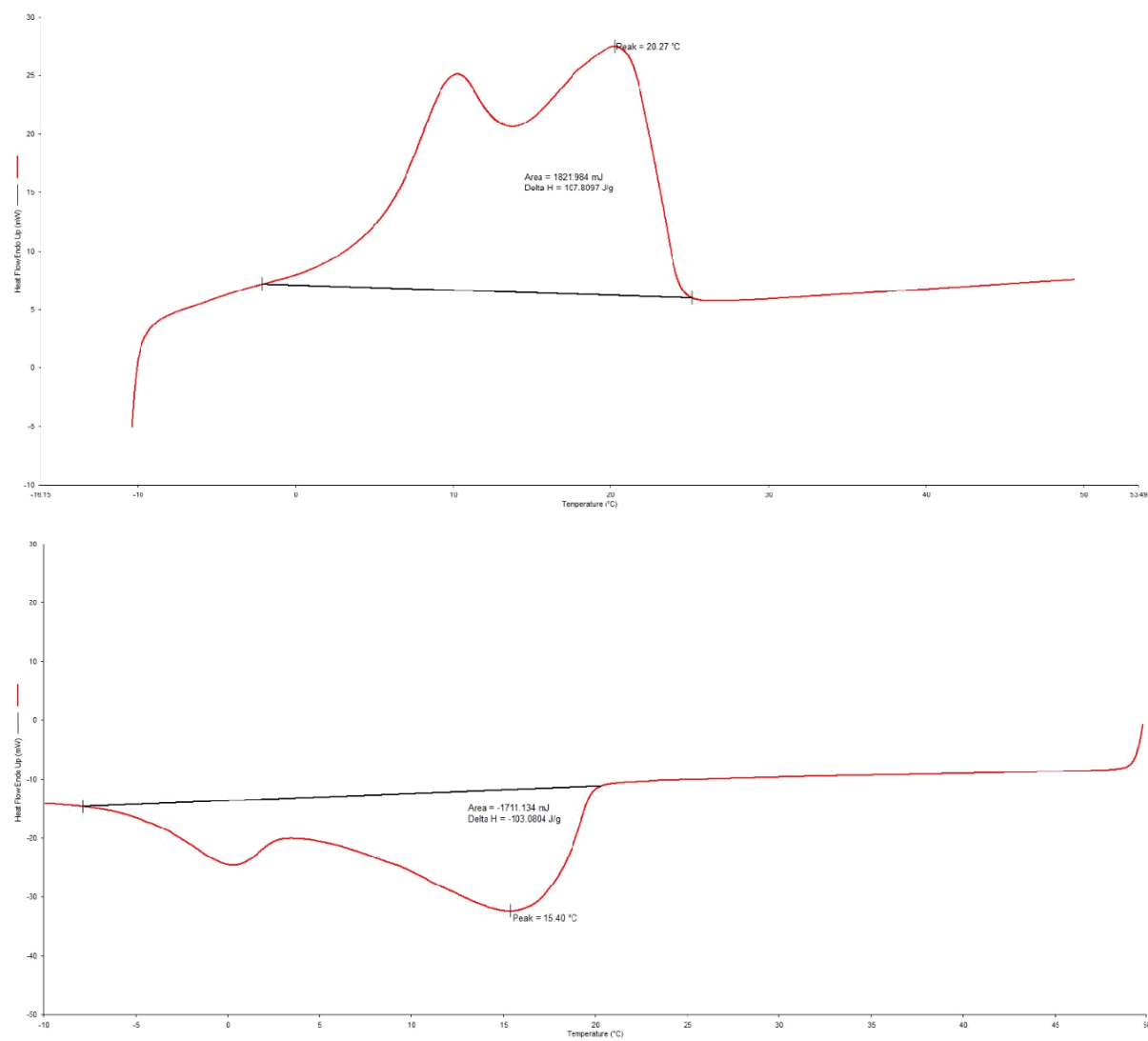


Figure 4: DSC Curve for F.HFAME

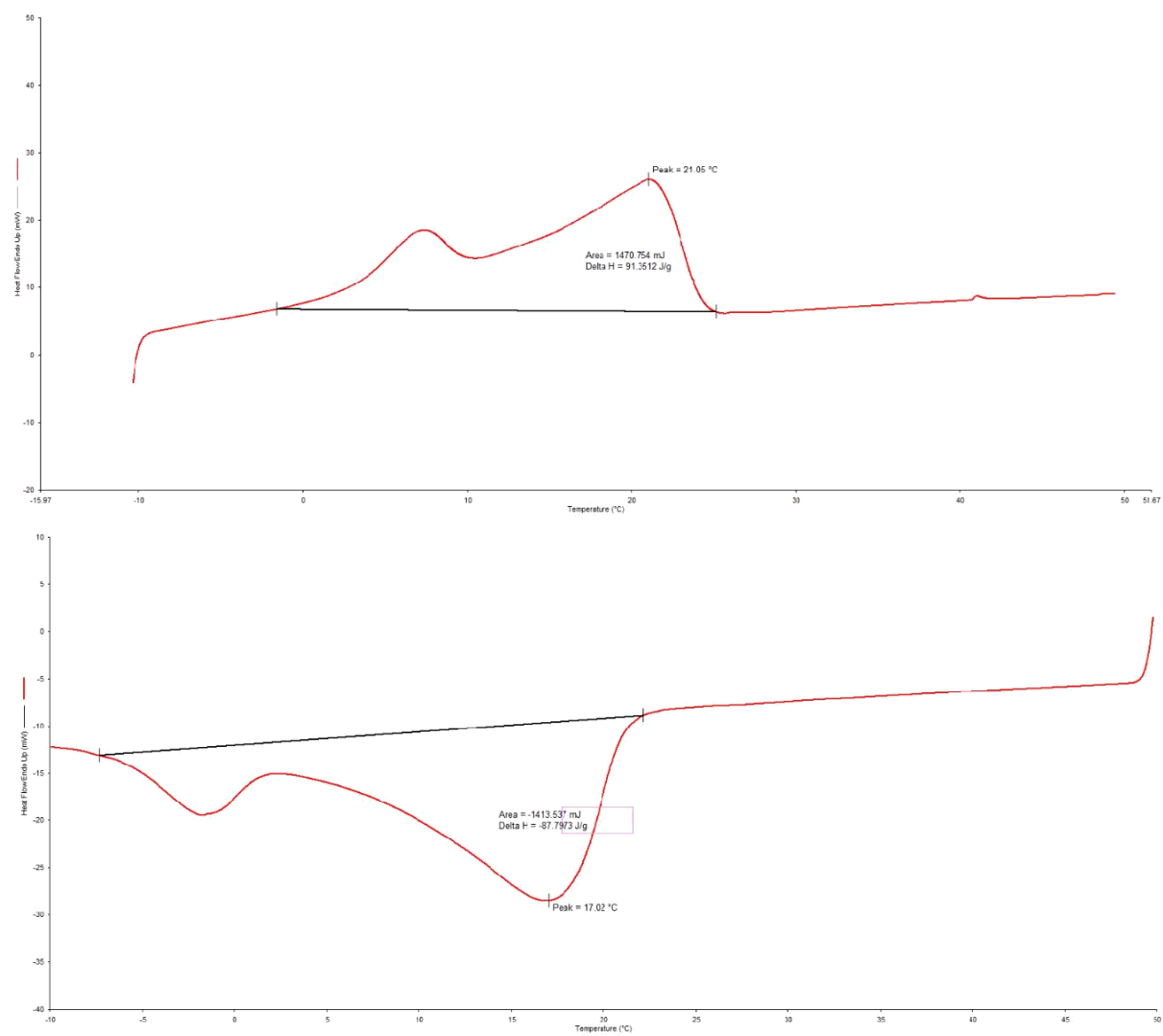


Figure 5: DSC Curve for W.HFAME

Table 3: The latent of energy, melting and freezing temperature for different samples

Sample	Melting Temperature (°C)	Freezing Temperature (°C)	Latent heat of Fusion (J/g)	Latent heat of Crystallization (J/g)
F.FAME	14.82	7.23	66.73	-47.96
F.HFAME	20.27	15.40	107.81	-103.08
W.FAME	12.79	6.03	62.87	-32.02
W.HFAME	21.05	17.62	91.35	-87.80

3.2 Thermal Durability

From the STA curve (see Figure 6), the F.HFAME and W.HFAME sample is thermally stable before 100°C. After 100°C, minor weight loss is observed for both samples. The F.HFAME and W.HFAME reached 5wt% loss at around 190°C and 210°C. Starting from 190°C, the W.HFAME is showing significant weight reduction until 300°C. For the F.HFAME, the significant weight reduction is happened after 210 °C until 340°C. The W.HFAME and F.HFAME reached 90 wt% loss when they approximate to 400°C.

In overall, the thermal durability of the F.HFAME is better than the W.HFAME due to its higher purity fatty acids content. The W.HFAME has higher unsaturated fatty acid composition if compared to F.HFAME. The cis-configuration in unsaturated fats which causes the intermolecular force between the molecules become weaker. Thus W.HFAME requires less energy requirement for the bond breaking process when compared to F.HFAME. The significant weight losses is due to this condition approaches to the fatty acid boiling point. Those liquid fatty acids have enough latent heat of energy to overcome the bonding between the molecules convert into gas phase. This means the F.HFAME and W.HFAME are not appropriate to be used on higher temperature applications. But they are proper material for lower temperature range applications due to their thermal stability.

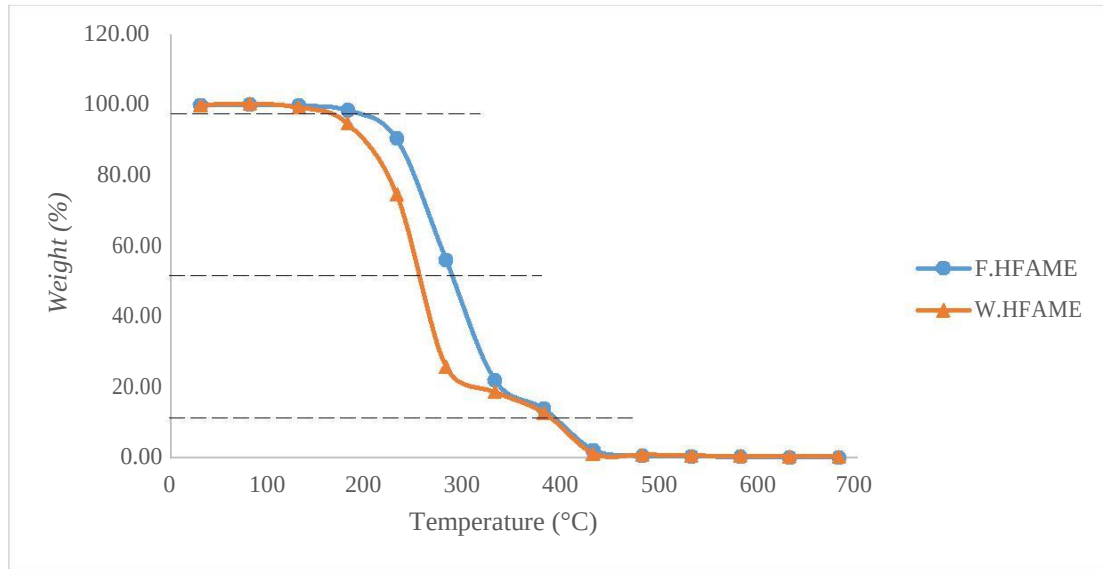


Figure 6: The graph of weight loss for F.HFAME and W.HFAME against temperature

3.3 Density

Figure 7 shows the density of the F.HFAME and W.HFAME decreases as its temperature increasing. This is due to the volume expansion of liquid (the mass of both samples are presumed constant at below 100°C). The increased percentage of thermal expansion for F.HFAME and W.HFAME as its temperature increased from 25°C to 50°C is 2.25% and 2.13%, respectively. Whereas both samples have the same increased percentage of thermal expansion of 4.98% when its temperature increased from 25°C to 80°C. Serious volume expansion is potential to cause leakage during the phase change process especially when the ambient temperature is higher than its design temperature. However, the F.HFAME and W.HFAME are suitable to be used in low temperature applications (<50°C) where the effect of thermal expansion is minor and can be prevented by microencapsulation [37].

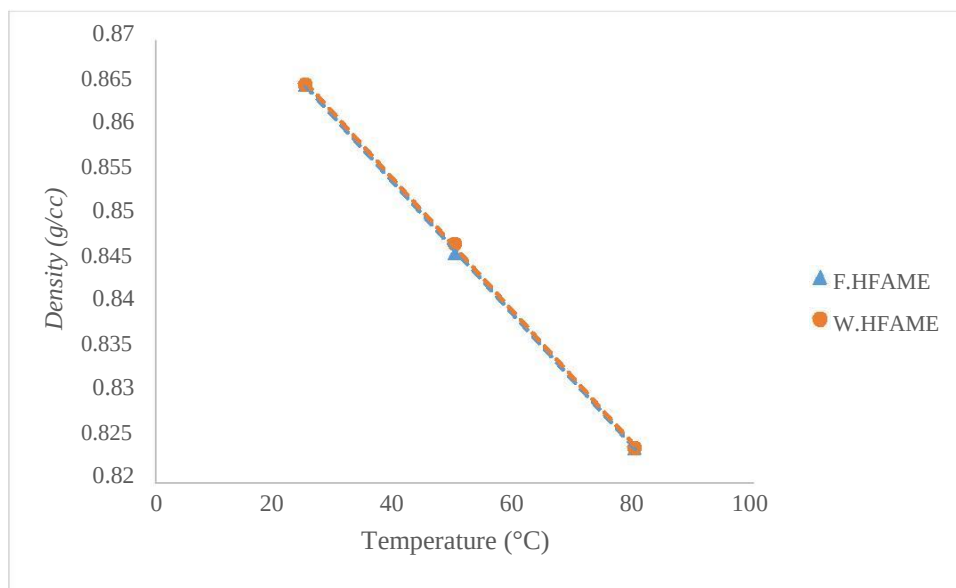


Figure 7: The graph of F.HFAME and W.HFAME density against temperature

3.3 Thermal Conductivity

From Figure 8, the thermal conductivity of the F.HFAME and W.HFAME increases as their temperature increasing. But both samples showed low conductivity behavior (<0.5 W/m.K) and this result match to the most researcher's result [35–38]. The low thermal conductivity means the heat transfer between the heat source and the material is slow. The F.HFAME and W.HFAME require longer time to store or release the thermal energy.

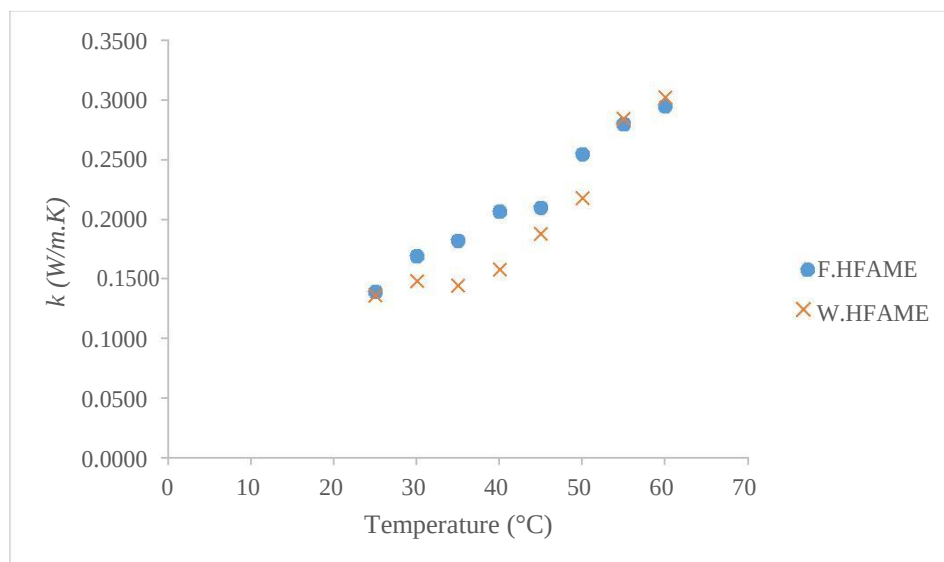


Figure 8: The graph of thermal conductivity of F.HFAME and W.FHAME against temperature

4.0 Conclusion

The FCO and WCO has successfully converted into the F.FAME and W.FAME through two steps transesterification reaction. The thermal property of both F.FAME and W.FAME are further enhanced by the hydrogenation reaction. The F.HFAME and W.HFAME have a final latent heat of fusion of 107.81 J/g and 91.35 J/g, whereas the corresponding melting point are 20.27°C and 21.05°C, respectively. For cooling process, the latent heat of crystallization of F.HFAME and W.FAME are 103.08 J/g and 87.80 J/g, whereas the corresponding freezing point are 15.40 °C and 17.62 °C, respectively. The thermal durability for both F.HFAME and W.HFAME are thermally stable at below 100°C, but both samples are observed reached 5wt% loss at temperature 190°C and 210°C. The density for both F.HFAME and W.HFAME at 15°C are 873 kg/m³ which is acceptable on PCM usage. Moreover, the effect of thermal expansion for both F.HFAME and W.HFAME are minor if they are used on low temperature applications (i.e. 25→50°C). The current study also proves that the F.HFAME and W.HFAME have poor performance on thermal conductivity which might limit their applicability.

In overall, the W.HFAME is justified to be a good participant in PCM for its high latent heat of energy when compared to the F.HFAME. The melting point and freezing point of W.HFAME is also fall between the human comfort temperature range (16-26°C). In addition, the W.HFAME is thermally stable at low temperature application where its density also closes to the F.HFAME. But the disadvantages of the W.HFAME are little supercooling effect and relatively low thermal conductivity. But these drawbacks can be eliminated by the addition of nucleating agents or dispersion of high conductivity solid particles (micro/nano size) in the PCM. From the economic analysis, the overall production cost for W.HFAME is cheaper than the F.HFAME and the availability of waste palm cooking oils are easily accessible in Malaysia. The utilization of waste cooking oils into palm oil methyl ester is potentially to be used on the domestic heating applications, building material and textile industry.

The present study only cover the thermal and physical properties. For a better understanding on its practicability, the study should further proceed into other characteristics such as economic, kinetic, and chemical properties as well as the microencapsulation technology.

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Enhancing the Enzymatic Reaction Rate in Synthetic Jet Mixer

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Abstract

Biomolecular materials such as enzymes play an important role in bio-based products. In fact, these materials can get easily damaged due to the nature of the mixing process; consequently, this will result on a drop of the activeness of these materials. From here, the concept of synthetic jet mixing plays its critical role in solving the challenge. However, the substrate that takes places to be converted to a product has to be enhanced so that the product will be formed at a faster rate. This research contributes in developing the performance of the synthetic jet system by enhancing the mixing quality. In detail, the reaction rate will be optimized by optimizing the area of the orifice where the fluid is shot out through. The study goes through the behavior of mixing process by studying the relationship between the reaction rate and the surface area. Six orifices with different diameters are tested and analyzed. The tested orifice diameters are from 5 mm to 30 mm with an interval of 5 mm. The enzymatic reaction used in this study is the hydrolysis of tributyrin oil using lipase enzyme. As a result of this investigation, as the area decreases, the rate of reaction occurs faster. Besides, some other parameters affecting the result such as solution amount, viscosity and permeability flow through the orifice. In this study the optimum orifice diameter is found to be a 15 mm in length, as the rate of reaction is enhanced with a percentage of 128% compared to the previous study. Finally, synthetic jet mixer is been compared with other mixers such as mechanical agitator and magnetic stirrer in term of mixing performance, and the result shows that synthetic jet has the best mixing.

Keywords

Biomolecular Materials, Enzymatic Reaction, Synthetic Jet, Orifice, Rate of Reaction, Mixing Process

1. Introduction

A bimolecular material is any molecule that consists mainly of carbon and hydrogen and it is produced by a living organism [1]. bimolecular materials such as enzymes can be implemented in various field of industrial application like biochemical, food and pharmaceuticals industries [2]. Enzymes are used to speed up the rate of reaction and do not cause any chemical change in the position of the reaction equilibrium [3]. The process of the enzymatic reaction occurs by attaching the substrate into the active site of the enzyme [3]. Then the enzyme enhances it to convert it into a product. The active site of an enzyme is the binding point where a substrate attaches tightly to make the reaction takes a place.

Activity of enzyme can be dropped due to various factors such as exceeding in temperature and pH level which will damage the active site of enzyme, hence enzymes will be denaturalized [4]. In addition to that, enzyme materials are sensitive and can get easily damaged of using high shear mixer such as impeller [5]. Various researches have been studied to investigate the effect of high shear mixer on enzyme activities; as a result, high shear stress causes more enzymes loss. [6].

Synthetic jet is a novel technology with a relatively new concept. This technology has a well effective and basic operation to perform the mixing process without causing high shear stress on enzymes. The concept of synthetic jet mixer is that, jet flow motion is generated by oscillating actuator as jet fluid is launched from a cavity chamber through an orifice into the upper section of the vessel by suction and ejection motion caused by the diaphragm deflection, Fig. 1 illustrates a schematic design of the synthetic jet process [7].

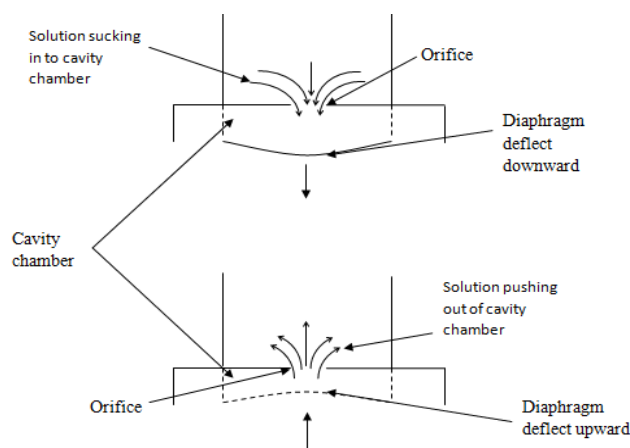


Figure 1. A Schematic design of synthetic jet mixer [4].

Main objectives of the synthetic jet are that it has no net mass flux, which eliminates the need for plumbing as it forms a creation of closed recirculation and low-pressure regions [8].

A study was investigated at Taylor's University involving comparison between the mechanical overhead stirrers at speed of 300 rpm and 600 rpm with the synthetic jet [7]. The study was on hydrolyzing tributyrin oil to produce butyric acid using lipase enzyme. As a result, the synthetic jet mixer gives higher performance compared to the other mixer due to less shear stress applied on enzyme. Fig. 2 shows the rate result between the two mixers.

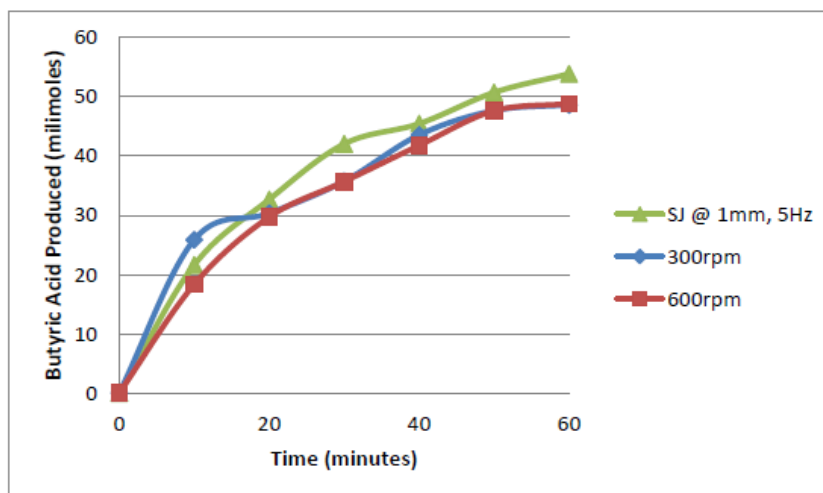


Figure 2. Comparison between Synthetic Jet Mixer and Mechanical Agitator [7].

Another study was made on synthetic jet to test the optimal frequency of actuator used to give the highest reaction rate. The tested frequencies are 5, 10, 15 Hz were investigated also on hydrolyzing the tributyrin oil. As a result, frequency of 5 Hz gives the highest released amount of NaOH which is the amount of butyric acid produced within 5 minutes, as it is seen in Fig. 3.

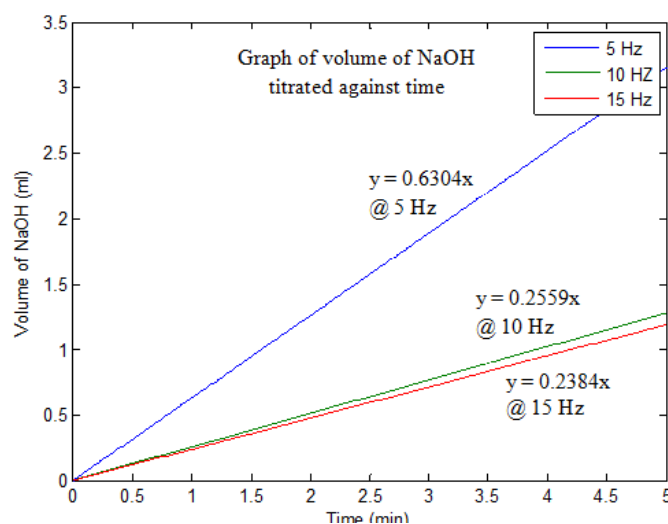


Figure 3. Comparison between 5, 10, 15 Hz of Actuator on Synthetic Jet [9].

Orifice is the plate that located above the cavity chamber and it covers up the entry cavity chamber where the solution jet is allowed to be shot out through the suction and ejection process of the actuator.

In the current study, a study on the effect of the areas of orifice along with the rate of reaction will be investigated to enhance the rate of reaction. Six orifices with different diameters from 5 mm to 30 mm with an interval of 5 mm are tested and analyzed. Hence, synthetic jet mixer will be compared with conventional overhead stirrers and magnetic stirrers.

1.2 Objectives

Achieving this objective would contribute to ensure that the concept of synthetic jet mixer can be enhanced by optimizing the orifice. The main objectives of this project are:

- Enhancing the rate of reaction by optimizing the diameter of orifices and compare the results with conventional overhead stirrers.
- Understand the behavior of mixing process by studying the relationship between the reaction rate and the orifice diameter.

2. Research Methodology

The previous study conducted at Taylor's University used a diameter of 25 mm. In the current study, six orifices with different diameters from 5 mm to 30 mm with an interval of 5 mm are investigated and analyzed. The mechanical drawing of the orifice plate is shown in Fig. 4.

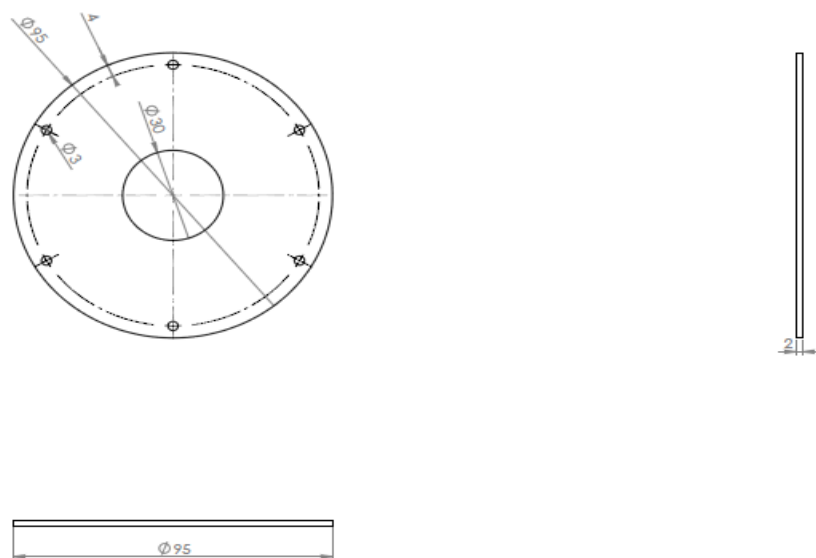


Figure 4. Mechanical Drawing of the Orifice Plate

The previous study used lipase enzyme extracted from *lipozyme tl* bacteria with an activity of 100 kLU/g (kilo-lipase unit per gram). Due to the unavailability of using the same enzyme from the same source, lipase enzyme extracted from *Candida Rugosa* bacteria with an activity of 700 UL/mg will be used instead. Hence, the enhanced reaction rate will be compared with the reaction rate made by 25 mm orifice diameter, which is considered as the same diameter used during the previous study.

Method

The method of this procedure is on the basis of the hydrolysis of tributyrin using lipase enzyme in distilled water to produce butyric acid, Fig. 5.

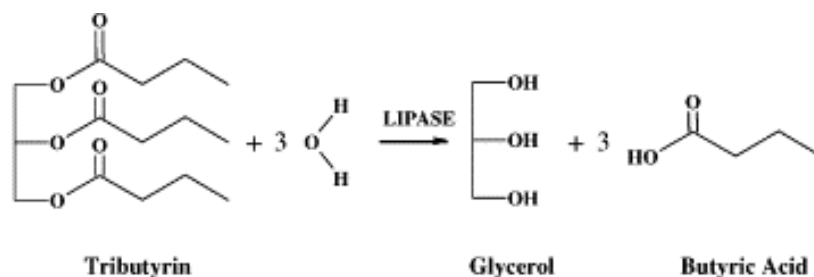


Figure 5. Hydrolysis of tributyrin expressed in structural formula [6].

The produced butyric acid is titrated through an alkali reagent, NaOH, with a concentration of 0.0525 M. The procedure is carried out and repeated six times. Each run different orifice will be used to determine the rate of reaction; hence, the result of each orifice will be analyzed and compared. The process of the method is reviewed in Fig. 6.

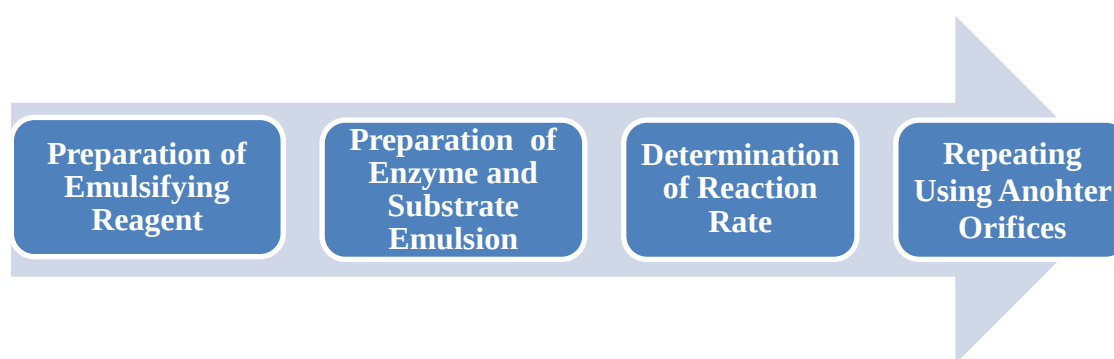


Figure 6. Flowchart of the overall method.

2.1 Materials and Equipments

In this investigation study, the chemical used in preparing the enzymatic reaction are sodium hydroxide (NaOH) with a concentration of 0.0525 M to be prepared as a titration reagent, tributyrin ($C_{15}H_{26}O_6$) works as a substrate, lipase (extracted from *Candida Rugosa* fungus) work as a catalysis to speed up the reaction and distilled water (H_2O). For preparing the emulsifying reagent that it works as a co-catalyst, the chemical used are sodium chloride (NaCl), potassium dihydrogen phosphate (KH_2PO_4), gum Arabic from Pharmacognosy of acacia and glycerol.

Equipment used in this investigation are auto-titration apparatus (848 Titrino Plus) and pH Meter (HI 110 Series) to measure the change in concentration of the product and its pH level. Besides, a homogenizer (IKA® ULTRA-TURRAX T18) is also used to homogenize the substrate and form it as a one layer solution. Power generator and function generator are used to set the voltage and frequency of the actuator at 24 V and 5 Hz respectively. Amplifier (LCAM 5/15) was also used to increase the current, and signal power at an optimum level. Last the synthetic jet mixer is used where the enzymatic reaction takes a place using the oscillation frequency waveform. These materials and equipments are available in the chemical and reaction laboratory at Taylor's University. The experimental setup is shown in Fig. 7.

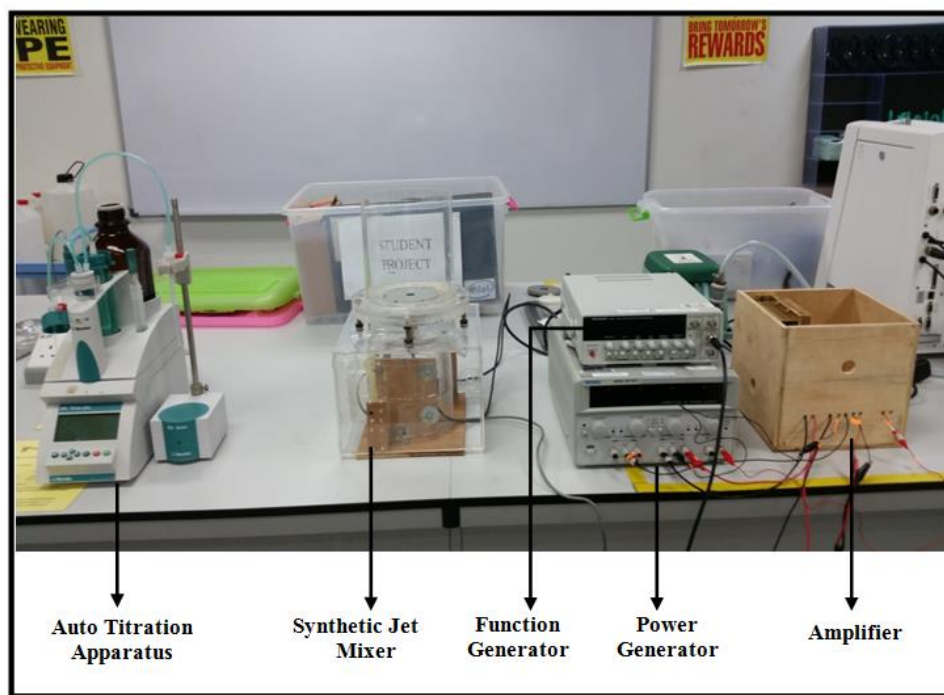


Figure 7. Experimental setup of tributyrin hydrolysis using synthetic jet.

2.2 Procedures.

Three solutions are to be prepared before carrying out the experiments. The mixture solutions are the emulsifying reagent, substrate and the enzyme solution. After the solutions are prepared, experiment is ready to be carried out.

2.2.1 Preparation of Emulsifying Reagent.

8.95 g of NaCl, 0.2 g of KH_2PO_4 and 3.0 g of Gum Arabic is dissolved in 230 mL of distilled water. After that, the solution is mixed with 270 mL of glycerol using the homogenizer until the solution is well homogenized.

2.2.2 Preparation of Substrate Emulsion.

50 mL the emulsifying reagent is mixed well with 8 mL of tributyrin oil and 742 mL of distilled water. The total volume of solution is 800 mL.

2.2.3 Preparation of Enzyme.

The lipase enzyme is in a powder phase and has a fixed unit activity of 700 UL/mg. In this experiment 10,000 ppm of lipase solution is prepared. So, 1 g of the lipase powder is mixed with 100 mL of distilled water.

2.2.4 Determination of the rate of reaction.

After preparing the substrate emulsion solution, the following steps are performed to achieve the investigation.

- i. The solution is poured into the synthetic jet vessel.

- ii. By using the auto titration apparatus the pH probe and the NaOH dispenser are placed into the mixture.
- iii. The pH of the mixture is adjusted to 7.0 ± 0.5 with a concentration of 0.0525M
- iv. Once the pH is fixed at 7, the lipase solution is added up and the titration apparatus is run.
- v. The frequency of the synthetic jet is adjusted at 5 Hz as it is the optimal value that gives the highest released amount of NaOH as was shown earlier [9]. The amount of NaOH added to the vessel is recorded for every 50 second until it reaches 300 second.
- vi. Rate of reaction can be determined using the following Eq. (1) :

$$-r = \frac{(\text{Normality of alkali}) \times (\text{Slope of the concentration various with time})}{(\text{Volume of the solution})} \quad (1)$$

where $-r$ is the reaction rate ($\text{mol/m}^3 \cdot \text{min}$), normality of NaOH is the concentration of the NaOH solution which is 0.0525×10^{-3} (mol/mL), slope is the ratio of the vertical change of the plot of the amount of NaOH against time with a unit of mL/min , and the volume of the solution is the volume of the substrate which is 800 mL.

3 Result and Discussion

3.1 The Effect of the Diameter on the Orifice

The titrated amount of the alkali reagent, NaOH, is recorded from 0 s to 300 s for each orifice plate, as the result is shown in table 1.

Table 1. Titrated Amount of NaOH Varied with Time

	5 mm	10 mm	15 mm	20 mm	25 mm	30 mm
Time (s)	Volume of NaOH (mL)					
0	0	0	0	0	0	0
10	0.5	0.6	0.7	0.5	0.5	0.7
30	2.8	3.0	4.2	3.8	2.3	3.9
50	6.4	6.2	7.7	7.1	5.4	7.2
100	13.1	14.6	16.0	13.9	13.7	15.6
150	19.5	20.0	29.1	20.1	20.0	20.7
200	22.3	27.0	39.1	32.8	26.4	28.1
250	28.3	35.4	43.3	37.9	34.7	36.5
300	34.0	40.0	47.0	44.6	40.0	40.0

The result of the released NaOH of each orifice diameter is plotted in a diagram for comparison, as it is shown in Fig. 8.

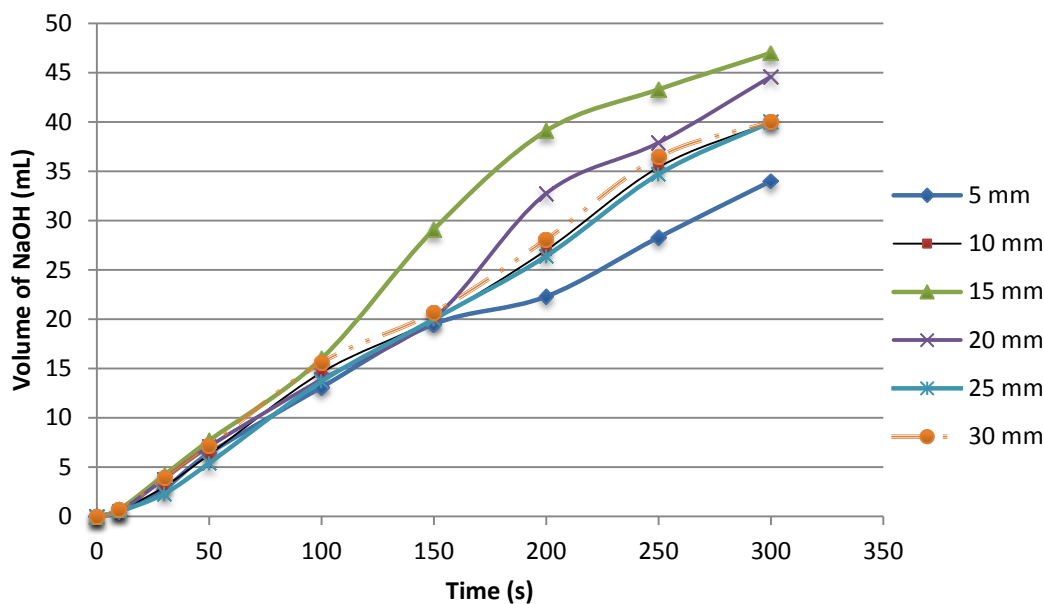


Figure 8. Volume of NaOH (mL) titrated against time for each diameter.

From the graph above it is clearly shown that the plot of the diameter of 15 mm has the highest released amount of NaOH. On the contrary, the lowest amount of NaOH is dosed by using the diameter of 5 mm. For further illustration the graph above is clarified by dividing it into parts in Fig. 9, 10 and 11, so that it will be easy to be visualized. Besides, the slope of the straight line of each orifice is displayed along with its coefficient of determination.

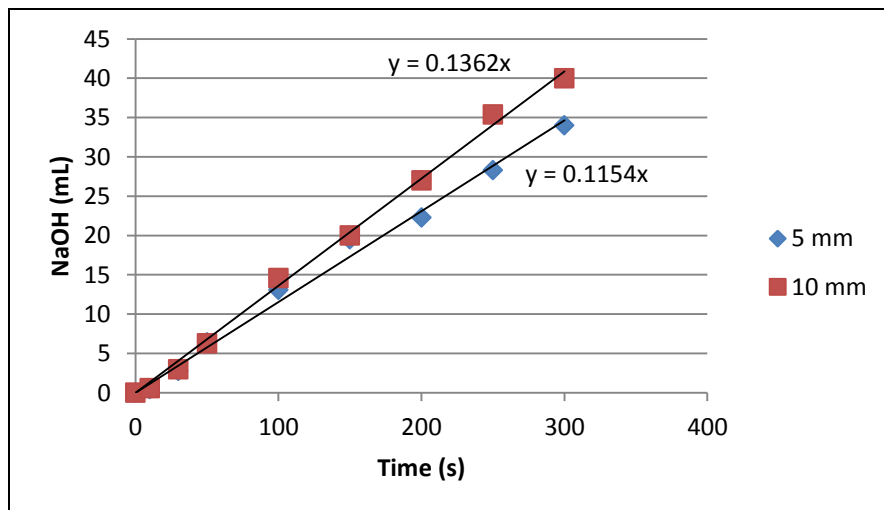


Figure 9. Comparison between 5 mm and 10 mm of the orifice diameter volume of NaOH titrated against time.

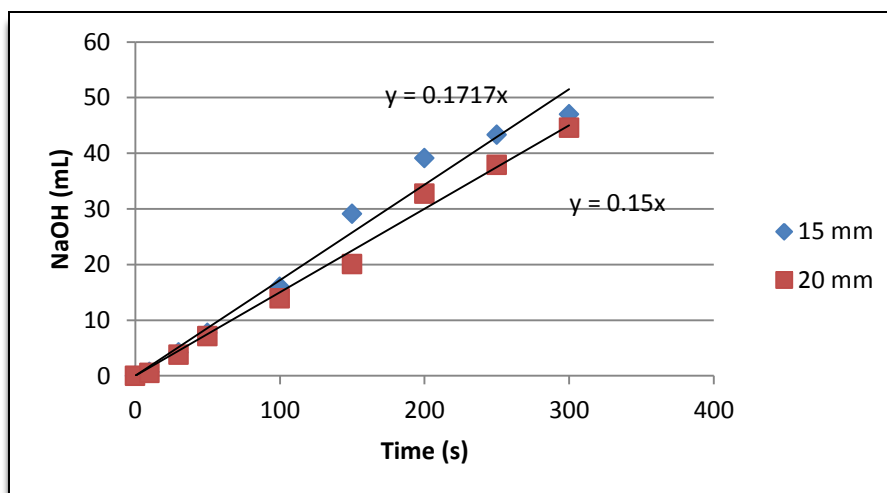


Figure 10. Comparison between 15 mm and 20 mm of the orifice diameter volume of NaOH titrated against time

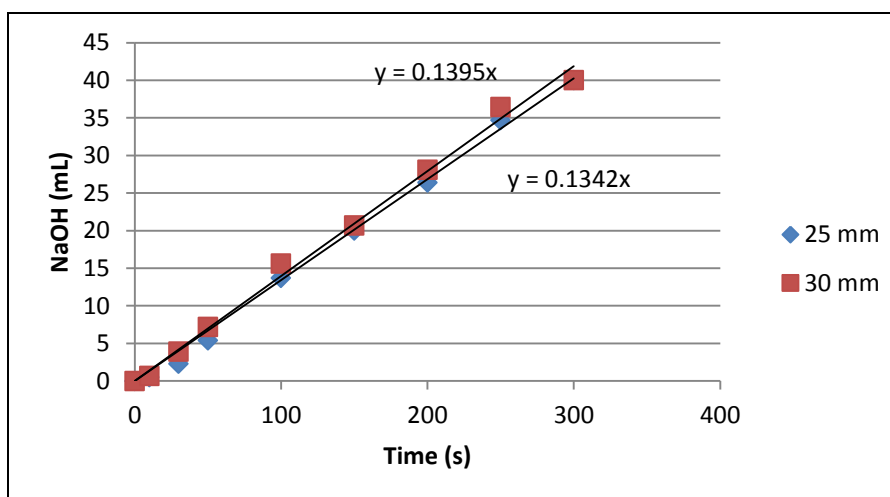


Figure 11. Comparison between 25 mm and 30 mm of the orifice diameter volume of NaOH titrated against time

According to the results, a number of indications can be observed. In Fig. 9, both diameters 5 and 10 mm have the lowest slopes compared to others. At the same time, Fig. 10, the orifice of 15 and 20 mm diameters are relatively considered the highest among others. While in Fig. 11, the both diameters 25 and 30 mm have almost the same amount and slopes. In the following table and graph the rate of reaction is determined, compared and analyzed.

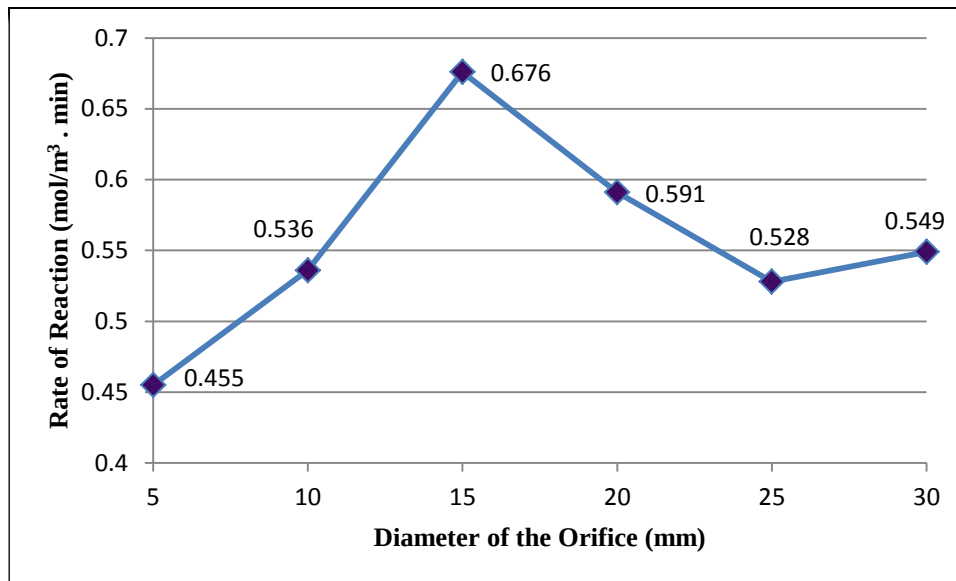


Figure 12. Comparison between the orifices.

As it is depicted by the Fig. 12, the plot can be divided into three parts. First, at the diameter of 25 to 30 mm the plot remains relatively static at approximately 0.55 (mol/m³.min). It then rises gradually from the 25 to 15 mm, as the reaction rate is at its highest level at 15 mm diameter. Third, a significant drop occurred from 15 to 5 mm diameter. Reynold number of the fluid flow of each orifice diameter is calculated using Eq. 2.

$$Re = \frac{\rho D v}{\mu}$$

(2)

where Re is Reynold number, D is the diameter of the orifice in (m), v is the fluid velocity (m/s), ρ is the fluid density which is 1010 (kg/m³) and μ is the viscosity of the solution, which is 0.00102 (Pa.s). Reynold number of the fluid flow of each orifice diameter is shown in Table 2.

Table 2. Velocity and Re of the fluid flow of each orifice

	Diameter (m)	Area (m ²)	Velocity (m/s)	Re
Diaphragm	0.08	0.005024	0.1	7918.887
Orifice	0.005	1.96E-05	25.6	494.9304
	0.010	7.85E-05	6.4	989.8608
	0.015	0.000177	2.84	1484.791
	0.020	0.000314	1.6	1979.722
	0.025	0.000491	1.02	2474.652
	0.030	0.000707	0.71	2969.583

In the first case the plot of the largest two diameters 25 and 30 mm is comparatively stable. When the orifice has a large cross sectional area the jet solution will not fully fill the cross area efficiently [10]. Thus, the mixing process will not reach its optimum level, as mixing will not be well dispersed randomly throughout the system resulting in slower

changes in molecular structure. So, even if the orifice has a bigger diameter than 30 mm it will be expected to give the same result. The flow structure changes from turbulent to transition condition as the Re at the diaphragm > 4000 and after it is shot out the flow is in transition condition. The turbulent flow will not well disperse around the vessel, which leads the tributary to take a period of time to undergo hydrolysis.

On the other hand, the second part of the diameter the rate of reaction gets higher as the orifice sectional area gets smaller. This can also be illustrated using the continuity equation, Eq. (3).

$$\dot{Q} = v_1 A_{\text{Diaphragm}} = v_2 A_{\text{Orifice}} \quad (3)$$

where: $\dot{Q}$ is the flow rate of the fluid (m^3/s), $v_{1,2}$ are the velocities of the fluid at the diaphragm and orifice region (m/s) and $A_{\text{Diaphragm, Orifice}}$ are the areas of the diaphragm and orifice (m^2).

The orifice at this part speeds up to the velocity of the fluid as the cross area gets decrease [10]. The flow structure at this stage has a laminar condition since Re is < 2100 . Hence, it is deduced that as the flow structure has parallel layers with no disturbance between the layers the flow gets mixed due to the well dispersion. Another elaboration on this case could be due to the bias error made during carrying out the procedure. The experiment could not be repeated for verification due to the limitation of time.

Last but not least, this stage has the lowest value, despite it has smallest Re and diameter with the highest velocity. The decrease in the two smallest orifices could be clarified as following, after the solution is poured into the synthetic jet, it will be confined inside the cavity chamber. At this point three factors affect the flow; first, as the solution is restricted at the chamber, this will oppose the motion of fluid generated by the actuator which will lead to drop its motion efficiency to drop; hence less oscillating frequency waveform will be supplied. In this stage the actual velocity will differ from the calculated one due to the opposing force created by the weight will supply stress on the actuator, hence the velocity will not preformed efficiently as it will be reduced to a certain level.

The second factor is caused by the viscous force, as this force exerted by the fluid on the particle [11]. So this force will work as a resistance which will not let the flow to be shot out the orifice. Consequently, there will be less mixing inside the vessel and the lipase enzyme will not efficiently take place in the enzymatic reaction to form the product in a fast period of time. Therefore, the rate of reaction will take longer time to be achieved.

The third factor could be due to the collision flow on orifice plate, since the orifice area is small and the chance of the fluid to escape from the orifice is low [12]. And this can be illustrated by comparing the orifice of 5 mm and 10 mm diameter, as the area gets small the changes of the fluid to launch out is small. Other than that, this could also be occurred due to the bias error made during carrying out the procedure.

The previous studies on synthetic jet mixer used an orifice with a diameter of 25 mm, as it has a reaction rate of $0.528 (\text{mol}/\text{m}^3 \cdot \text{min})$. However, this study has enhanced the rate of reaction to be $0.676 (\text{mol}/\text{m}^3 \cdot \text{min})$ with an enhancement percentage of 128%.

3.2 Comparison between Synthetic jet with Other Mixers.

After the mixing is been studied and enhanced on synthetic jet, the reaction is tested using different mixers. The tested equipments are Magnetic Stirrer with rate of 8 Hz, overhead mechanical agitator 500 rpm with 2 blades, overhead mechanical agitator 500 rpm with 4 blades and overhead mechanical agitator 1000 rpm with 4 blades.

Mixing rate of each is selected for a particular purpose, that 8 Hz is almost equivalent to 500 rpm; hence 500 rpm is compared with the three mixers. Besides that, the 1000 rpm with 4 blades is selected to compare with 500 rpm with 4 blades to see how effect the result speed. The first two mixers equipments are not tested with 1000 rate are due to the limitation of their speed. These mixer equipments are been compared with synthetic jet mixer using orifices of 15 and 5 mm diameter , the fastest and lowest rate of reaction producer, to see how synthetic jet is well effective compared to the other mixer and to visualize the effectiveness of synthetic jet after is been enhanced as is shown in Fig. 13.

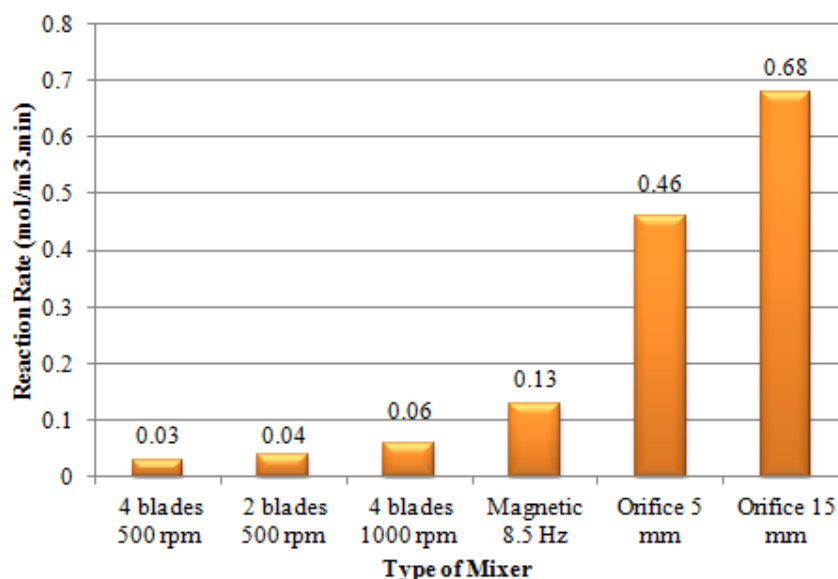


Figure 13. Comparison between mixing

The result shows that, the synthetic jet mixer is largely better compared to the other mixer in term of reaction rate. Synthetic jet with 15 mm orifice diameter is better with 2200 % compared to the lowest one, 4 blades at 500 rpm, as this validate the efficacy of synthetic jet compared to tradition mixing. Although the amount of solution are same in each one, but the synthetic jet vessel have a bigger diameter which could affect the result. It also shows that, the 2 blades agitator is better than the 4 blades, as it indicates that more enzymes are denaturalized using the 4 blades agitator. Reaction rate at 1000 rpm is more enhanced compared to 500 rpm, this is due to the turbulent flow is more at 1000 rpm. Last, the magnetic agitation has the highest reaction rate compared to the mechanical mixers, which indicates that less shear stress are applied, hence less denaturalizing occurs.

4. Conclusions

In conclusion, the enhancement of the rate of reaction in synthetic jet mixer is been achieved by 128%. Besides, the study has also dealt with the impact of orifice area on the reaction rate. There is an inverse relation between them in such a way that the area decreases

as the rate of reaction increases. Nevertheless, the smallest area does not increase the reaction rate due to restriction in the solution inside the cavity chamber as the solution will not spread well all over the vessel. In addition, viscous force has also an inverse relation with the rate of reaction, as it is considered as an obstacle inside the cavity chamber that does not allow the solution to be shot out through the orifice. Over and above, synthetic jet mixer has the best performance in term of mixing quality compared with other mixers such as mechanical agitator and magnetic stirrer.

For future work, it is recommended to test different enzymatic reactions with different viscosities to study the effects on viscous force on enzymatic reaction using synthetic jet mixer. Moreover, in term of mechanical design of synthetic jet, an ergonomic vessel is recommended to be designed, which will result in the easiness of handling and cleaning to the investigator. Finally, synthetic jet mixer studies are been performed in a small reactor, so scaling up the reactor will positively contribute to apply it in industrial field.

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The Fundamental Study on Solubility of Heavy Metal Oxides in Ammonium and Phosphonium based Deep Eutectic Solvents

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Abstract

Water pollution has become increasingly prevalent in our daily lives and has caused a serious threat at a global level. Among the various pollutants that exist, heavy metal pollution has become an issue of great concern due to their high toxicity, greater bioaccumulation in human body and food chain, non-biodegradability nature, and carcinogenic effects to humans. This study aims to address the heavy metal ion contamination in wastewater by providing a low cost and efficient removal technique using DESs. In this investigation, the solubility of CuO and ZnO heavy metal oxide ions with concentration of 20g/L was studied in ammonium and phosphonium based DESs. The samples were left to stir at 250 rpm at 28, 45 and 65°C respectively for four hours in an incubator orbital shaker and the solubility of the heavy metal ions were analysed using Atomic Absorption Spectrometer (AAS) using serial dilution technique. Phosphonium based DES which contain MTPB showed higher solubility of CuO and ZnO ions. Based on the results obtained, DES 6 (MTPB: Glycerol) has the highest solubility of CuO, 0.197 mg/L at 65°C and the solubility of ZnO was found to be the highest in DES 7 (MTPB: Glycerol), 1.225 mg/L at at 65°C.

Keywords: Heavy metals, Deep Eutectic Solvent, solubility, wastewater, removal.

1. Introduction

Water covers almost 70% of the earth's surface and is an important resource to the people and environment. Today, water pollution has become increasingly prevalent in our daily lives and has caused a serious threat at a global level. Water pollution occurs when contaminants enters and dissolve in water bodies like oceans, rivers and lakes which result in the degradation of the water quality (Kabir et al. 2014). According to the Sick Water report by the United Nations Environmental Program (UNEP), up to 90 % of waste water in developing countries flow untreated into catchment areas and highly productive coastal zones, threatening the health food security and access to safe drinking and bathing water (Cocoran et al. 2010). The Sick Water report also revealed that an estimated 245,000 kilometres squared of marine ecosystems are affected by hypoxia (Oxygen depletion caused by coastal eutrophication) and has brought a severe impact on fisheries and the livelihood of people. The number of people suffering from water related diseases have increased tremendously and around 2.2 million people die each year from diarrhoeal conditions in which 1.8 million of them are children under 5 years old (Cocoran et al. 2010).

Water pollution poses a serious challenge due to its impact on various types of economic activities (Reddy & Behera 2006). Major pollutants can be classified into several categories such as anions and cations (nitrates, phosphate, sulphates, Ca^{+2} , Mg^{+2} and F^-), inorganic pollutants (acids, salts and toxic metals), pathogens (bacteria, viruses and protozoa) and water soluble radioactive substances (Azizullah et al. 2011). Among these classified pollutants, heavy metal pollution has become a global issue due to their high toxicity level, high bioaccumulation in human body and food chain, non-biodegradable property and carcinogenic effects to humans (He & Chen 2014). The high concentration of transition metals like Cd, Cu, Pb and Zn in urban topsoil and dusts tend to washout from infrastructures and contaminate the water sources (Kabir et al. 2014).

Removal of pollutants in waste water is the fundamental goal of waste water treatment systems. Gupta and Ali (2013) summarised the different methods involved in wastewater treatments which include adsorption, centrifugation and filtration, micro and ultrafiltration, coagulation, crystallization, electro dialysis, electrolysis, evaporation and many more. Adsorption is an example of a heavy metal removal technique that has been commonly used and researched extensively. The adsorption capacities of heavy metal ions that are commonly found in wastewater sources such as Zn^{2+} , Cu^{2+} and Cd^{2+} are compiled in Table 1. Among the adsorbents used, agricultural wastes were found to have high adsorption capacity of these ions.

In general, physicochemical waste water treatments offer several benefits such as fast separation process and easy to operate. However, the advantages of these systems are often outweighed by a number of disadvantages. The main drawbacks identified from conventional physiochemical treatment systems requires a more proficient separation technique that is low in cost and easy to operate. Some of the main advantages and disadvantages of conventional wastewater treatment techniques are summarized in Table 2.

Table 3. Adsorption Capacities of Heavy Metals using Different Types of Adsorbents

Adsorbent	Adsorbent capacity (mg/g)	References

	Pb^{2+}	Cd^{2+}	Zn^{2+}	Cu^{2+}	Ni^{2+}	
Zeolite, clinoptilolite	1.6	2.4	0.5	1.64	0.4	(Babel & Kurniawan 2003)
Clay/poly(methoxyethyl) acrylamide	81.02	-	20.6	29.8	80.9	(Şölener et al. 2008)
Maize cobe and husk	456	493.7	495.9	-	-	(Igwe & Abia 2007)
Pecan shells activated carbon	-	-	13.9	31.7	-	(Bansode et al. 2003)
<i>Bacillus</i> -bacterial biomass	467	85.3	418	381	-	(Ahluwalia & Goyal 2007)

The main drawbacks identified from conventional physiochemical treatment systems requires a more proficient separation technique that is low in cost and easy to operate. Some of the main advantages and disadvantages of conventional wastewater treatment techniques are summarized in Table 2.

Table 4. The Main Advantages and Disadvantages of Different Physiochemical Methods for Treatment of Heavy Metal in Wastewater

Treatment Method	Advantages	Disadvantages	References
Adsorption using new adsorbents	• Easy operating conditions • Low cost of adsorbent • Wide range of pH • High metal binding capabilities	• Low selectivity • Cause production of waste products	(Babel & Kurniawan 2003)
Chemical precipitation	• Low capital cost • Simple operation	• Generation of sludge • Extra operational cost for sludge disposal	(Kurniawan et al. 2006)
Electrodialysis	• High separation selectivity	• High operational cost due to energy consumption and membrane fouling	(Mohammadi et al. 2004)
Membrane filtration	• Small space requirement • Low pressure • High reparation selectivity	• High operational cost due to membrane fouling	(Kurniawan et al. 2006)

Fuerhacker et al. (2012) performed an investigation on the application of ILs for the removal of heavy metals from waste water and activated sludge. The removal of heavy metals from activated sludge using quaternary ammonium and phosphonium ILs has proven to be more successful than conventional methods (Fuerhacker et al. 2012). The removal rate of heavy metals by sorption to ILs was complex and could not be predicted using standard solutions. However, more than 90% of removal was successfully achieved for Cu, Ni and Zn by both ILs, [PR4][MTBA] and [PR4][TS] from the extraction of activated sludge

(Fuerhacker et al. 2012). The success in the removal of heavy metals using ILs has provided an opportunity to perform further research on other cheaper alternatives of ILs.

Unfortunately, in recent years the environmental aspects related to ILs have been strongly addressed, stating that many ILs commonly used cannot be regarded as ‘green derivatives’ (Domínguez de María & Maugeri 2011). It has been demonstrated that some ILs, based on imidazolium or pyridinium cations, turned out to be as toxic as conventional solvents, and caused adverse effects to microorganisms as well as the environment (Kislik 2012; Wu et al. 2013; Biczak et al. 2014). In addition, the synthesis of ILs is far from being environmentally friendly as it typically requires a large amount of salts and solvents in order to completely exchange the anions (Zhang et al. 2012).

One of the key breakthroughs in the development of ionic liquids was identified when 1 mol equivalent N-ethylpyridinium bromide: 2 AlCl₃ was successfully synthesised by Hurley and Weir in 1951 which was a eutectic liquid at 20°C (Abbott et al. 2011). The term “deep eutectic solvent” was first invented a decade ago by Abbott, a notable pioneer in the field (Wagle et al. 2014). Abbott discovered the concept of mixing two solid organic materials to produce a free flowing fluid with a freezing temperature far below the individual components (Wagle et al. 2014). The fusing of the mixtures resulted in the formation of a eutectic mixture with a melting point lower than its original components which led to the mixture being called a DES (Abbott et al. 2004; Shahbaz et al. 2011; Zhang et al. 2012). DESs belong to a class of ionic liquids which are mixtures of a quaternary salt with either a hydrogen bond donor (HBD), metal halide (Lewis acid) or a hydrated salt (Bagh et al. 2013). The HBD can consist of an alcohol, amide or a carboxylic acid which act as a complexing agent (Bagh et al. 2013).

DESs have been considered an alternative to ILs as they are able to overcome some of the disadvantages of ILs. DESs have been regarded as an environmentally friendly solvent that is able to be synthesised at high purity and low cost compared to ILs (Bagh et al. 2013; Shahbaz et al. 2011; Zhang et al. 2012). DESs has been identified to overcome some of the principle disadvantages of ILS, as they are easy to synthesise in pure state, chemical inertness with water, non-toxic, biocompatible and biodegradable properties (Abbott et al. 2004; Shahbaz et al. 2011; Zhang et al. 2012; Bahadori et al. 2013). The unique features of DESs has found its way into various applications such as electrochemical processes (Abbott et al. 2007), production and purification of biodiesel (Shahbaz, Mjalli, et al. 2011; Gu et al. 2015), biological catalysis (Durand et al. 2012), synthesis of solar cells (Steichen et al. 2011), separation of aliphatic and aromatics (Kareem et al. 2012) and many other potential applications.

In this study, different types of ammonium and phosphonium based DESs was synthesised and investigated for their ability to dissolve heavy metal ions of Copper (II) Oxide (CuO) and Zinc (II) Oxide (ZnO). Ammonium and phosphonium were selected as the source of quaternary salt ions in the synthesis of DESs as they are low cost and easy to synthesise at high purity (Abbott et al. 2004; Shahbaz et al. 2011). Various combination of ammonium and phosphonium based DESs were synthesised and their characteristics were analysed. A quantitative investigation was performed to identify a specific DES as a novel, efficient, safe, simple and most importantly cost effective solvent to dissolve heavy metal oxides. Findings from this research study can be useful in the application of DESs for the removal of heavy metal oxides from wastewater.

2. Experimental Methodology

The solubility of heavy metals in different ammonium and phosphonium based DESs was investigated in this research. The overall experimental methodology of the investigation is summarized in the flow chart shown below.

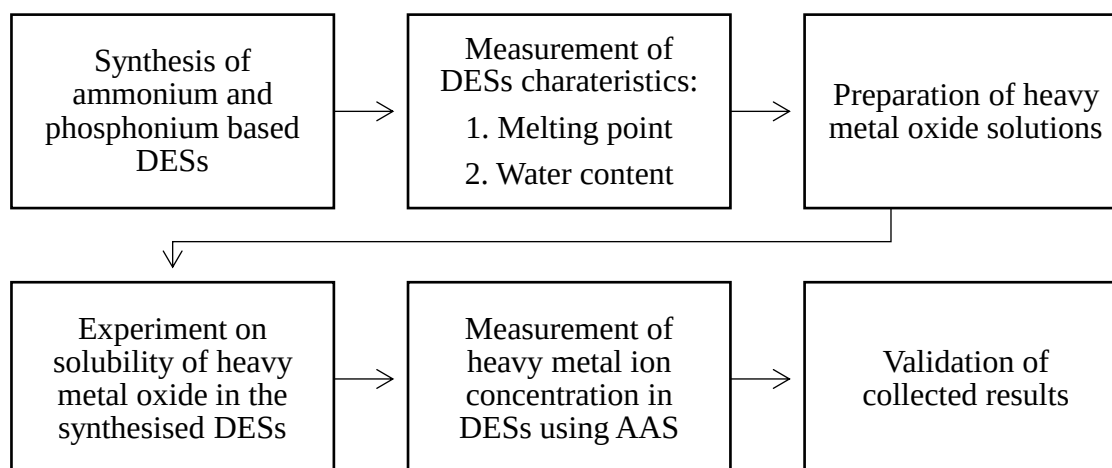


Figure 4. Summarized Research Methodology

2.1 Chemicals

The chemicals used in this research study are listed in the table shown below. All utilised chemicals are of high purity (>99%).

Table 5. List of Chemicals Used

No.	Chemical Name	Chemical Formula	Use	Supplier
1.	Choline Chloride (ChCl)	C ₅ H ₁₄ ClNO	Salt	Merck
2.	Methyl Triphenyl Phosphonium Bromide (MTPB)	C ₁₉ H ₁₈ PBr	Salt	Merck
3.	Glycerol	C ₃ H ₈ O ₃	HBD	Merck
4.	Triethylene glycol (TEG)	C ₆ H ₁₄ O ₄	HBD	Merck
5.	Copper (II) Oxide	CuO	Heavy metal oxide for solubility analysis	Ajax Chemicals
6.	Zinc (II) Oxide	ZnO	Heavy metal oxide for solubility analysis	R&M Chemicals

2.2 Synthesis of DES

In this study, 10 types of DESs based on ammonium and phosphonium based salts were synthesised to investigate the solubility of heavy metal oxides. ChCl and MTPB were selected as the source of quaternary salts for the synthesis of DESs. Two different HBDs, glycerol and TEG were selected to fuse with the quaternary salts for the synthesis of DESs. In order to increase the number of possible combinations, the DESs were prepared with different molar ratios of ChCl and MTPB salts to the HBDs. The preparation of DESs for this investigation was done according to the method used by Shahbaz et al. (2011).

To synthesise the DES, the mass of salt and the corresponding HBD were first weighed accurately using an electronic balance. Then, the weighed salt and HBD were carefully filled into 150ml Schott bottles and sealed with Parafilm to prevent any moisture from mixing with the contents. The Schott bottles were then allowed to heat at 70°C at 300 rpm until a homogenous and transparent liquid is formed Shahbaz et al. (2011). Table 2 shows the details of the DESs which were synthesised in this study. The synthesised DESs were given abbreviations.

Table 6. Compositions and Abbreviations of the Synthesised DES

Salt	Hydrogen Bond Donor (HBD)	Molar Ratio (Salt: HBD)	Abbreviation
Choline Chloride (ChCl)	Glycerol	1:2	DES 1
	Glycerol	1:3	DES 2
	TEG	1:3	DES 3
	TEG	1:4	DES 4
	TEG	1:5	DES 5
Methyl triphenyl phosphonium bromide (MTBP)	Glycerol	1:2	DES 6
	Glycerol	1:3	DES 7
	TEG	1:3	DES 8
	TEG	1:4	DES 9
	TEG	1:5	DES 10

2.3 Heavy Metal Ion Solubility in DES

Heavy metal ion solubility was determined by mixing 0.1 g of the metal oxide (CuO and ZnO with >99% purity) in 5 ml of the synthesised DES. Samples were prepared for 10 combinations of DESs with 2 combinations of heavy metal oxide ions separately. The samples were left to stir at 250 rpm at 28, 45 and 65°C respectively for four hours in an incubator orbital shaker. The stirred samples were then left overnight for settling before being analysed using the AAS.

2.3.1 Atomic Absorption Spectrometer Analysis (AAS)

The samples containing DESs and heavy metal oxide ions was analysed for heavy metal ion content using the AAS equipment. The samples for AAS analysis were prepared by performing a serial dilution technique, in which 1 ml of DES containing heavy metal oxide is diluted in 9 ml of distilled water three times before being analysed. The specification of the AAS equipment are shown in the table below.

Table 7. AAS Analytical Conditions

Atomic Absorption	
Oxidant	Air
Oxidant flow rate	10.0 L/min
Acetylene flow rate	2.5 L/min
Flame Emission	
Oxidant	Nitrogen oxide, N ₂ O
Oxidant flow rate	6.0 L/min
Acetylene flow rate	7.5 L/min
Replicates	3

3. Results and Discussion

3.1 Synthesis of DES

In this study, ChCl and MTPB were used to synthesis DESs by mixing these quaternary salts with two different HBDs, glycerol and triethylene glycol. The DESs were prepared with different molar ratios to form ChCl based DESs (DES 1- DES 5) and MTPB based DESs (DES 6 – DES 10). The selection of molar ratios used to synthesise the DESs was done based on the research performed by Shahbaz et al. (2011). All 10 types of DESs that were synthesised formed colourless eutectic mixtures with no salt present inside the solvent. The DESs formed a clear homogenous solution and there were no undissolved salts left in the solvent. The freezing point and water content of the DESs was measured using a Differential Scanning Calorimeter (DSC) and Karl Fischer Titration (KF). All the synthesised DESs showed low water content and the solvents formed have lower freezing points compared to their individual constituents. The formation of the eutectic mixtures are a result of hydrogen bonding between its constituents.

4.2 Solubility of Heavy Metal Oxides in DESs

Based on this research investigation, all the synthesised DESs are capable in dissolving both CuO and ZnO heavy metal oxides at different temperatures. The analysis performed using AAS was successful and showed significant results in this study. There are several factors that influenced the solving ability of the DES during this research. These factors include, effect of temperature, type of DES and type of heavy metal oxide ions. The details of each factor are explained in the following section of this paper.

4.2.1 Effect of Temperature

In general, it is known that when a solvent is subjected to additional heating, the particles of the solute present in that solution tend to move more easily between the solid phase and the

solution. The heavy metal oxides that are solid in room temperature and pressure tend to become more soluble when the temperature is increased. Heating the DESs with the heavy metal oxides at different temperatures makes it easier for the particles of solid to move between the DES solution and the solid phase. This can be proven based on the Second Law of Thermodynamics which predicts that the solutes will tend to shift to the more disordered and dispersed state resulting into the two components being in a solution form (Ghareh Bagh et al. 2014).

Figure 2 shows the solubility profile of CuO in DES 1 (ChCl: Glycerol) and DES 6 (MTPB: Glycerol) at 28, 45 and 65°C. Both DES have the same molar ratio of salt to HBD, 1:2. Based on the graph, DES 1 and DES 6 exhibit an increasing trend in solubility with increase in temperature. DES 6 has the highest value of solubility at 65°C (0.197 mg/L) followed by DES 1 (0.098 mg/L).

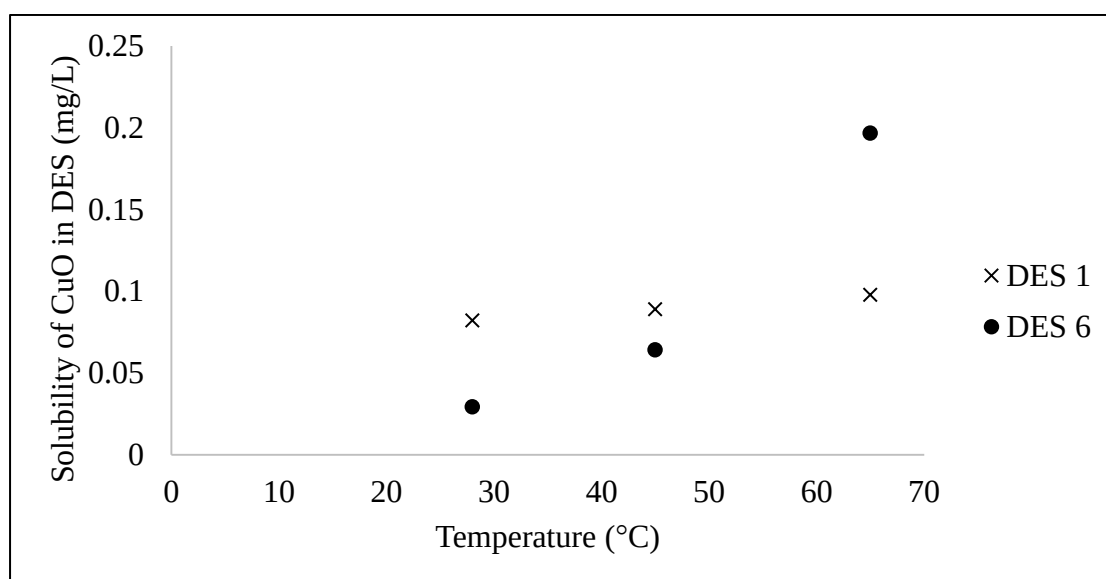


Figure 5. Solubility Profile of CuO in DES 1 (ChCl: Glycerol) and DES 6 (MTPB: Glycerol) as a Function of Temperature

The increase in solubility of CuO in the DESs is due to the increase in kinetic energy among the particles when subjected to higher temperature in which the solids move readily between the solution and the solid phase. It is apparent that both the DESs show increase in solubility with increase in temperature as mentioned in the second law of thermodynamics.

Figure 3 represents the results for the solubility of ZnO in DES 1 and DES 6 at 28, 45 and 65°C. It is observed that the solubility of ZnO exhibits an increasing trend in DES 6 but shows a decreasing trend in DES 1. ZnO is most soluble in DES 6 (0.575 mg/L) and least soluble in DES 1 (0.267 mg/L) at 65°C.

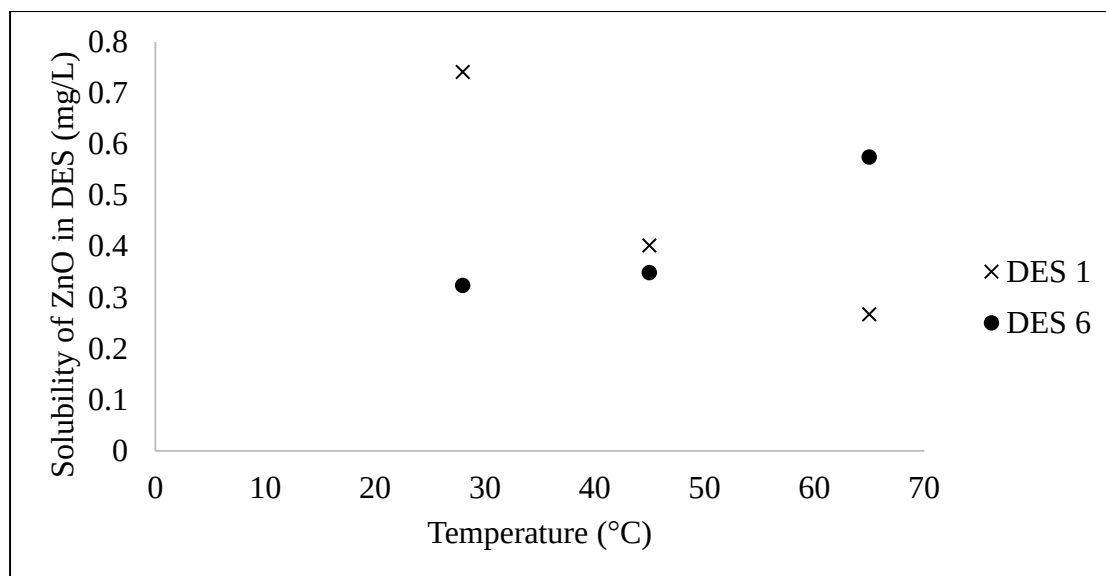


Figure 6. Solubility Profile of ZnO in DES 1 (ChCl: Glycerol) and DES 6 (MTPB: Glycerol) as a Function of Temperature

As mentioned earlier, the increase in heavy metal solubility in the DESs are due to the increase in kinetic energy among the particles at high temperatures. However, the trend observed with ZnO differs from the trend observed with CuO for DES 1 and DES 6. The difference in solubility can be due to the presence of different anion groups in the DES in which DES 1 has Chloride (Cl^-) ions whereas DES 6 has bromide (Br^-) ions. Since both DESs are comprised of the same HBD, glycerol, the solubility is also affected by the presence of three hydroxyl group in glycerol.

Similarly, Figure 6 below shows the solubility profile of CuO in DES 2 (ChCl: Glycerol) and DES 7 (MTPB: Glycerol). Both the DESs were synthesised with salt to HBD ratio of 1:3. Based on the figure, DES 7 shows an increasing trend in solubility with respect to temperature, however, the increasing trend in DES 2 experiences a decline in solubility at 65°C. The highest solubility was achieved by DES 7 (0.169 mg/L) whereas the lowest solubility was achieved by DES 2 (0.116 mg/L).

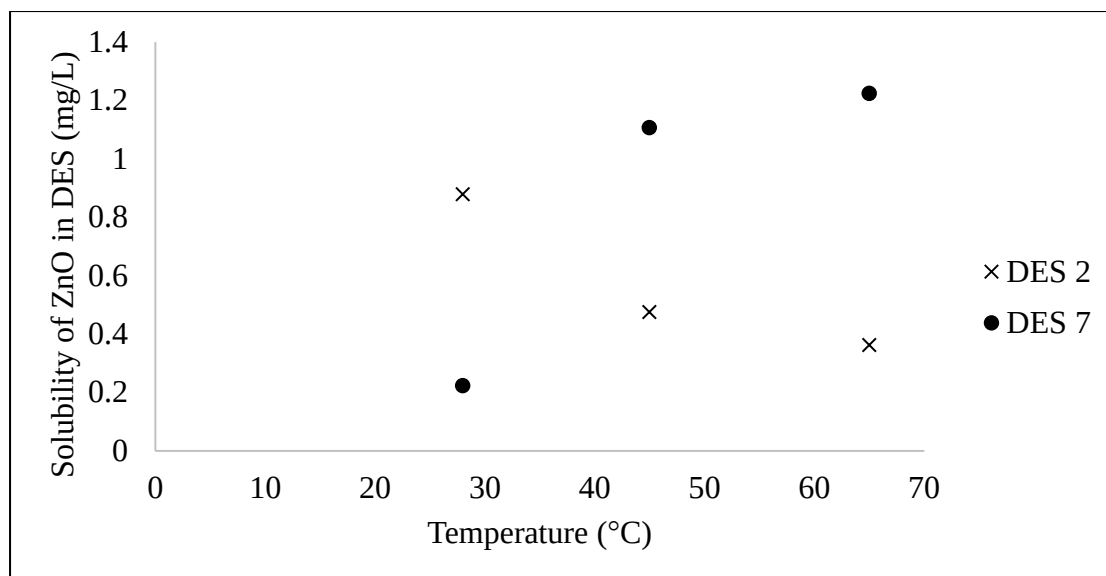


Figure 7. Solubility Profile of CuO in DES 2 (ChCl: Glycerol) and DES 7 (MTPB: Glycerol) as a Function of Temperature

The variation in the trend of solubility depends on the increase in temperature. It can be observed that DES 2, which is the ChCl based DES experiences a decline after 45°C. This indicates that this type of DES does not exhibit good solving properties at high temperature. However, DES 7, which is a MTPB based DES showed better solving properties when subjected to higher temperature.

Based on the solubilities of CuO and ZnO in all the synthesised DESs, it can be seen that the difference of solubility between each temperature show variation as small as 0.001 mg/L. Besides that, the range of temperature that was studied, 28, 45 and 65°C should be increased in order to understand the significance of temperature in the solubility of these metal oxides. This is because the incubator shaker equipment is also subjected to heat losses and may have caused slight deviation in the readings obtained. However, higher solubility readings at 45°C compared to 65°C in some DES combination requires further investigation to justify the sudden decline in solubility.

4.2.1 Effect of Type of DES

The 10 types of DES which were synthesised in this research study each have a unique combination of salt to HBD molar ratio. Figure 5 illustrates the solubility profile of CuO in DES 3, 4 and 5 with salt to HBD ratio of 1:3, 1:4 and 1:5 respectively. These DESs are made up of ChCl and TEG. The solubility profile shows an increasing trend as the temperature increases from 28 to 45°C, but experiences a decline at 65°C. DES 5 which has the highest HBD content compared to DES 3 and 4 exhibits the highest solubility at 45°C (0.0602 mg/L) followed by DES 3 (0.0503 mg/L) and DES 4 (0.0325 mg/L).

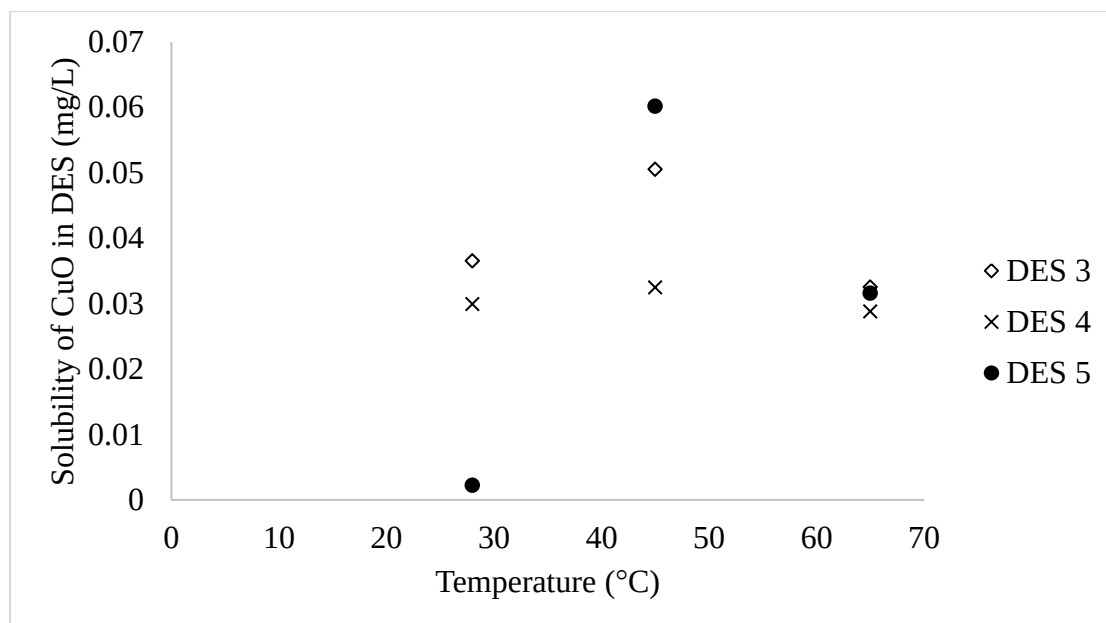


Figure 8. Solubility Profiles of CuO in DES 3- DES 5 (ChCl: Triethylene Glycol)
as a Function of Temperature

The increase in the amount of HBD in a particular DES plays a significant role in affecting the solubility properties of the solvent. In this case, DES 5 which has the highest amount of TEG content exhibits the highest solubility at 45°C. The presence of two hydroxyl functional groups in TEG affects the solubility of CuO. The higher number of hydroxyl group present in the DES increases the strength of the intermolecular forces formed between the heavy metal oxides and DES.

Figure 6 shows the solubility profile of CuO in DES 8, 9 and 10 which comprise of MTPB and TEG with salt to HBD ratio of 1:3, 1:4 and 1:5 respectively. DES 8 exhibits the highest solubility among the rest at 45°C (0.105 mg/L). However, CuO showed the lowest solubility in all three DES at 65°C where DES 10 has the lowest solubility (0.017 mg/L) compared to DES 9 (0.021 mg/L) followed by DES 8 (0.030 mg/L).

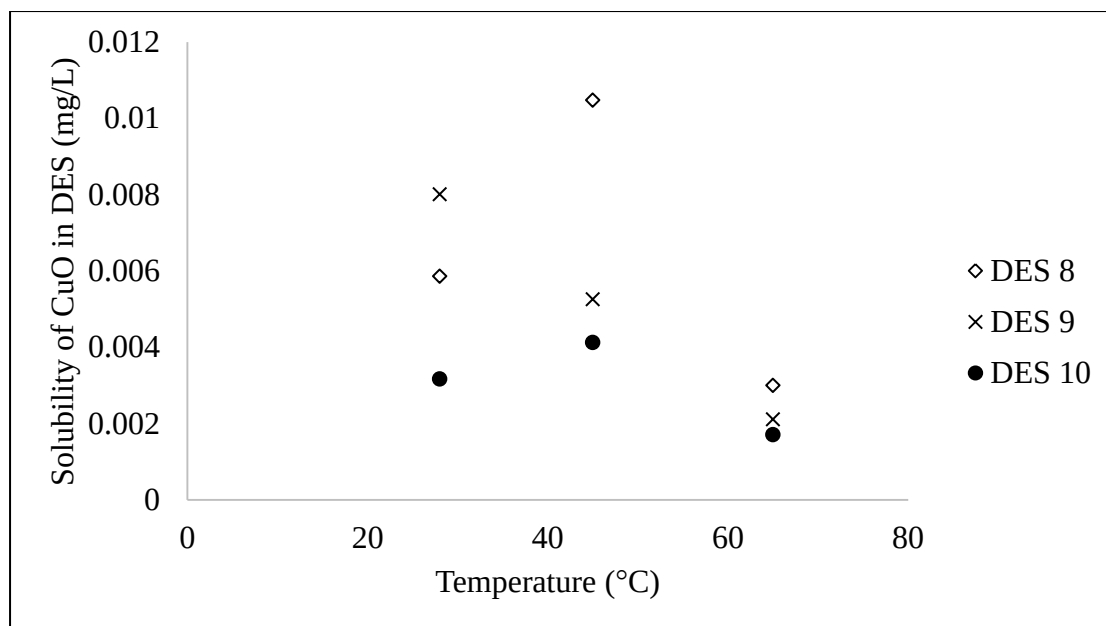


Figure 9. Solubility Profiles of CuO in DES 8- DES 10 (MTPB: Triethylene Glycol) as a Function of Temperature

The solubility of CuO in ChCl based DESs (DES 3- 5) and MTPB based DESs (DES 8- 10) showed a similar trend in which the solubility was the highest at 45°C compared to 28 and 65°C. However, the solubility readings for MTPB based DESs were slightly higher compared the ChCl based DESs.

4.2.3 Effect of Type of Heavy Metal Oxides

The solving ability of the DESs is influenced by the type of heavy metal ion present in the solution. The heavy metal oxides, CuO and ZnO belong in the transition elements group in the periodic table. The ions that constitute the metal oxides, Cu^{2+} and Zn^{2+} are metal cations which are also known as Lewis acids. These metal cations act as electron pair acceptors when mixed with the DES.

Figure 8 shows the comparison between the solubility of CuO and ZnO in the synthesised DESs at 28°C. Based on the figure, it is apparent that the solubility of ZnO is significantly higher compared to CuO in all the DESs. The solubility of ZnO was found to be the highest in DES 2 (0.879 mg/L) followed by DES 1 (0.744 mg/L). In contrast, the solubility of CuO was found to be the highest in DES 1 (0.089 mg/L) followed by DES 2 (0.082 mg/L).

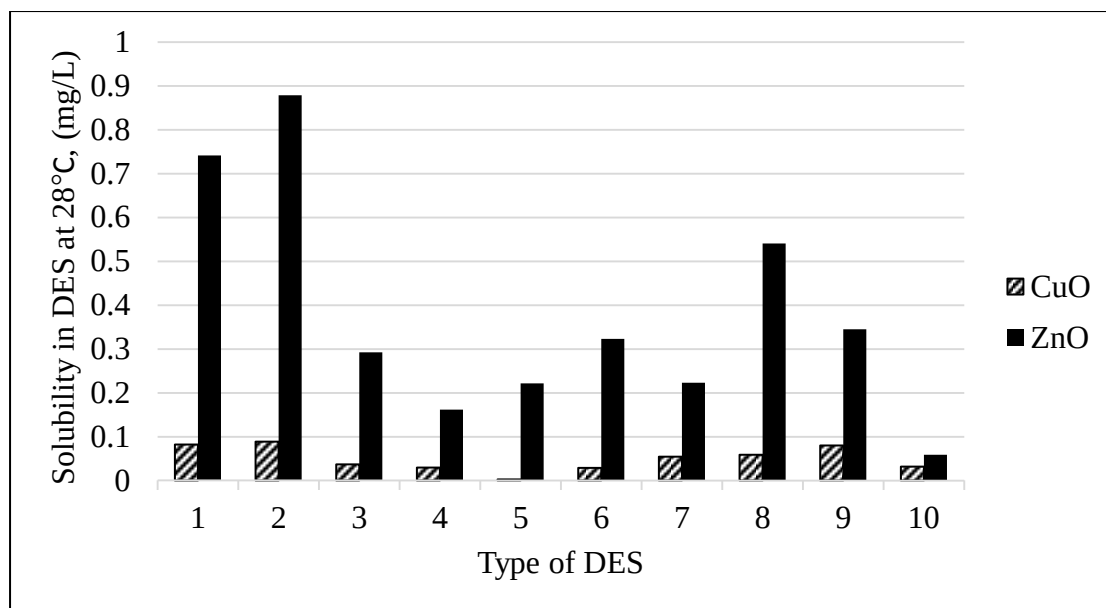


Figure 10. Solubility of CuO and ZnO in DESs at 28°C

Based on the results obtained, ZnO was found to be more soluble in the DES when compared to CuO. Higher solubility is observed in samples containing ZnO as they are more ionic compared to CuO (Abbott et al. 2006). However, further studies have to be performed in order to understand the complexation of the heavy metal oxides to form a soluble compound in the synthesised DESs.

4. Conclusion

The solubility of heavy metal oxides, CuO and ZnO in ChCl and MTPB based DESs with different salt to HBD combinations was investigated and analysed using AAS. It was found that CuO has the highest solubility in MTPB-Glycerol (1:2) with 0.197 mg/L at 65°C and the lowest solubility in MTPB-TEG (1:5) with 0.017 mg/L. ZnO was found to have the highest solubility in MTPB-Glycerol (1:3) with 1.225 mg/L and the lowest solubility in MTPB-TEG (1:5) with 0.017 mg/L. The findings obtained from this research study can be enhanced in future work in order to identify a particular DES that exhibit the highest heavy metal oxide solving property since the analysed ions was soluble in all the synthesized DES. Firstly, additional analytical techniques can be applied to understand the behaviour of heavy metal oxide ions in DESs at different temperature conditions. FAB-MS analysis can be employed to understand the binding of DESs with the metal ions during the solubility experiment (Abbott et al. 2006). The measurement of pH must also be performed as it is a crucial analysis for wastewater treatment procedures. Besides that, further study can be done to identify a suitable separation method after DESs are used to dissolve heavy metal ions. The recovery of the spent DESs after allowing the solvent to dissolve the ions is crucial to ensure that the proposed method is suitable to the environment.

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Stability and Characterization of CNT Nanofluids Using Polyvinyl Alcohol Dispersant

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Abstract

In this research, CNT-water nanofluids are synthesized using polyvinyl alcohol (PVA) dispersant where each of the CNT concentration ranging from 0.01 to 0.1 wt% is tested with 0.25 to 3.00 wt% of PVA to optimize the dispersion and stability of nanofluids. The nanofluids are sonicated for 4 hours using ultrasonic water bath and the stability is analyzed using UV-Vis spectrophotometer. The dispersion state of the CNT-water nanofluid is further examined using optical microscope. The stable nanofluids of each CNT concentration identified were then tested for their thermo-physical properties such as thermal conductivity and viscosity with respect to temperature ranging from 25 to 70 °C. The results revealed that 0.5 to 1.5 wt% of PVA dispersant give the optimum stability to the entire range of CNT concentration studied. It was found that the thermal conductivity enhancement of CNT-water nanofluid stabilized by PVA increased non-linearly with temperature. Although PVA suppressed the thermal conductivity of water, the addition of CNT is able to surpass its effect and the results showed that there is approximately 1 to 44 % enhancement for the range of CNT concentration and temperature studied. It was also observed that the viscosity for 1.5 wt% of PVA aqueous solution at 25 °C is approximately 7.5 mPa.s, which is significantly greater than water. However, the presence of CNT nanoparticles is able to reduce the viscosity of its respective optimum PVA solution by 2 to 6% for the entire range of CNT concentrations investigated, showcasing self-lubrication effect of CNT. Moreover, the viscosity of the nanofluids decreases significantly with increasing temperature.

Keywords: Nanofluid, Carbon Nanotube, Polyvinyl Alcohol, Stability, Thermal Conductivity

1. Introduction

Heat transfer fluids such as water, ethylene glycol (EG) and mineral oils are commonly used in the industries as the medium to exchange the thermal energy in heat exchanger, engines, electrical devices, transformer, etc. A fluid with excellent heat transfer properties such as thermal conductivity will significantly enhance the rate of heat transfer and

thus the efficiency of the equipment. However, these conventional fluids often have poor thermal properties which limit their performances and thus the size of the heat transfer equipment need to be increased in order to compensate for its efficiency. Therefore, the approach is to utilize the superior thermal characteristics of solid nanoparticles by dispersing them into the traditional heat transfer fluids. The stable colloidal suspensions with nano-size particles are known as nanofluids. This is due to the facts that the thermal conductivity of solid particle is greater than the water and the nanoparticles have high surface to volume ratio which increases the effective heat transfer surface area [1]. For instance, the thermal conductivity of copper (Cu) nanoparticle is 390 W/mK, which is considerably greater than the thermal conductivity of water of 0.6 W/mK [2].

Different types of metal, metal oxides and carbon based nanoparticles such as are Cu, aluminium (Al), silver (Au), aluminium oxide (Al_2O_3), copper oxide (CuO), titanium oxide (TiO_2), silicon oxide (SiO_2), carbon nanotube (CNT), etc. have been studied extensively to maximize the heat transfer performance of the conventional base fluids. Based on the research done by Choi et al. [3], the dispersion of 1 vol% of CNT nanoparticles in oil without the addition of dispersant is able to enhance the thermal conductivity of oil by 2.5 times. Assael et al. [4] and Wang et al. [5] studied the effect of CNT and CuO nanoparticles in the thermal conductivity of water respectively. The findings reported by Assael et al. [4] showed that the addition of 0.6 vol% of CNT in water is able to show 34% enhancement in thermal conductivity. On the contrary, Wang et al. [5] discovered that 9.7 vol% of CuO is required to produce the same value of thermal conductivity enhancement. This shows that CNT has better thermal performance due to its high aspect ratio which allows them to arrange in three dimensional networks that promote rapid heat flow, thus small fractions of CNT is sufficient to show a significant enhancement in the thermal conductivity of nanofluid [6]. Moreover, the thermal conductivity of CNT is approximately 3000 W/mK, which is remarkably greater than the thermal conductivity of metal oxides nanoparticles with the values ranging from 10 to 50 W/mK [7].

However, CNT nanoparticles are more prone to agglomerations compared to other nanoparticles when there are dispersed in polar base fluids such as water. This is due to the large surface area and high van der Waals forces between the hydrophobic surfaces of the CNT [8]. Therefore, CNT nanoparticles are insoluble in most of the base fluids as they cannot interact with the polar molecules to overcome the large inter-tube attractive forces. Besides causing clogging and erosion in the piping systems and micro-channels, the formation of clusters also increase the sedimentation rate of nanoparticles and thus reducing its heat transfer efficiency [1]. Till now, many efforts have been conducted to maximize and maintain the stability of nanofluid. In general, there are two methods used to disperse the nanoparticles, namely physical and chemical methods. Physical methods involve the usage of mechanical stirrer, homogenizer and ultrasonic agitation to break the agglomerates under high shear rate. However, the suspension will settle down after a short period of time, thus it is normally accompanied by chemical methods to strengthen the stability [9].

Chemical methods can be further divided into surface modification and surface coating. In terms of surface modification, the nanoparticle such as CNT will be oxidized under the presence of acid at high temperature to attach the functional group such as hydroxyl (OH), carboxyl (COOH) or amine (NH_2) to its surface via covalent bond [8]. The polar functional group will increase the interaction of the functionalized CNT with the water molecules. However, the structures of CNT are often damage due to the extreme pH and temperature during the oxidation [10]. Hence, surface coating offers a simpler procedure

where surfactants or dispersant are added to act as a barrier between the nanoparticles. In CNT-water nanofluid, the hydrophobic tail of dispersant will adsorb onto its non-polar surface, while the hydrophilic head extends to the water to provide repulsion between the nanoparticles. Previous researches shown that the addition of dispersant such as Gum Arabic (GA) [8, 11], sodium dodecyl sulfate (SDS) [12-13], sodium dodecyl benzene sulphate (SDBS) [13-14], etc. are able to improve the stability of CNT nanofluid remarkably. To date, GA is the best dispersing agent for CNT nanofluids due to its high hydrophobic polysaccharides content which increases the chances of adsorption onto the nanoparticle surfaces [15-16]. However, GA has low decomposition temperature where the protein compounds tend to precipitate at approximately 90 °C. This will limit the application of the nanofluid dispersed with GA as it cannot be used for high temperature applications.

Therefore, this research involves the study of alternative dispersing agent, which is polyvinyl alcohol (PVA) on the stability of CNT-water nanofluids. The long hydrocarbon chain of PVA with hydroxyl groups is able to withstand temperature up to 200 °C, which makes it a good candidate for dispersing the nanofluids in heat transfer application [17]. The hydroxyl group is responsible for the formation of hydrogen bond with water and thus increasing the solubility of CNT in water. Although the effect of PVA on nanofluids have been studied by Wang et al. [18] and Singh et al. [19], none of it involves the application of PVA on CNT-water nanofluid. Also, the effect of PVA on the stability, thermal conductivity and viscosity of CNT-water nanofluid are still unknown. The viscosity of nanofluid plays an important role in the applications involving fluid flow as it will affect the pumping cost and pressure drop in pipes. This objective of this study is to optimize the amount of PVA dispersant (0 to 3 wt%) in different concentrations of CNT nanoparticles (0.01 to 0.10 wt%) in order to synthesize the nanofluids with maximum stability. This is because excess dispersant will have adverse effect on the stability, thermal conductivity and viscosity of the nanofluid [20]. Moreover, the effect of PVA and CNT on the thermo-physical properties of stable CNT-water nanofluids such as thermal conductivity and viscosity are investigated with respect to temperature.

2. Research Methodology

2.1 Materials

The MWCNT with the purity $\geq 95\%$ is obtained from Laboratory and Scientific Enterprise, Malaysia. The average dimensions of the individual tube in terms of outer diameter and length is 25 nm and 20 μm respectively. The PVA dispersant is obtained from Ever Gainful Enterprise Sdn. Bhd., Malaysia. The thermal conductivity of CNT and PVA is 3000W/mK and 0.2 W/mK respectively, while the decomposition temperature of PVA is 200 °C.

2.2 Preparation of Samples

A low range of CNT concentrations, 0.01 wt%, 0.02 wt%, 0.04 wt%, 0.08 wt% and 0.10 wt% are used in this study to minimize the tendency of agglomeration as the stability of nanofluids tend to decrease due to the formation of dense solution as CNT concentration increases [21]. Each CNT concentration is tested with a wide range of PVA concentrations which are 0.25 wt%, 0.50 wt%, 1.0 wt%, 1.5 wt%, 2.0 wt%, 2.5 wt% and 3.0 wt% respectively so that the optimum PVA concentration required to produce a CNT-water nanofluid with maximum stability can be obtained [8, 22]. The amount of CNT, PVA and

water are measured using a four decimal point electronic weighing balance (BEL M164A, Italy) to make up a total weight of 40 grams. Then, the nanofluids are sonicated for 4 hours at temperature and frequency of 60 °C and 35 kHz respectively using ultrasonic bath (Elma Transsonic TI-H-15, USA) to detangle the CNT for the adsorption of PVA dispersant on the surface. The sonication temperature is set at 60 °C to improve the diffusional rates and the frequency of collision between the individual tubes and PVA molecule. It must be noted that the temperature of water bath must not exceed 80 °C as it may change the properties of nanoparticles [23-24]. Based on previous studies, 4 hours sonication time at 35 kHz is the optimum duration to maximize the adsorption of dispersant on the CNT [8]. Prolonged sonication can lead to dislocation of carbon structure and reduces the aspect ratio of CNT which will affect the thermal properties of CNT [25].

2.3 Stability Study of Nanofluids

The stability of each sample is analyzed for a period of 20 days using UV-vis spectroscopy (Shimadzu UV-1800, Japan). The nanofluids and their respective blanks are transferred into the cuvette cells immediately after sonication. The function of blanks which consist of water and PVA is to eliminate the absorbance of both water and PVA in the nanofluid so that the absorbance value obtained is purely based on CNT. One of the samples and its respectively blank containing the same PVA concentration are used to determine the absorbance spectrum of the CNT. Based on the absorbance curve shown in Fig. 1, CNT nanoparticles absorbed most of the light energy at the peak of the spectrum, which is 267 nm. The wavelength obtained is used throughout the stability study. Note that the applicable wavelength of the cuvettes used is 220 to 900 nm. Hence, the peaks and fluctuations of the absorbance below 220 nm are not taken into account. A linear calibration curve of absorbance versus CNT concentration as shown in Fig. 2 is constructed to convert the absorbance value into concentration of CNT. Therefore, the optimum concentration of PVA required to produce the most stable nanofluid for each CNT concentration can be determined based on the graph of CNT concentration against sedimentation time.

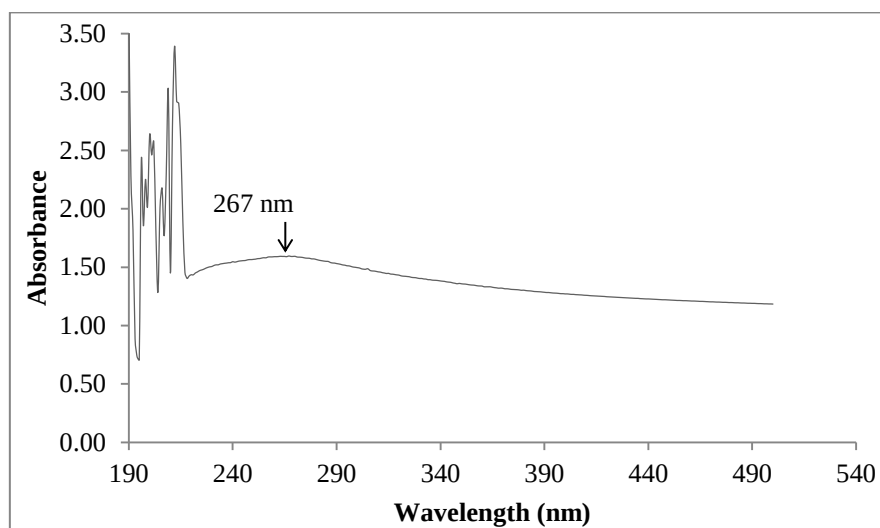


Figure 1. Absorption spectrum of CNT.

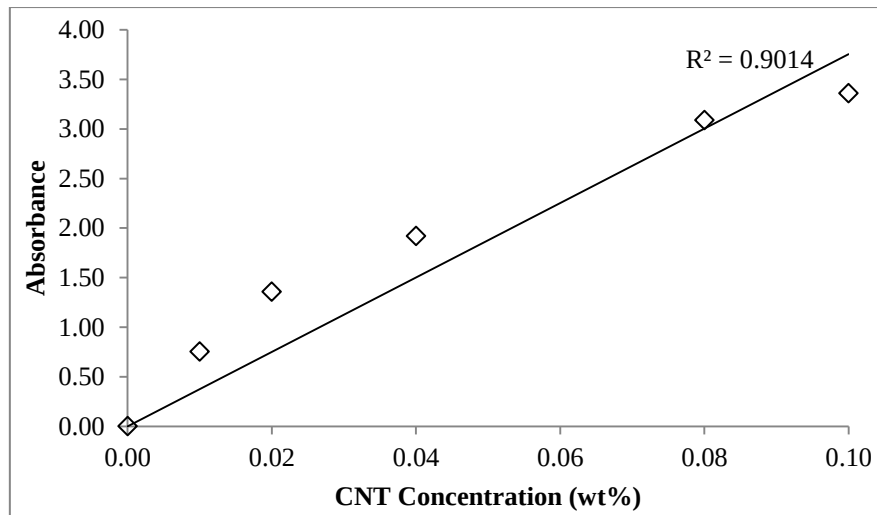


Figure 2. Calibration curve of CNT-water nanofluid at 267 nm.

2.4 Characterization of Nanofluid

The five stable samples of different CNT concentrations with its optimum amount of dispersant identified from the stability study were further characterized using optical microscope (Swift M10D, USA) at 40X magnification. This is to estimate the dispersion characteristic of the nanofluid by examining the size of the cluster formed in the range of micrometres because stable nanofluid will have lesser and smaller agglomerates [22].

2.5 Thermo-Physical Properties of Nanofluids

The thermo-physical properties such as thermal conductivity and viscosity of stable nanofluids are measured with respect to temperatures at 25 °C, 40 °C, 55 °C and 70 °C.

2.5.1 Thermal Conductivity

The thermal conductivity of stable nanofluids are measured using a transient line source (TLS) thermal conductivity meter (Decagon KD2 Pro Thermal Analyzer, USA) with a 6 cm needle sensor (KS-1) which is suitable for water based fluid. The thermal conductivity meter is calibrated with a standard glycerin solution at room temperature each time before measurement and the samples are placed in an enclosed water bath to control the temperature throughout the experiment. Due to the high sensitivity of the thermal conductivity meter to slight changes in the surrounding such as temperature, vibrations and air flow, the experiment was conducted in a quiet and still environment to reduce fluctuations. First few readings were ignored until equilibrium in temperature was reached. Further, at least 10 readings were recorded at 15 minutes interval with error value smaller than 0.01 and averaged.

2.5.2 Viscosity

The viscosity of stable nanofluids for 0.01, 0.04 and 0.10 wt% are measured using a viscometer (Brookfield DV-II+ Pro, USA) with UL adapter which is suitable for viscosity range of 1 to 10 cP. 20 mL of the samples are transferred into the adapter and the rotational speed of the cylindrical spindle is set at 100 rpm (122 s^{-1}), which is the optimum speed for

low viscous and water based fluid. A circulating water bath is used to flow the water across the adapter in order to maintain the temperatures of the samples throughout the experiment. The experiment was repeated 3 times and averaged.

3. Results and Discussion

3.1 Stability Study of Nanofluids

Fig. 3 to Fig. 7 shows the effect of dispersant concentration on the stability of CNT-water nanofluid with respect to sedimentation time. Lack of dispersant might have little or no effects on the stability of nanofluid as the hydrophobic surface of CNT is not fully coated with dispersant. On the contrary, too much dispersant will have adverse effect on the stability of nanofluid because it will weight down the CNT particles and increases the rate of sedimentation [22]. Therefore, it is essential to determine the optimum concentration of PVA dispersant in CNT nanofluid in order to maintain the long term stability of CNT-water nanofluid. Based on the graphs, there were slight sedimentations observed at the beginning of the study period as the concentration of CNT in the suspension decreases with time. This is due to the agglomeration and settlement of uncoated CNT nanoparticles when the dispersion is not agitated [26]. However, the sedimentation rate decreases and reaches a constant value after the suspension and the bonding between the CNT and PVA is stabilised.

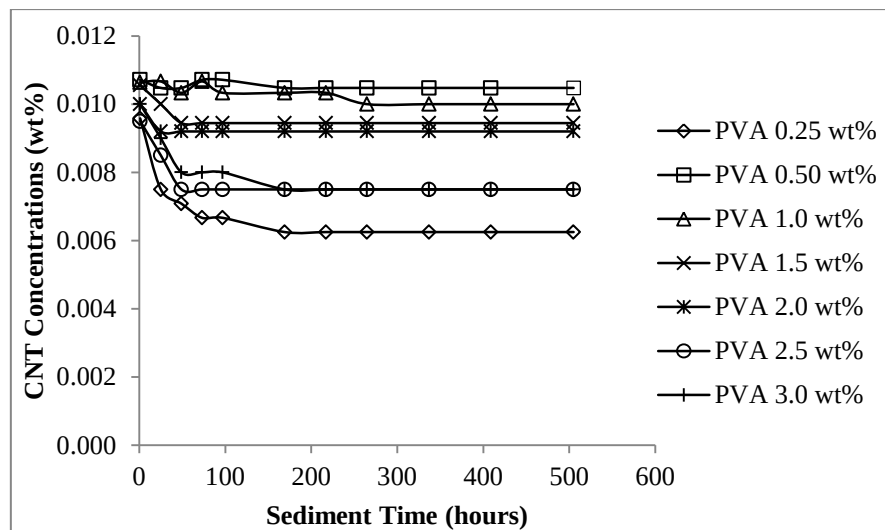


Figure 3. Effect of PVA concentration on 0.01 wt% of CNT.

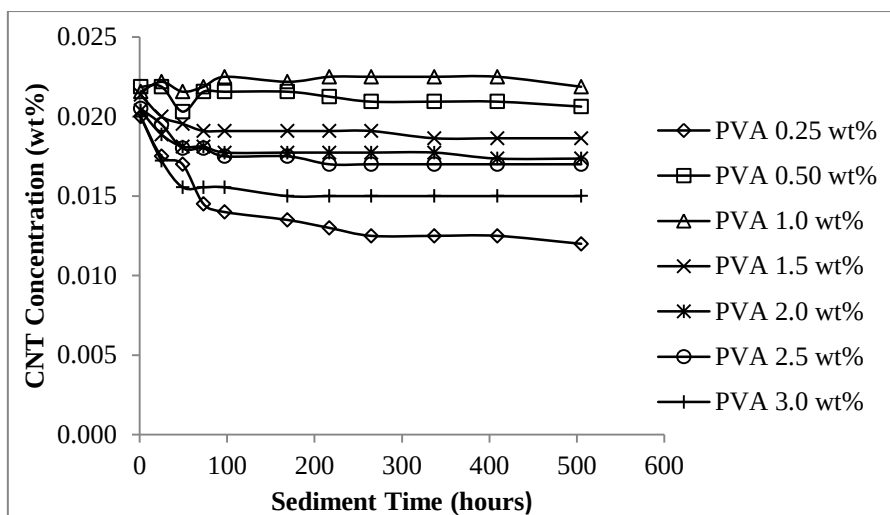


Figure 4. Effect of PVA concentration on 0.02 wt% of CNT.

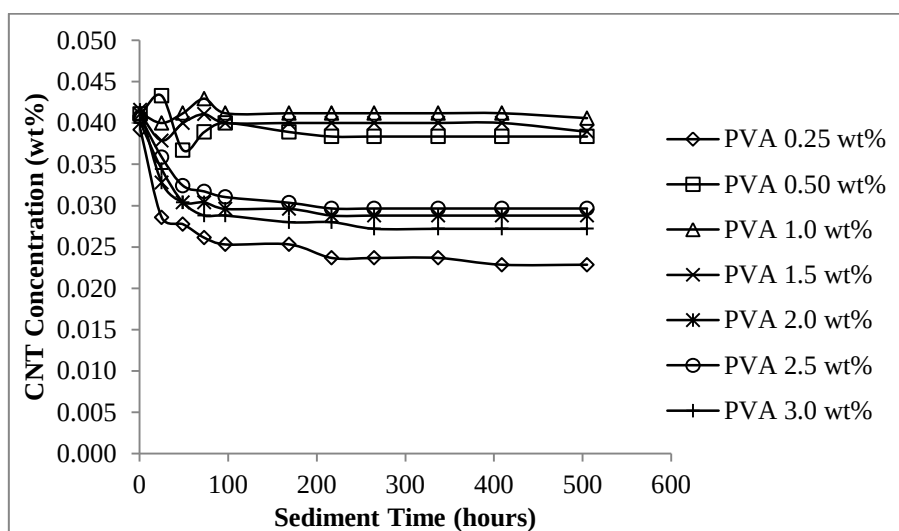


Figure 5. Effect of PVA concentration on 0.04 wt% of CNT.

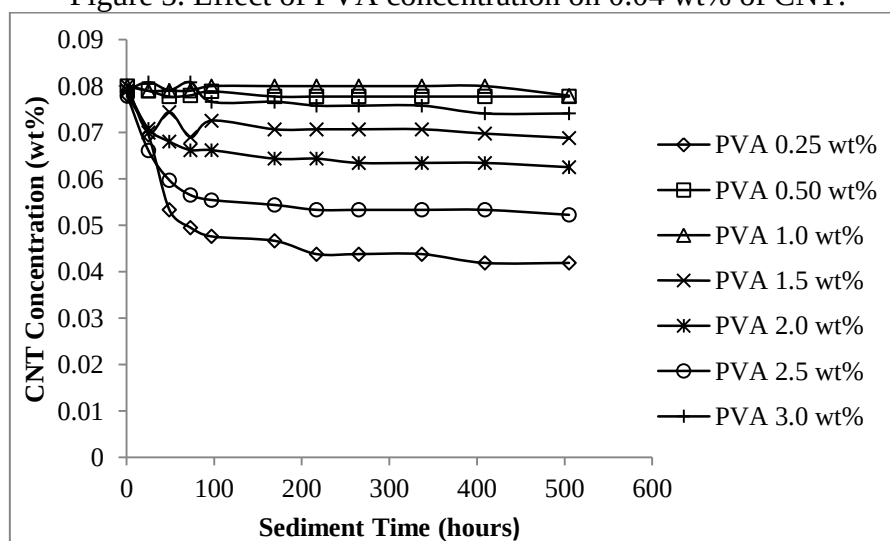


Figure 6. Effect of PVA concentration on 0.08 wt% of CNT.

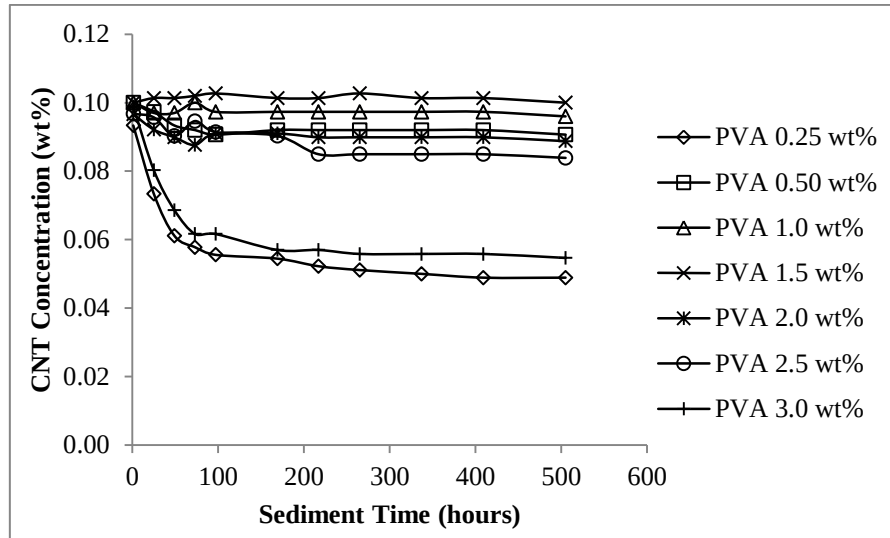


Figure 7. Effect of PVA concentration on 0.10 wt% of CNT.

It is observed that the optimum PVA concentration needed to stabilize the nanofluid increases with CNT concentration. As the CNT concentration increases, more amount of PVA is required to adsorb onto the hydrophobic site in order to fully separate the individual tube during ultrasonication. However, increasing the concentration of PVA beyond its optimum value will have adverse effect on the nanofluid dispersion. The PVA molecules will tend to self-aggregate and form reverse micelles due to the presence of additional dispersant molecules which is not adsorbed onto the CNT [20, 27]. In this study, it is proven that PVA dispersant is able to maintain the dispersion of CNT nanoparticles in the water by overcoming the attractive forces or Van der Waals forces between the neighboring tubes via steric repulsion. The optimum concentration of PVA dispersant for each CNT concentration is summarized in Table 1.

Table 1. Optimum concentration of PVA dispersant for each CNT concentration.

CNT Concentration (wt%)	PVA Concentration (wt%)
0.01	0.5
0.02	1.0
0.04	1.0
0.08	1.0
0.10	1.5

3.2 Characterization of Nanofluid

The optical images of stable nanofluid samples with its optimum amount of PVA are shown in Fig. 8.

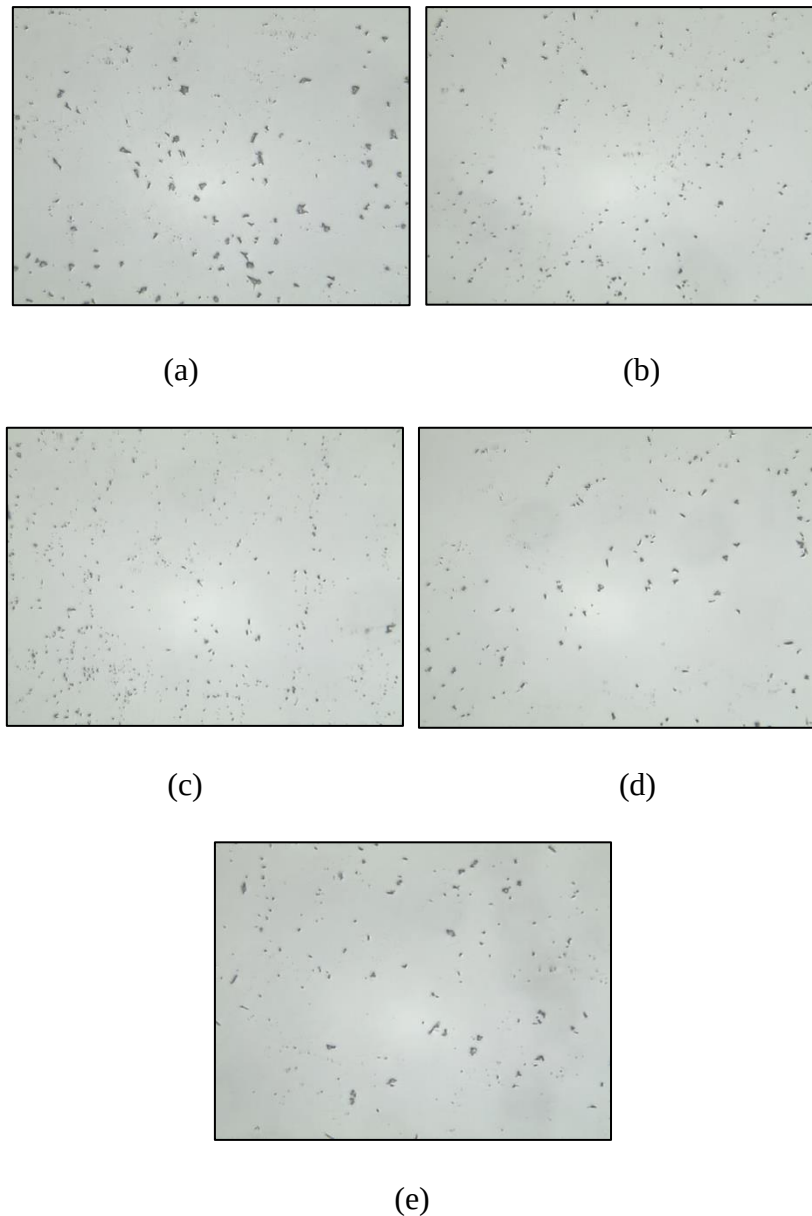


Figure 8. Optical images of nanofluids with difference amount of CNT, (a) 0.01 wt%, (b) 0.02 wt%, (c) 0.04 wt%, (d) 0.08 wt%, (e) 0.10 wt%.

Based on Fig. 8, it is observed that 0.01 wt% CNT has the largest size of agglomerates compared to the rest. This might be due to the low concentration of CNT in water which reduces its chances of collision with the PVA dispersant during the sonication process. Hence, the individual nanotubes which are not attached to the dispersant molecules are most likely to re-aggregate [28]. It is further observed that 0.02 wt% and 0.04 wt% of CNT has the smallest size of agglomerates. However, the size of the agglomerates appears to be larger as the CNT concentration increases. This is because the high concentration of CNT in the base fluid gives rise to a more dense nanofluid, which reduces the stability of the suspension as dense particles are more prone to sedimentation [29]. Thus the settled particles will re-aggregate once they accumulated at the bottom of the tube. Note that all the optical microscope images are taken after 2 months where the fresh samples of nanofluids are more likely to have smaller size of agglomerates.

3.3 Thermo-Physical Properties of Nanofluids

3.3.1 Thermal Conductivity

The effect of PVA on the thermal conductivity of water is shown in Fig. 9. It can be seen that the addition of PVA suppresses the thermal conductivity of water due to the lower thermal conductivity of PVA (0.2 W/mK) compared the water (0.6 W/mK). On the other hand, Fig. 10 shows the effect of temperature and CNT concentrations with its optimum amount of PVA on the thermal conductivity of water. The percentage of enhancement in the thermal conductivity of nanofluids is shown in Fig. 11 where it is calculated using Eq.1, where k_{eff} and k_f is the effective thermal conductivity of nanofluid and the thermal conductivity of base fluid (water) respectively.

$$\text{Percentage Enhancement} = \frac{k_{eff} - k_f}{k_f} \times 100\% \quad (1)$$

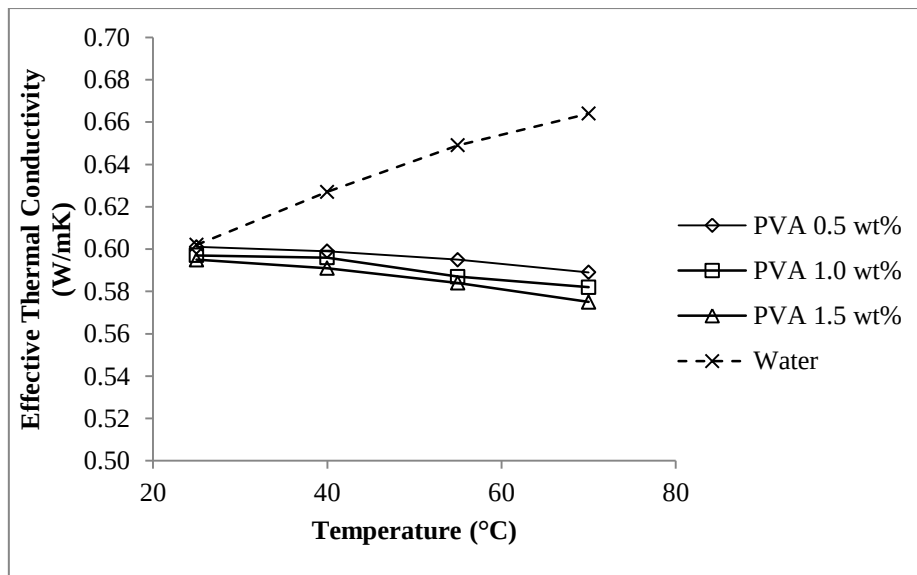


Figure 9. Thermal conductivity of PVA aqueous solution with respect to temperature.

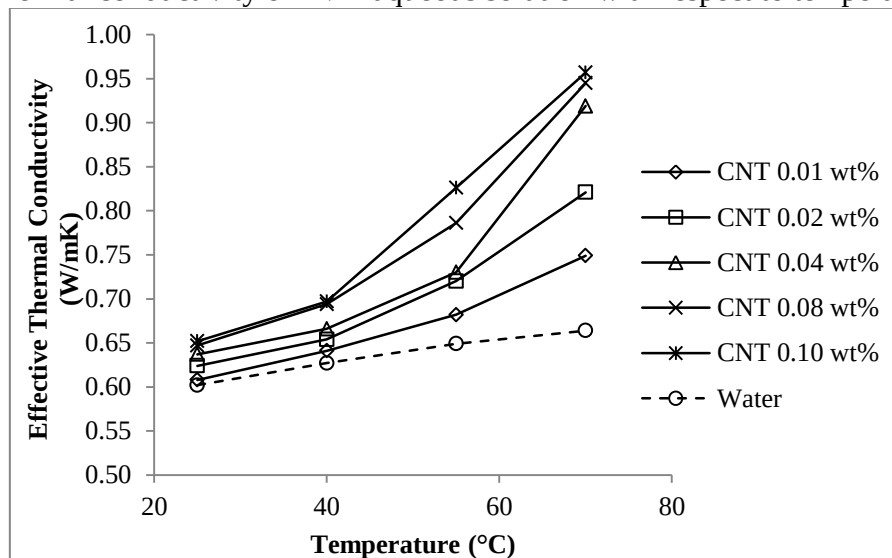


Figure 9. Effective thermal conductivity of CNT-water nanofluids with its optimum PVA concentrations with respect to temperature.

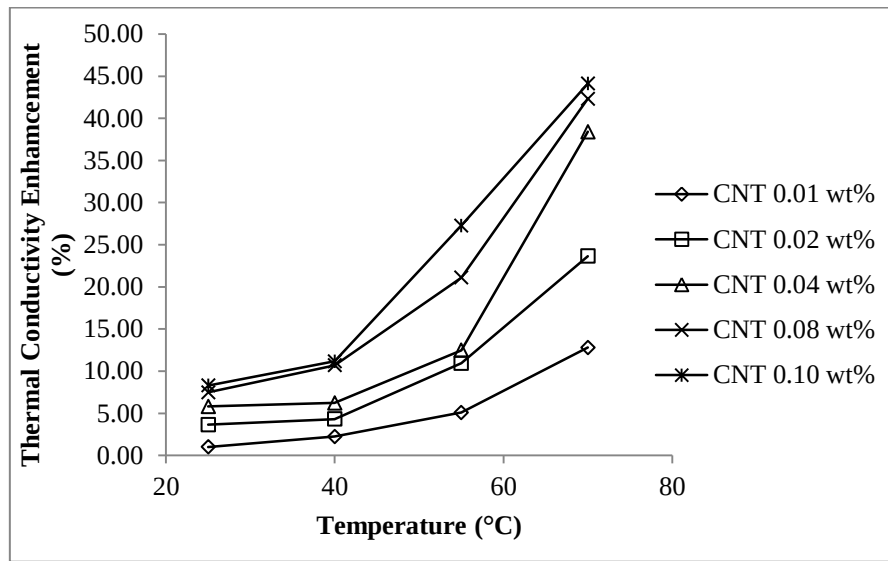


Figure 10. Percentage enhancement in thermal conductivity of nanofluids with its optimum PVA concentrations with respect to temperature.

It can be observed that the effective thermal conductivity and the thermal conductivity enhancement of the stable nanofluids with its optimum amount of PVA increases with increasing CNT concentration. At 25 °C, the enhancement increases from 1 to 8.3 % at CNT concentration of 0.01 to 0.10 wt%. Although PVA suppress the thermal conductivity of water, the addition of CNT enhances the thermal conductivity of water. This is attributed by the excellent thermal conductivity of CNT nanoparticles where the increasing amount of CNT in water base fluid raises the resulting thermal conductivity of the nanofluids [8]. In short, the greater the amount of CNT suspended in the solution, the higher the thermal conductivity of nanofluid. The CNT-water nanofluid stabilized with optimum amount of GA studied by Rashmi et al. [21] showed a greater percentage enhancement, which is 4 to 37% at 25 °C for the same range of CNT concentration tested. This is because GA further enhances the thermal conductivity of water by 1.2% at 1.0 wt% of GA aqueous solution instead of suppressing it. However, this study showed greater enhancement in CNT-water thermal conductivity compared to other literatures due to the high stability of nanofluids with optimum amount of dispersant.

Moreover, the thermal conductivity of nanofluids also increases with temperature and the effect is much pronounced at 40 °C. This is due to the Brownian motion of the nanoparticles where the nanoparticles are able to gain more kinetic energy at higher temperature. The CNT with high energy content will tend to move faster and bombard with each other, leading to a substantial increase in the thermal conductivity of nanofluids [30]. Overall, the CNT-water nanofluids stabilized with its optimum PVA concentration respectively are able to show 1 to 44% enhancement in thermal conductivity for the range of CNT concentration and temperature studied.

3.3.2 Viscosity

Fig. 11 shows the effect of PVA and CNT-water nanofluids with optimum amount of PVA on the viscosity of water. It is observed that the addition of PVA increases the viscosity of water significantly. This is due to the high molecular weight and long polymeric chain of PVA molecules where the hydroxyl groups will form inter and intra hydrogen bonding with each other as well the hydrogen bonding with water molecules [31]. The presence of such linkages leads to the enhancement of viscosity of water. However, the addition of CNT into their corresponding optimum PVA solution decreases the viscosity of PVA aqueous solution by approximately 2 to 6%. This is can be explained by the self-lubricating effects of the CNT where the nanotubes are able to arrange themselves in the same orientation along the flow direction and slide against each other when forces are applied, causing the viscosity to decrease [32].

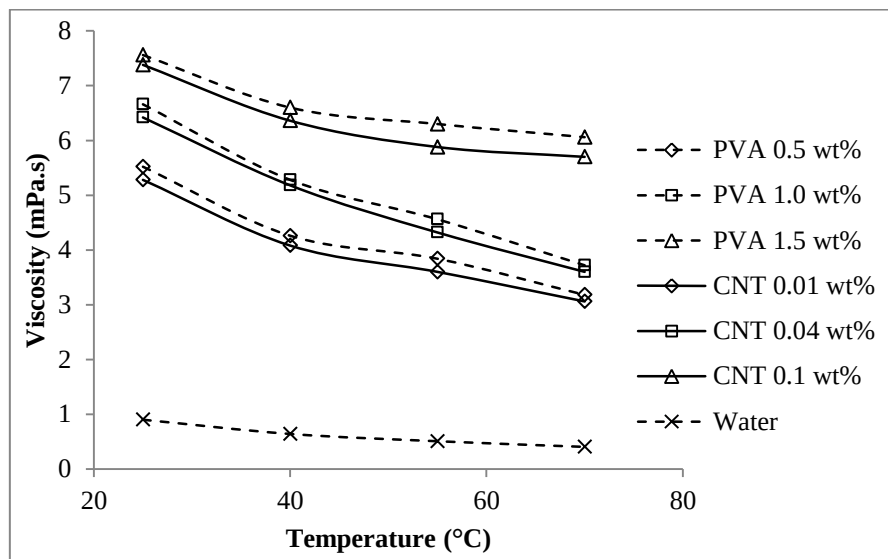


Figure 11. Viscosity of PVA aqueous solution and CNT-water nanofluid stabilized with optimum PVA at different temperature.

In addition, the increase in temperature reduces the viscosity of PVA aqueous solution and nanofluid due to the increase in kinetic energy and movement of the molecules where it will weakens the hydrogen bonds and thus reducing the viscosity [31]. The viscosity of CNT-water nanofluids stabilized with its corresponding PVA dispersant is remarkably greater than the water base fluid. Although high viscosity is undesirable as it will increase the pressure drop along the pipes and pumping cost, the rheological behavior can be further tested in the future as the CNT-water nanofluid stabilized by PVA may exhibit shear thinning behaviors where the viscosity will decrease with increasing shear rate. This parameter is important as the heat transfer fluid in real life application will be constantly subjected to different forces and shear rates under certain circumstances where it will alter the viscosity of nanofluid.

4.0 Conclusion

In conclusion, nanofluid has a promising potential to enhance the heat transfer properties of the conventional base fluid, given that the appropriate dispersant is used to stabilize the nanoparticles. In this case, PVA is able to maintain the stability of CNT-water nanofluid for the entire research period of approximately 3 months. Although PVA suppresses the thermal conductivity of water, the effect is being counterbalanced by the

addition of CNT. The CNT-water nanofluid stabilized with its optimum amount of PVA showed 1 to 44% enhancement in thermal conductivity for 0.01 to 0.10 wt% of CNT at temperatures of 25 to 70 °C. Also, the nanofluids studied possess high viscosity at low shear rate of 122 s^{-1} . Hence, detail investigations on the rheological properties and nanoparticle Brownian motion should be performed in the future to understand the effect of shear rate on the viscosity of nanofluids and the non-linear behavior of thermal conductivity enhancement of nanofluids as a function of temperature respectively.

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The thermal degradation effect on Thermoplastic Starch (TPS) / Montmorillonite nano-clay (MMT) / Alumina Trihydrate (ATH) nanocomposites

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Abstract

In the chase of enhance performance and characteristics of polymers in terms of thermal degradation, one of the answer is introducing nanoclay and flame-retardant component to produce nanocomposites. Although cross-linking is a common approach to enhance the properties of starch films, current starch cross-linking methods are either expensive, toxic or does not offer desired properties. In this research, TPS based nanocomposites is prepared using ATH and MMT by solution casting method with citric acid (CA) as cross-linking agent. The mechanical disadvantage of TPS can be improved by introducing MMT and ATH whereas ATH is capable to reduce thermal decomposition and acts as fire retardant in polymer. This study aims to determine the effect of thermal degradation of TPS/MMT/ATH blends. Moreover, the combined interaction between the nano-clay, ATH and CA component in weight loss of thermoplastic starch are analysed using a Design of Experiment approach. The prepared nanocomposites are characterized through Differential Scanning Calorimetry (DSC) and method of Weight Loss at Different Temperature is introduced to determine thermal properties and weight loss of blends, respectively. In addition, the formation of crosslinking networks in polymer matrix could enhance the thermal stability when CA is used. Meanwhile, high loading level of ATH will result of better thermal stability effect as the weight loss % reduces. However, MMT offer the optimum thermal stability at medium loading level given that it delayed the thermal decomposition temperature and also increased formation of the char residue which is able to slow down the combustion process. Consequently, nanocomposite has result an overall improvement in terms of thermal stability thus presenting new class of biodegradable and environmental acceptable material.

Keywords: Nanoclay, Nanocomposite, Citric Acid, Thermal Degradation, Cassava Starch.

1. Introduction

In recent years, synthetic polymers are produced from petrochemicals and are non-biodegradable. These polymers are the origin of environmental pollution, endangering human-welfare and wildlife when implemented into nature. Apart from this, plastics also play a role in waste management where the society responsible with large amount of waste discharging expenses. To overcome this drawback, by introducing biodegradable polymers would be another alternative way to overcome restriction of the petrochemical resources in the future. There are some abundant biodegradable polymers that originates from biomass, micro-organisms, biotechnology and petrochemicals such as chitin, protein, polyhydroxyalkanoates as well as poly(lactic acid)[1].

Starch is economically competitive with polymers originated from petroleum manufactured packaging materials since starch can be biodegrade in soil and water entirely and it is rather low cost. Starch is comprised of repeating α -D-glucopyranosyl units which include of a mixture of a linear polysaccharide-amylose and a highly branched polysaccharide-amylopectin. Unfortunately, starch has poor mechanical properties, brittle, sensitive to environmental humidity and difficulty in processing when compared with synthetic polymers since they have the nature of hydrophilic. Besides, starch exists in granular form where the molecular order within the granules must be destroyed to enhance its processability [2]. Cassava starch is chosen for research since cassava starch or commonly named as tapioca starch is widely cultivated and commercialized in Malaysia due to sufficient availability and this type of starch is proven to be highly effective for TPS production [3].

Native starch can be converted into thermoplastic materials via addition of plasticisers (e.g. glycerol) under high temperature and extensive shear stress conditions, which results in the gel like material which is thermoplastic starch (TPS). Hence, plasticiser is used to modify properties of polymer matrix by heating polymer and mixed well with plasticiser in order to ensure resin is completely dispersed in plasticiser. At the meantime, it opens up free volume between molecular chains as well as molecular mobility of polymers [4]. Glycerol is the most common used plasticiser when blended with cassava starch that could increase the molecular mobility of glucan chain which indirectly enhance starch characteristics for this promising bio-polymer based film formulation [5].

The mechanical weakness of TPS can be ameliorate by introducing inorganic reinforcing material, nanoclay or more specifically known as Montmorillonite (MMT). Despite of these, MMT has nowadays arise as grand interest for science researchers due to its nature and low content could achieve favourable mechanical properties. Due to its large specific surface area, high swelling capacity, adsorption capacity, high cation exchange; hence, outstanding mechanical and its thermal resistance characters can be achieved [6]. Modification of natural clays using organic cations is taken place in order to favour dispersion of clay nanolayers within the polymer matrix to form organo-modified nanoclays. As Huang et al. [7] has been said that the mass loss of composites with 30wt% of MMT is 11.64% which is relatively lower than only glycerol plasticised TPS. Chang et al. [8] indicated that thermal stability of composite sample containing ATH and MMT performed better at higher temperature since MMT offer better barrier in EVA matrix.

The widespread synthetic polymer has raised the flammability of human's environment that accompanied by releasing of corrosive or toxic gases and smoke during combustion. Aluminum Trihydroxide (ATH) blends could improve fire retardancy of polymer. For physical action, endothermic decomposition of flame retardant additives will reduce the temperature by heat consumption. These additives is the reason to form protective solid or gaseous layer between the gaseous phases where combustion process occur [9]. Protective layer formed enable to restrict the transfer of substance such as oxygen and combustible volatile gases. Hence, the amount of decomposition gases released will reduce. ATH filler enhance the stiffness of the polymer matrix, heat resistance significantly as well as cut down the expenses of material [10]. It is also known as non-halogen flame retardants which is used to replaced halogen-flame retardants that would emit hazardous gases during combustion and reduce smoke emission [11]. Chang et al. [8] revealed that EVA/ATH/Organic MMT(OMMT) sample exhibited a two-stage weight loss. It is also realized that ATH enhances flame retardancy by delaying the oxidation of material, decomposition of material are non-combustible and eventually, EVA will be more stable.

In order to overcome hydrophilic and hygroscopic character of thermoplastic starch, barrier properties against both water vapour and liquid water is improved by cross-linking method [12]. Citric acid is selected because it is biodegradable and renewable since it can be obtained from fruit. Cross-linking starch with citric acid could enhance tensile strength, thermal stability and reduce dissolution of starch films in water. Several researchers reported that citric acid could form ester bond with starch, it enhance thermal and water stability to hinder retrogradation to occur [13]. The thermal degradation effect of starch films can be observed using thermogravimetric analyzer (TGA) where about 20% lower weight loss than the non-cross-linked films after heating the films to 600 °C which indicate better resistance to thermal degradation when citric acid used as cross-linking agent [14]. Citric acid is more favourable for starch cross-linking as low amount (5% or less) are needed for cross-linking reaction.

In this research, TPS based nanocomposites can be prepared using two different nano fillers: ATH and MMT via solution casting method. Sample preparation might be an intricate process; the interaction of the fillers may result in complex conclusions. Hence, a design method known as full factorial design is employed to interpret the data. Characterization of TPS nanocomposite takes place to investigate the properties of thermal stability by using Differential Scanning Calorimetry (DSC) and also applying method of Weight Loss at Different Temperature to determine thermal degradation as well as weight loss effect. This research is mainly focused on the thermal degradation of TPS/ATH/MMT composite with two major objectives as shown:

- To study the thermal degradation of TPS/MMT/ATH blends.
- To analyse the combined interaction between the nano-clay, ATH and citric acid component in weight loss of thermoplastic starch using Design of Experiment approach.

2. Materials and methods

2.1 Design of Experiments

This approach required multiple runs of experiment to investigate the complete parameter space. The experimental design approach of factorial design is implemented as valid method to compare and contrast factorial experiments to randomized controlled trials and maintain quality of data collection. In the research, a 3^3 full factorial is implemented and thus, 27 runs of experiment are conducted with accompanied of 2 controls for better research purpose. It is essential to determine the proper selection of factors and levels. In this research, three main factors: loading levels of MMT, ATH and citric acid are experimented in three levels (eg. low, medium, high) based on literature review on similar field of publications. One of two control samples is composed with nanocomposite of TPS and citric acid with no MMT and ATH as well as nanocomposite of TPS with no addition of ATH and citric acid. The loading level of MMT varied from 1 to 3wt.% [8][15], ATH varied from 14 to 18 wt.% [8] [16], glycerol loading is fixed at 27 wt% (to be further discussed in Preliminary Test) whereas citric acid varied in the range from 1 to 5wt.% [13]. In order to perform detailed data analysis, Minitab17 is utilised for visual analysis which accommodates the best way to correspond with statistical data.

2.2 Materials

Regular cassava starch containing 17% amylose is kindly supplied by SCS Food Manufacturing Sdn. Bhd., Malaysia for preparation of Thermoplastic Starch (TPS). Citric acid ($C_6H_8O_7$) with $1.665g/cm^3$ density and 99% purity is used as cross-linking agent for starch based material purchased from Evergreen Engineering Resources, Malaysia. Glycerol (about 99.8% purity) is used as plasticizer for TPS are obtained from Merck Sdn. Bhd., Malaysia. Treated Montmorillonite nanoclay (Nanolin DK® nanoclay) is purchased from FCC®, Inc., China. The Alumina Trihydrate, $Al_2O_3 \cdot 3H_2O$ (ATH) with purity of 90% flame retardant was also purchased from Evergreen Engineering Resources, Malaysia and used as received.

2.3 Sample Preparation

[1] 2.3.1 Preliminary Test

The samples are prepared as shown in Table 1. The objective of conducting preliminary test is to determine the optimum loading level of glycerol as plasticizers to be added into the nanocomposites of TPS, MMT and ATH. Given there is no related published results regarding to the nanocomposite of TPS, MMT and ATH, it is necessary to conduct a preliminary test to determine the optimum processing weightage of glycerol in order to formulate optimum samples. The glycerol content is yet to be determined in this preliminary test and it is estimated by selecting the range of glycerol based on the percentage proportion to the starch which ranged about 40, 50 and 60 wt.%. To ease formulation of nanocomposite during preparation, loading level of each additive are represent in phr which imply for parts per hundred parts of resin. Literally mean 0.32phr of MMT corresponds to put in 0.32g of MMT nanoclay into a 10g of starch based polymer or resin. The formulation corresponding with dose rate of additives is shown in Table 1. As removing the nanocomposite films from the rectangular Teflon molds, it can be noticed from physical appearance whether it is brittle or soft. In fact, if the film appeared to be brittle indicated that addition of glycerol is too less. In a contrary, excess addition of glycerol into the suspension will turn the film appeared to be soft. As a result, nanocomposite film appeared in best physical appearance, the loading level of glycerol is chosen to be utilized in the following sample preparation.

Table 8. Formulation of Preliminary Test

Experiment	Starch	Nano-clay	Alumina Trihydrate	Citric Acid	Glycerol
	phr	phr	phr	phr	phr
1	10.00	0.32	3.00	0.48	4.00
2	10.00	0.32	3.00	0.48	5.00
3	10.00	0.32	3.00	0.48	6.00

**Note: Composition as shown in table above is represent by phr, where MMT loading of 1, 2 and 3 wt.% is equivalent to 0.16, 0.32 and 0.48 phr, ATH loading of 14, 16, and 18 wt.% is equivalent to 2.5, 3.0 and 3.5 phr, CA loading of 1, 3 and 5wt.% is equivalent to 0.16, 0.48 and 0.8 phr as well as glycerol loading of 23, 27 and 31 wt.% is equivalent to 40, 50 and 60 phr respectively.*

[2] 2.3.2 Preparation of TPS/ MMT/ ATH Nanocomposites Film

Cassava starch/MMT/ATH composite films are prepared by solution casting technique. It is proven that TPS nanocomposite films prepared by solution casting method where transparent and homogenous appearance are formed without breaks, fractures, insoluble particles or bubbles [17]. Optimum loading level of glycerol and starch can be determined earlier during preliminary test. 10g of cassava starch, powder form of MMT (0.16, 0.32 and 0.48phr), ATH (2.5, 3.0 and 3.5phr) and citric acid (0.16, 0.48 and 0.8 phr) are added simultaneously into the suspension of glycerol for dispersion. The suspension is then dissolved and dispersed in 400ml of distilled water and stirred with a glass rod until the all the particles are not clumped together. Then, the suspension is heated to 70°C and stirred under hot plate stirrer (SMHS-3 WiseStir) with appropriate speed (600rpm) for 1 hour to gelatinize the cassava starch

granules. The hot suspension is casted pour into rectangular Teflon molds and the cast film is dried overnight at 60°C in an air-circulating oven. After water completely evaporated, nanocomposite films are removed and conditioned according to requirements the of the characterization method followed. The obtained nanocomposites films are stored tightly in a sealed polyethylene zipper bags contained silica gels to avoid moisture absorption. The formulation of nanocomposite is shown in Table 2.

Table 9. Formulation of TPS/ MMT/ ATH nanocomposites film

Experiment	Starch	Nano-clay	Alumina Trihydrate	Citric Acid	Glycerol
	phr	phr	phr	phr	phr
1	10.00	0.16	2.50	0.16	5.00
2	10.00	0.32	2.50	0.16	5.00
3	10.00	0.48	2.50	0.16	5.00
4	10.00	0.16	2.50	0.48	5.00
5	10.00	0.32	2.50	0.48	5.00
6	10.00	0.48	2.50	0.48	5.00
7	10.00	0.16	2.50	0.80	5.00
8	10.00	0.32	2.50	0.80	5.00
9	10.00	0.48	2.50	0.80	5.00
10	10.00	0.16	3.00	0.16	5.00
11	10.00	0.32	3.00	0.16	5.00
12	10.00	0.48	3.00	0.16	5.00
13	10.00	0.16	3.00	0.48	5.00
14	10.00	0.32	3.00	0.48	5.00
15	10.00	0.48	3.00	0.48	5.00
16	10.00	0.16	3.00	0.80	5.00
17	10.00	0.32	3.00	0.80	5.00
18	10.00	0.48	3.00	0.80	5.00
19	10.00	0.16	3.50	0.16	5.00
20	10.00	0.32	3.50	0.16	5.00
21	10.00	0.48	3.50	0.16	5.00
22	10.00	0.16	3.50	0.48	5.00
23	10.00	0.32	3.50	0.48	5.00
24	10.00	0.48	3.50	0.48	5.00
25	10.00	0.16	3.50	0.80	5.00
26	10.00	0.32	3.50	0.80	5.00
27	10.00	0.48	3.50	0.80	5.00

**Note: Composition in the table above represent in phr, where MMT loading of 1, 2 and 3 wt.% is equivalent to 0.16, 0.32 and 0.48 phr, ATH loading of 14, 16, and 18 wt.% is equivalent to 2.5, 3.0 and 3.5 phr, CA loading of 1, 3 and 5wt.% of CA is equivalent to 0.16, 0.48 and 0.8 phr as well as glycerol loading of 27 wt.% is equivalent to 50 phr.*

2.4 Sample Characterization

2.4.1 Differential Scanning Calorimetry (DSC) and crystallinity

Differential scanning calorimetry (DSC) is performed using a differential scanning calorimeter (DSC 8500, Perkin Elmer) to study the thermal behaviour of nanocomposite films. Around 6 to 10mg of nanocomposite films were weighed into aluminium pans, sealed and then heated from 80°C to 220°C at 10°C per minute under nitrogen flow of 20mLmin⁻¹ and holding at 80°C for 1 minute to remove moisture before heated to 220°C.

2.4.2 Weight Loss at Different Temperature

All the nanocomposite films are cut manually with a stainless steel scissor into small pieces about (1 ± 0.010 g) and inserted into the universal bottles, in order to study the combined interaction between the TPS/MMT/ATH and citric acid in terms of weight loss effect. Samples that are not subjected to the procedure (drying and weighing) were store in a dessicator (silica gel). In each experiment, 87 samples (3 replicates) of nanocomposite film produce earlier during sample preparation are weighted using an electronic balance (M214Ai, BEL Engineering) with a range of 220g, linearity of ± 0.003 mg and readability to 0.0001g. Weighted samples are then placed into universal bottle and dried in the oven (Mettler, DO6836, Germany) for 1 week at 80°C. Then, the weight loss of samples was measured at the intervals of 2, 4, 8, 24, 72 and 168 hours treated at temperature of 80°C, 120°C and 200°C.

3. Results and Discussion

3.1 Differential Scanning Calorimetry Test (DSC)

Fig. 1 to 4 show the DSC curves of the TPS/MMT/ATH blend nanocomposites where endothermal peaks were observed indicating melting state can be found at 170 to 190°C. However, the presence of glass transition state¹ (T_g) was not noticeable meanwhile an obvious exothermic peak indicating melting state can be found ranging from 130 to 190°C. In this paper, the extent melting state of DSC is the major factor or issue to be investigated since this will directly delivered that magnitude of intermolecular bonding in the nanocomposite blend. It is also noticed that large peak area denotes more thermal energy is necessary to alter into kinetic energy to enable polymer molecules escape from the ordered crystalline structure [18]. It is expected that there is enhancement in the thermal stability by adding inorganic nanoparticles such as ATH and MMT would result to formation of barrier network and chars that inhibit transfer of volatile product and heat during degradation process [19].

¹ Glass transition, T_g : temperature at which the transition in the amorphous regions between the glassy and rubbery state occurred.

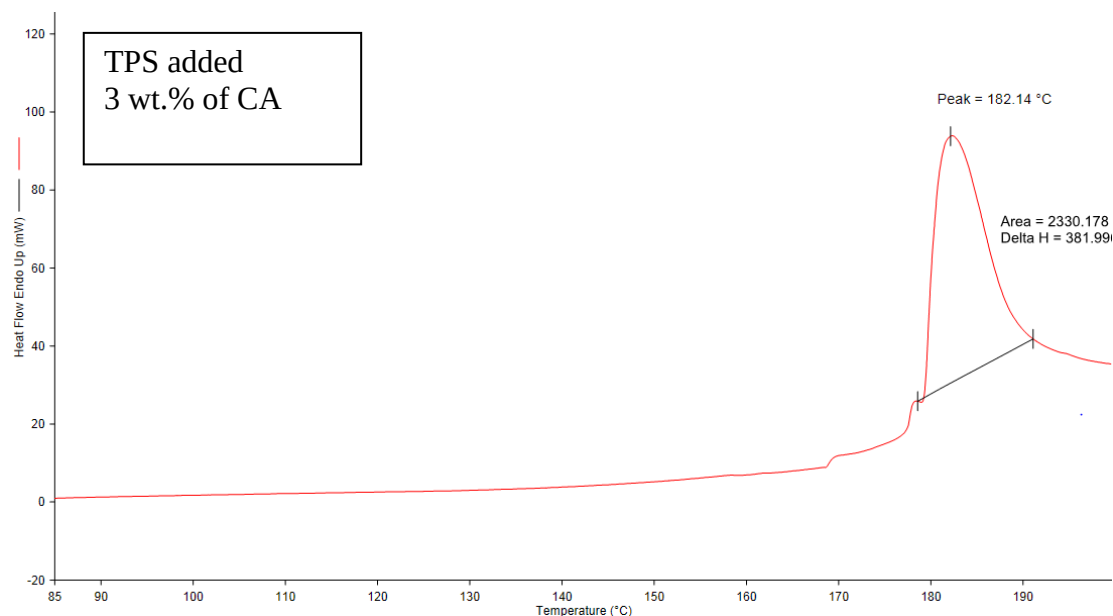


Figure 11. DSC Curve Of Cross-Linked Nanocomposite Film with 3 wt.% of Citric Acid

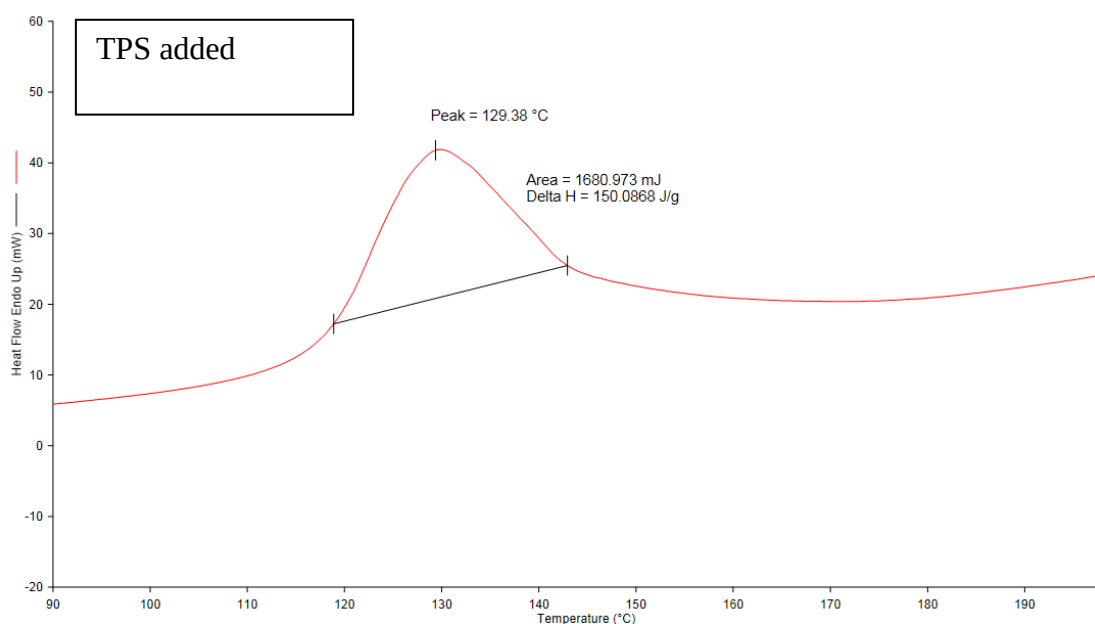


Figure 12. DSC Curve of Non-Cross-Linked Nannocomposite Film

The DSC curves of cross-linked and non-cross-linked film with 3wt.% of citric acid are shown in Fig. 1 and 2. The curve of the non-cross-linked film as shown in Fig. 2 show endothermic event that peaks at about 130°C whereas the cross-linked film show 50°C later than non-cross-linked film. This is due to citric acid formed ester bond with starch that able offer thermal stability enhancement [20]. Besides, the hydrophilic and hydrosopic characteristic of TPS also improved by cross-linking method that is done by citric acid. In spite of that, cross-linked film exhibit a broader peak area and fairly higher thermal stability (lower weight loss) compared to non-cross-linked film. Therefore, citric acid is more favourable for starch cross-linking as only low amount (5% or less) are needed for cross-linking reaction.

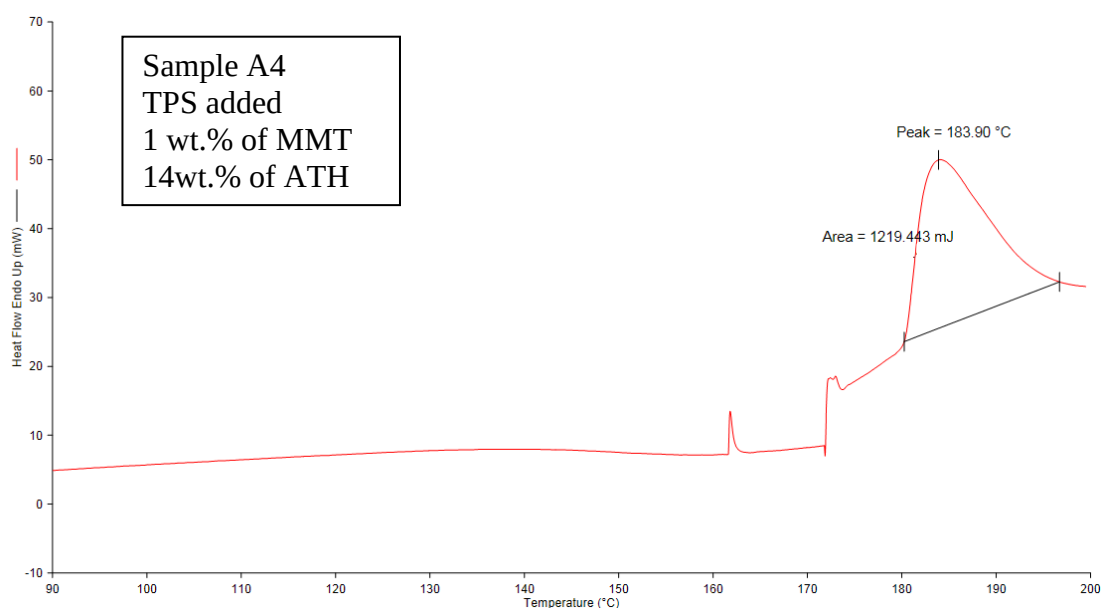


Figure 13. DSC Curve of Nanocomposite Film of Sample A4.

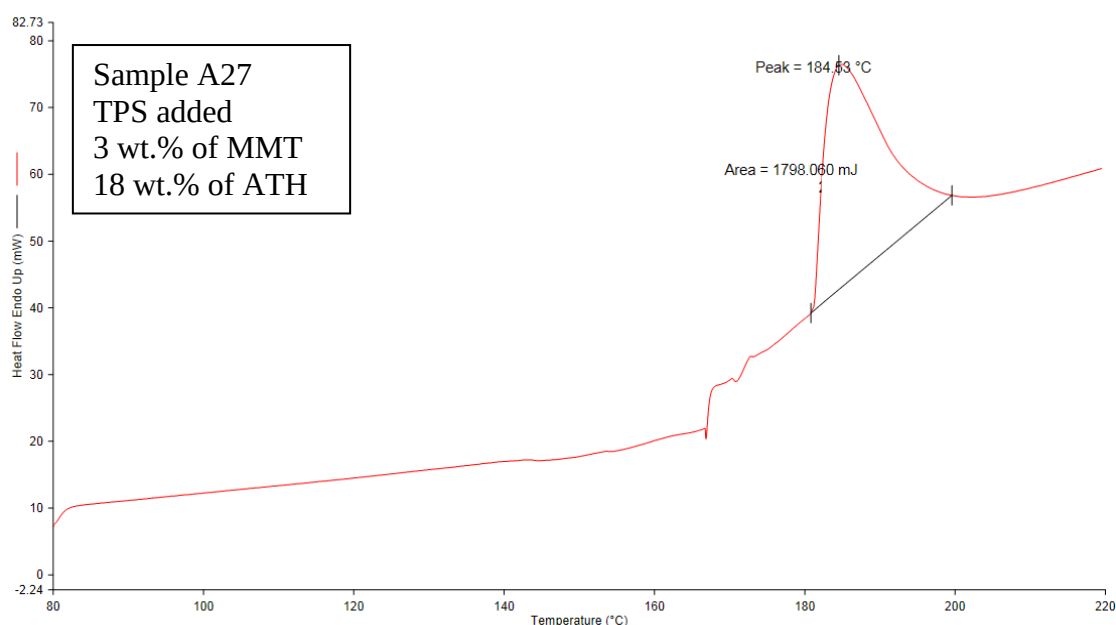
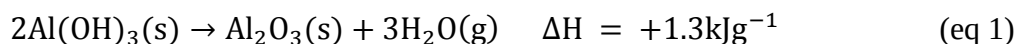


Figure 14. DSC Curve of Nanocomposite Film of Sample A27.

From the Fig. 3 and 4, it is noted that most of the melting peak as well as melting peak are sharp and broad. Given the process of melting nanocomposite film did absorbed heat, hence melting is recognized as endothermic transition. As the melting temperature reached, the nanocomposite's temperature would not rise until all the crystals have completely melted. However, it is clearly observed from Fig. 4 that the temperature continue to rise after the melting temperature, T_m due to presence of MMT since the expected melting point of MMT is 1450°C [21]. Hence, it could be further researched with the aid of Thermogravimetric Analysis (TGA) due to temperature limitation of DSC. Nevertheless, there is appearance of a small peak at 161°C as shown in Fig. 3. This is might be due to imperfect blending of citric acid into the nanocomposite film given that the melting point of citric acid is about 160°C [21].

Therefore, small peak appear indicated presence of small amount of citric acid in the film.

From Fig. 3 and 4, it could be observed that the T_m of nanocomposite peak rise from 183.90°C to 184.53°C when the ATH loading increased from low to high loading level (14 to 18 wt.%) as well as MMT loading increased from low to high loading level (1 to 3wt.%) too. The peak position changed mainly due to the endothermic decomposition of ATH that normally occurs between 180 to 200°C and at the same time, it released water and ended up by formation of alumina as shown in equation below:



During this endothermic decomposition, Boehmite, "ALOOH" is formed as intermediate product that mainly corresponding to the rather low endothermic energy [9]. This endothermic decomposition of ATH process is able to reduce the temperature by heat consumption. Hence, a protective layer formed that inhibited transfer of oxygen and combustible volatile gases which lead to reduction of corrosive or toxicity decomposition gases released. Similarly, the change of peak position also indicated that the MMT contents favour the formation of larger crystal domains and lowers down the mobility of polymer chains [22].

Besides, the melting area was comparatively larger at higher amount of MMT where it increase from 1219.443 to 1798.060mJ when the MMT loading level increase from 1 to 3wt.%. This exhibited that MMT actually cause effect on the formation of secondary bonding where two or more composite parts joined together during chemical or thermal reaction. Such phenomenon also observed by Tee et al.[18]. This deduce that there is increment of 19% of thermal energy that correspond to 1 to 3wt% of MMT loading level in order to transform into kinetic energy to enable polymer molecules escaped from the crystalline structure. This investigation inferred that introduction of MMT and ATH enhanced the thermal stability due to the presence of inorganic particles. In spite of that, sample A27 with high loading of nanoclay, flame retardant material and cross-linker agent (0.4wt.%/3.5wt.%/0.8 wt.%) shows the best thermal stability performance among all the composition. As a result, sample with high loading of nanoclay, flame retardant material and cross-linker agent arise as the best thermal stability among all the composition.

3.2 Weight Loss at Different Temperature

The combined interaction between the TPS/MMT/ATH nanocomposites in terms of weight loss effect is investigated by plotting out the weight loss % at different temperature with respect to loading level of ATH and MMT. When the samples exhibit low weight loss % literally means that the sample did not easily lose its weight corresponding to different thermal degradation temperature. In another word, this sample has better thermal stability effect given that the clay and flame retardant material acts as heat barrier that able to enhances the overall thermal stability of the nanocomposite. Besides, it was also noted that the samples ceased to be yellowish in colour after treated at high temperature or long periods of time that indicated changes

in chemical composition and morphology. Fig. 5 and 6 show the weight loss % at different temperature corresponding to loading level of ATH and MMT.

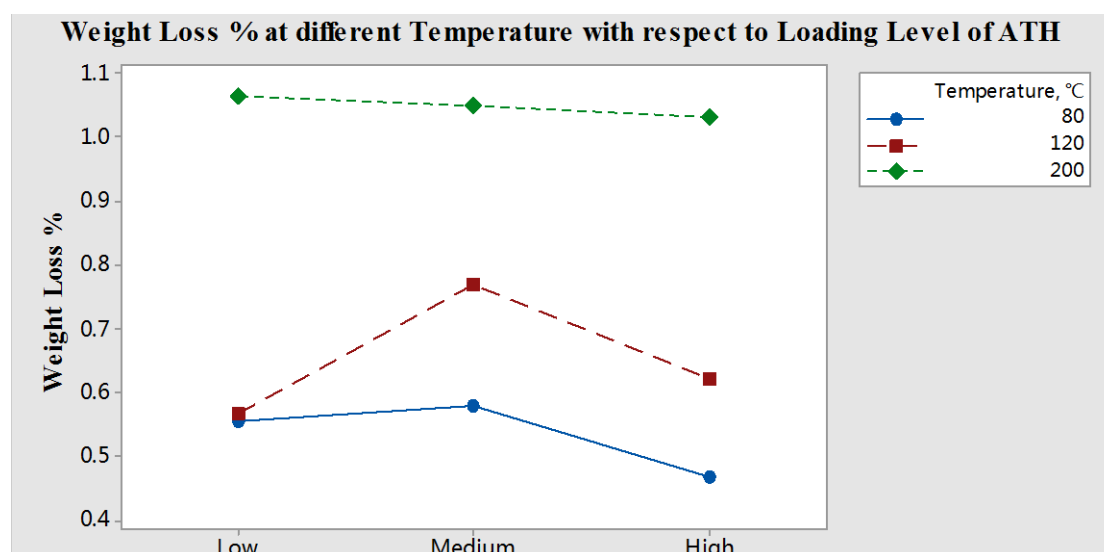


Figure 15. Weight Loss % at different Temperature with respect to Loading Level of ATH

The weight loss effect of samples at different temperature corresponding to loading level of ATH is shown in Fig. 5. From the observation, this satisfy the hypothesis where high loading level of ATH will give better thermal stability effect or in another word, the weight loss effect decrease when the loading level of ATH is at high level which is approximately 18 wt.%. Furthermore, the weight loss % that corresponds to different loading level of ATH is rather low which only range about 1.065% to 0.468% weight loss %. However, the weight loss % between 80°C and 120°C is almost similar; this possibly due to water inside the sample started to evaporate out at 120°C since water's boiling point at 100°C. At 200°C, weight loss % decrease when loading level of ATH increases which exhibit an inversely proportional relationship. ATH as flame retardant element could lead formation of carbonized or vitreous layer at the surface of polymer by chemical transformation of polymer chain degradation which indicates by the colour change of sample as mentioned earlier.

It exhibits a relatively high weight loss % which is approximately 0.578 weight loss % at medium loading level at 16 wt.% during thermal degradation temperature at 80°C. This is due to presence of MMT where it takes the major role at that moment. It is considered that burning nanocomposite with low content of ATH, the nanoclay in the nanocomposite would not be able to integrate perfectly with ATH to constitute a rigid insulation layer on the ablating surface and might shed away the melting element. In a contrary, MMT is able to blend with high loading of ATH in order to produce solid insulation barrier when exhibited at high temperature [23]. This in turn created a synergistic effect with flame retardants material and nancoclay in the nanocomposite blend.

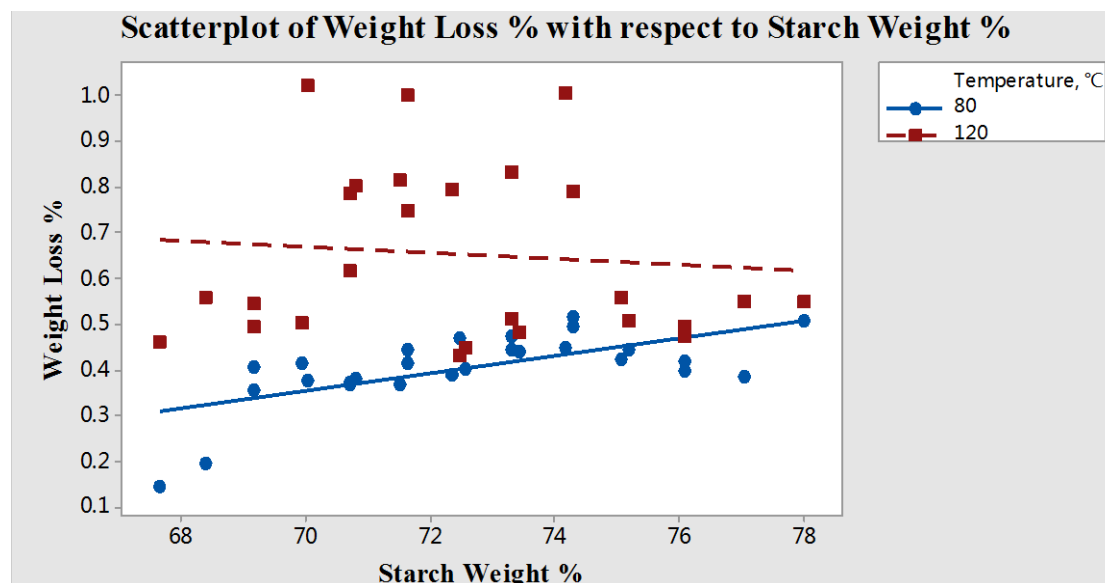


Figure 16. Scatter Plot of Weight Loss % with respect to Starch Weight %.

Fig. 6 is plotted in order to determine the effect of starch weight % in the specific temperature at 80°C and 120°C, given there is almost similar effect of weight loss as shown in Fig. 5. Moreover, it is shown that the weight loss % at 120°C scatter around and the two main variables (starch weight % and weight loss %) did not have correlation where no apparent relationship shown between this two main variables. Therefore, starch did not make a major role for the effect of weight loss at this temperature. As mentioned earlier, it might be due to water evaporated out at 120°C given water's boiling point occur at 100°C. However, weight loss % of 80°C shows an increasing effect when the starch weight % increases due to the loss of moisture content as proposed by other authors who also able to demonstrate mass loss of cassava bagasse occurred at 30°C [26].

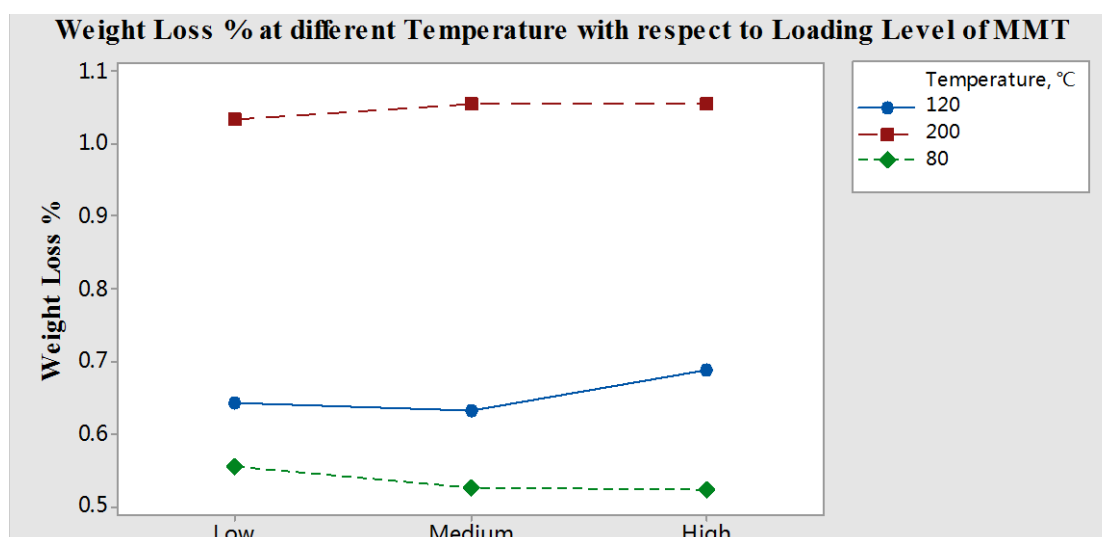


Figure 17. Weight Loss % at different Temperature with respect to Loading Level of MMT

The weight loss effect of samples at different temperature corresponding to loading level of MMT is shown in Fig. 7. It could be observed from the line plots

where the weight loss effect decrease when the loading level of MMT under medium level which is approximately 2wt.%. In another word, it offers the optimum thermal stability at the medium level of MMT loading. Incorporation of MMT delayed the thermal decomposition temperature, at the same time increased formation of the char residue that could delay the combustion process as well as improvement of mechanical properties [24]. An almost constant effect of weight loss % is shown at 200°C which only offer difference of 0.02% of weight loss since MMT is expected to be decomposing at high temperature. However, a high loading of MMT (3%) offer a deterioration effect or literally means that effect of thermal stability is lower which brought about 0.685% weight loss that could be clearly demonstrated at 120°C. This can be attributed by the fact of increasing clay content up to a percent at which the silicate layers cannot be exfoliated anymore [25]. Hence, addition of more amount of nanoclay into matrix leads to appearance of clay stacks and even aggregates that deteriorate the thermal properties.

4.0 Conclusion

Nanocomposite films were prepared using the method of solution casting using thermoplastic starch, montmorillonite (MMT) and alumina trihydrate (ATH) with existence of citric acid as cross linking agent. DSC showed that cross-linked nanocomposite film larger area and fairly high thermal stability compared to non-cross-linked nanocomposite film from 182.14°C to 129.38°C. Besides, it was also possible to conclude that T_m of nanocomposite peak rise from 183.90°C to 184.53°C when the ATH and MMT loading increased. This indicated that endothermic decomposition of ATH taken place and MMT content favour formation of large crystal and reduced the mobility of the polymer chains. Meanwhile, the melting area offered increment of 19% when the MMT loading level increase from 1 to 3wt.% where MMT cause an effect on the formation of secondary bonding. It also can be deduced that high loading level of ATH will give better thermal stability effect as weight loss % decrease. However, MMT offer the optimum thermal stability at medium level of MMT loading at 2wt.% given that incorporation of MMT delays the thermal decomposition temperature and also increases formation of the char residue which is able to slow down the combustion process. From all the findings, high loading of MMT, ATH and citric acid (0.4wt.%/3.5wt.%/0.8 wt.%) arise as the optimum formulation as proven by analysis in term of thermal stability conducted as mentioned. Therefore, elaboration of TPS/MMT/ATH nanocomposite film with citric acid as cross linking agent arise as an uprising alternative with its excellent thermal properties for application as fire-retardant coating materials in the future.

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Energy Harvesting from Human Vibrations

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Abstract

With the growth of electronic components into a more compact and energy efficient model by the reduction of size in component design, energy harvesting from the ambient sources for the operational of the electronic component without external power sources has become a heated subject for researchers. This project is focused on the approach of energy harvesting from human vibration, without taking other ambient energy sources into consideration. Human movements in the daily activities could be considered as a form of vibration, researchers has shown that human body is capable of generating 1.8 Hz of excitation frequency when walking and 4.2 Hz when running. Piezoelectric was chosen as the transducer for the energy harvester when compared with electromagnetic and electrostatic transducers due to its high power densities and capable of generating high output voltage by direct piezoelectric effect. Furthermore, electromagnetic transducer generally has low voltage output and more works have to be done to convert the harvested energy into usable input while electrostatic transducer would require external power source to charge up its capacitor before initiating energy conversion. A Lead Zirconate Titanate (PZT) bimorph energy harvester provided by Piezo System Inc (Model T220-A4-303Y) was used in this project. Analytical analysis of the bimorph energy harvester was done to estimate the power output of the system. Tip mass of 4.1 g is attached to the free end of the bimorph energy harvester and up to 100 m/s² of vibration acceleration was applied to the system. Frequency range of 0 Hz to 5 Hz is interested as it is attainable by human body. Result shows that the bimorph energy harvester could generate power output of 0.04106 mW at 1.8 Hz and 0.1451 mW at 4.2 Hz.

Keywords: Vibration, Energy, Harvesting, Piezoelectric, Bimorph.

1. Introduction

1.1 Background

The advances in technology have made human life easier by providing solutions to issues that could not be addressed by human beings decades ago. With the design of electronic component grown into more compact and energy efficient model in the recent years, the power requirement of small electronic devices also decreased tremendously. Hence, there is a growing interest in energy harvesting from surrounding sources for the operation of electronic microsystems. The idea of harvesting energy through the ambience will allows the microsystem to become self-powered without the need of battery or any external power sources. At the present time, electronic microsystem could be found everywhere in the modern world ranging from small biomedical implants to large wireless sensor networks actively operated in monitoring applications for both civilian and military usage [1].

The title of the project is self-explanatory as this project is only focused in the aspect of harvesting energy from human vibrations which ruled out other possible ambient energy sources. The daily life of human being is consists of movements which could be considered as a form of vibration, energy could be harvested from the vibration and further converted into electrical energy by various mechanisms. Williams and Yates mentioned that electromagnetic, electrostatic, and piezoelectric transductions are the three fundamental system which could harvest and convert vibration energy to electrical energy [2]. However, based on the trend in energy harvesting researches in the recent years, it could be seen that piezoelectric transduction received the most attention as the number of publications in piezoelectric transduction is far higher than the number of publications in the other two transductions. Piezoelectric energy harvester is recognized to be the most suitable transducer in harvesting ambient energy as it has largest power density when compared to other transducer and batteries, as shown in Figure 1 [3].

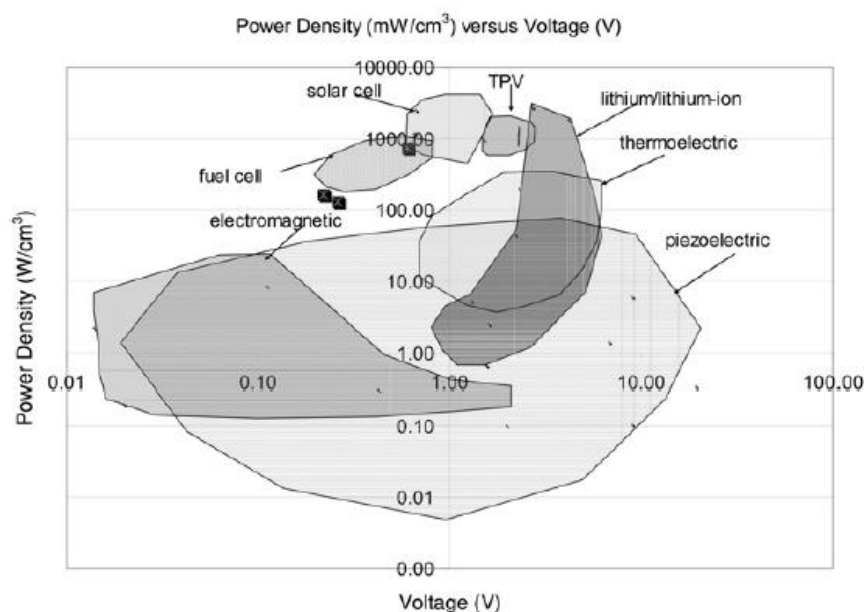


Figure 1: Comparison of power density versus voltage among several common transducers and batteries.

From Figure 1, it is clear that piezoelectric has the largest power density and capable of generating higher voltage output directly from the piezoelectric material. Electromagnetic transducer might be the most commonly found transducer used in a lot of applications, but it generally has lower voltage output. Furthermore, extra works have to be done to convert the harvested energy into usable energy [4]. In the other hand, external voltage source is needed by electrostatic transducer as the capacitor has to be charged up to a certain value before initiating the conversion of energy. Also, the high complexity of the design of electrostatic transducer limits the performance of the transducer and will causes reliability issues [5]. Hence, it is determined that piezoelectric will be the chosen transducer for this project as it has higher power density, higher voltage output and low design complexity. Piezoelectricity, discovered in 1880 by Pierre and Jacques Curie, is a property of material which produces an electric charge and voltage while external force is exerted and causes elastic strain to occur in the structure of the material. Direct piezoelectric effect is presented once current is produced by a material when subjected to external force while the inverse piezoelectric effect will causes the material to produce elastic strain when connected to electrical source [6].

1.2 Objectives

The purpose of this project is to determine the suitable piezoelectric material and excitation method of the energy harvester which could be deployed in harvesting energy from human vibrations. Analytical analysis to will be performed to evaluate and justify the capability of the energy harvester.

2. Methodology

This project is focused on exploring the suitable method of harvesting human vibration energy by using piezoelectric energy harvester. The initial stage of the project will consist of the adaptation of a Lead Zirconate Titanate (PZT) bimorph energy harvester provided in the works done by Ooi B.L. [7] The estimated power output of the energy harvester could be determined by using the power output equation shown in the following section.

2.1 Piezoelectric Energy Harvester

Generally, piezoelectric material operates in two different modes namely the 33 mode and 31 mode. Figure 2 below depicts the difference between 33 mode and 31 mode. As seen in Figure 2, the x, y, and z axes are labelled as 1, 2, and 3. Both 33 mode and 31 mode piezoelectric materials are poled in the 3 direction. Hence, voltage will acts in the 3 direction for both cases[5].

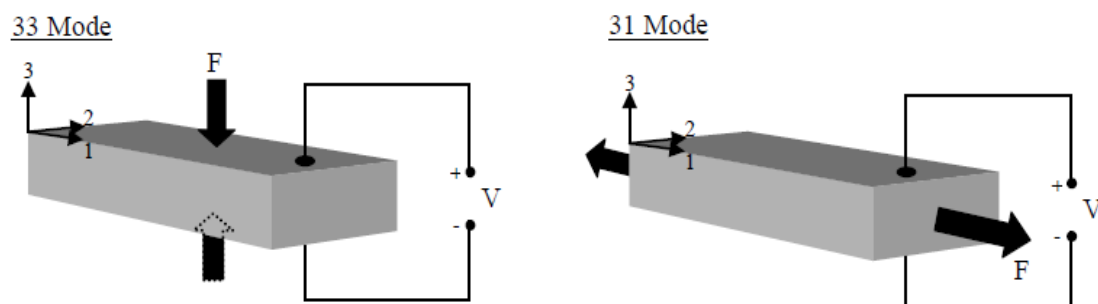


Figure 2: 33 Mode and 31 Mode in the operation of piezoelectric material.[5]

For 33 mode, both of the mechanical stress / strain and voltage act in the 3 direction while the mechanical stress / strain of 31 mode acts in direction 1 of the material. The 31 mode is chosen as the mode of operation in this project regardless that piezoelectric material operating in 31 mode will generally have lower electro-mechanical coupling coefficients than the same material operating in 33 mode. This decision was made in a sense that 31 mode is much more compliant when compared to 33 mode. Also, the amount of stress and strain in piezoelectric material is in direct proportion to the output voltage of the material, smaller input forces are required by the 31 mode to produce a large strain in the material, hence producing higher voltage output. Furthermore, resonant frequency of the model operating in 31 mode is much lower than model operating in 33 mode. Hence, a bimorph is chosen as the piezoelectric energy harvester in this project. A bimorph is a cantilever structure with both top and bottom of the rectangular surfaces attached with piezoelectric material. The advantages of a bimorph are such as low space requirement, compact design, low resonant frequencies and able to create a relatively large deflections hence higher power output [7].

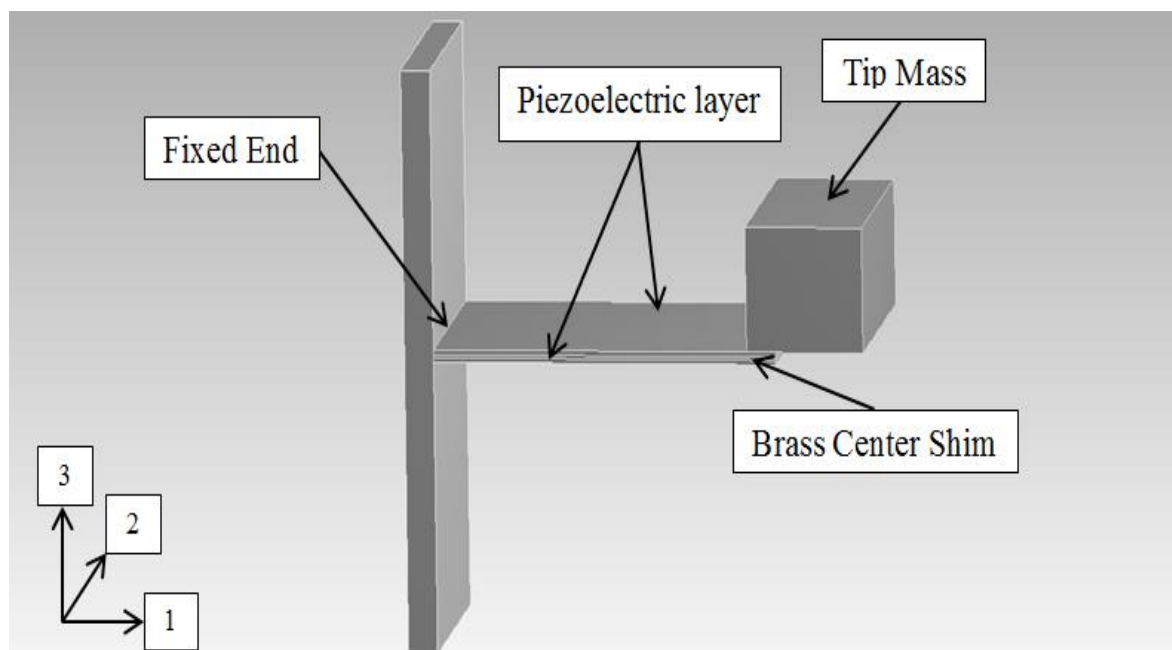


Figure 3: Illustration of bimorph energy harvester.

The bimorph piezoelectric bender used in this project is a bimorph made of Lead Zirconate Titanate, PZT (T220-A4-303Y) with a brass center shim supplied by Piezo System Inc.

Figure 3 shows the illustration of the bimorph energy harvester. The free end of the bimorph is fixed while a tip mass with a weight of 4.1 g is attached to the other end of the bimorph. The thickness of both layers of the piezoelectric material is 0.19 mm while the center shim is 0.13 mm thick. As shown in Figure 3, a tip mass with a weight of 4.1 g is attached to the final 2 mm of the free end. The bimorph has a total length of 23.5 mm and width of 12.7 mm as provided in the product catalog.

2.2 Analytical Analysis

In order to estimate the power output of the bimorph energy harvester, a resistive load is attached to the energy harvester to simulate a real electrical load. Output voltage of the bimorph energy harvester could be calculated from formula below [8]:

$$V = \frac{-j\omega \frac{Y_c d t_c b^*}{\varepsilon}}{\left[\frac{1}{RC_p} \omega_n^2 - \left(\frac{1}{RC_p} + 2\zeta \omega_n \right) \omega^2 \right] + j\omega \left[\omega_n^2 (1 + k_{co}^2) + \frac{2\zeta \omega_n}{RC_p} - \omega^2 \right]} A_{in} \quad (1)$$

and

$$b^* = \frac{3b}{l_b^2} \frac{(2l_b + l_m + l_e)}{(2l_b + \frac{3}{2}l_m)} \quad (2)$$

where R = Load resistance of the system
 Y_c = Young's modulus for the piezoelectric ceramic
 d = Piezoelectric strain coefficient
 C_p = Capacitance of the piezoelectric material
 t_c = Thickness of each piezoelectric layer
 ε = Dielectric constant of the piezoelectric material
 ω = Excitation frequency of the vibration
 ω_n = Natural frequency of the bimorph energy harvester
 ζ = Mechanical damping ratio of the system
 k_{co} = Electro-mechanical coupling coefficient of the piezoelectric material
 A_{in} = Acceleration magnitude of the vibration
 b^* = Distance between the center of the shim to center of piezoelectric layer
 l_b, l_e, l_m = Beam length setup

By acquiring the voltage output of the bimorph energy harvester, the root mean square power transferred to the simulated electrical load could be determined by using Equation (3) below [8]:

$$P_{rms} = \frac{|V|^2}{2R} \quad (3)$$

3. Results and Discussion

The results are validated through the comparison with the similar work done by Ooi [7], as shown in Figure 4 below. MATLAB was used in calculating Equation (1), (2), and (3), with the results of the calculation plotted in a graph to show the power output of the bimorph energy harvester under a wide range of excitation frequency. Figure 4 was plotted using the boundary conditions provided in the referred article. Through comparison with the referred article, the results of the calculation under human vibration show great accuracy. Hence, the coding of Equation (1), (2), and (3) in MATLAB is validated and could be used in this project by applying the acceleration magnitude and excitation frequency of human vibration into the equation.

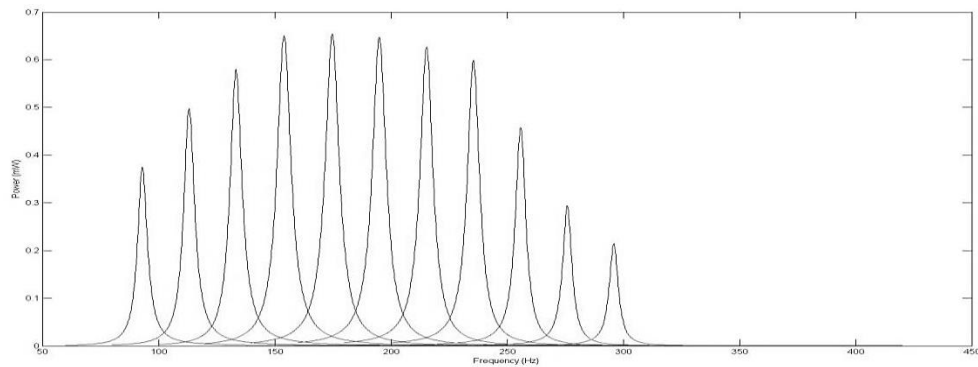


Figure 4: Validation of result.

With the MATLAB function validated, the project proceeds to the calculation of the bimorph energy harvester power output under parameters such as acceleration value of human vibration. Figure 5 below shows the frequency response of the bimorph energy harvester with varying resistive loads. All simulated result shows that the peak of the power output occurred at the resonance frequency 73 Hz of the bimorph energy harvester. Note that an offset frequency of 30 Hz was applied between each set of data in order to increase the clarity of the graph and prevent overlapping of result.

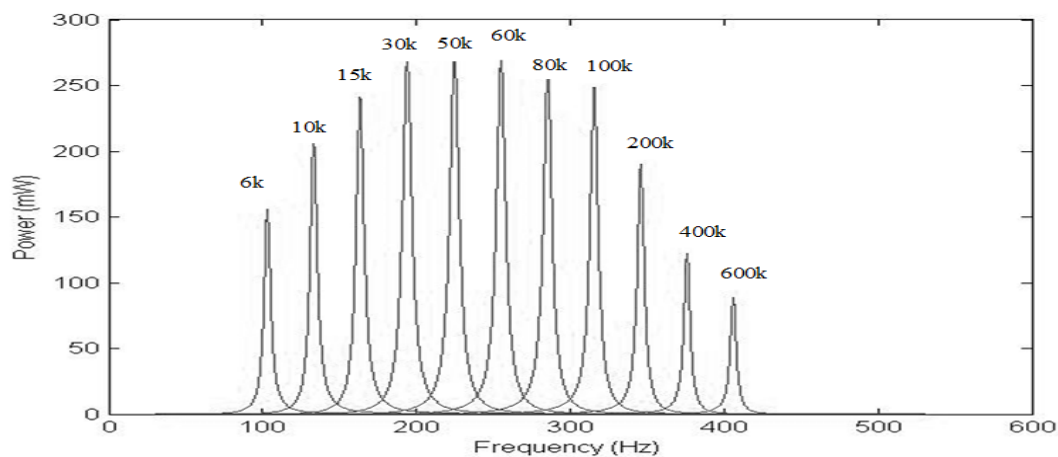


Figure 5: Simulated power output of bimorph energy harvester under varying excitation frequency and load resistance.

From Figure 5, it is clear that the bimorph energy harvester achieved the highest power output when the resistive load is 30 k Ω as it matches to the internal resistance of the system [7]. However, the high resonance frequency (73 Hz) of the simulated results will not be achievable in human motion as the excitation frequency of human during walking is 1.8 Hz and 4.2 Hz when running [9]. Although the excitation frequency achievable by human vibration is very low, high acceleration levels of up to 100 m/s² at 2 Hz could be found on the foot of a human while subjected to a jogging motion [10]. Therefore, the power output is focused on the frequency band between 2 Hz to 4 Hz as it is the practicable excitation frequency of human vibration. Also, it is shown that the bimorph energy harvester will have the lowest peak power output when the resistive load is at 600 k Ω . Nevertheless, when only the frequency band of 0 Hz to 5 Hz is interested, the power output of the bimorph energy harvester will be the

highest at 600 k Ω when compared with other lower experimental load resistant value, as shown in Figure 6 below.

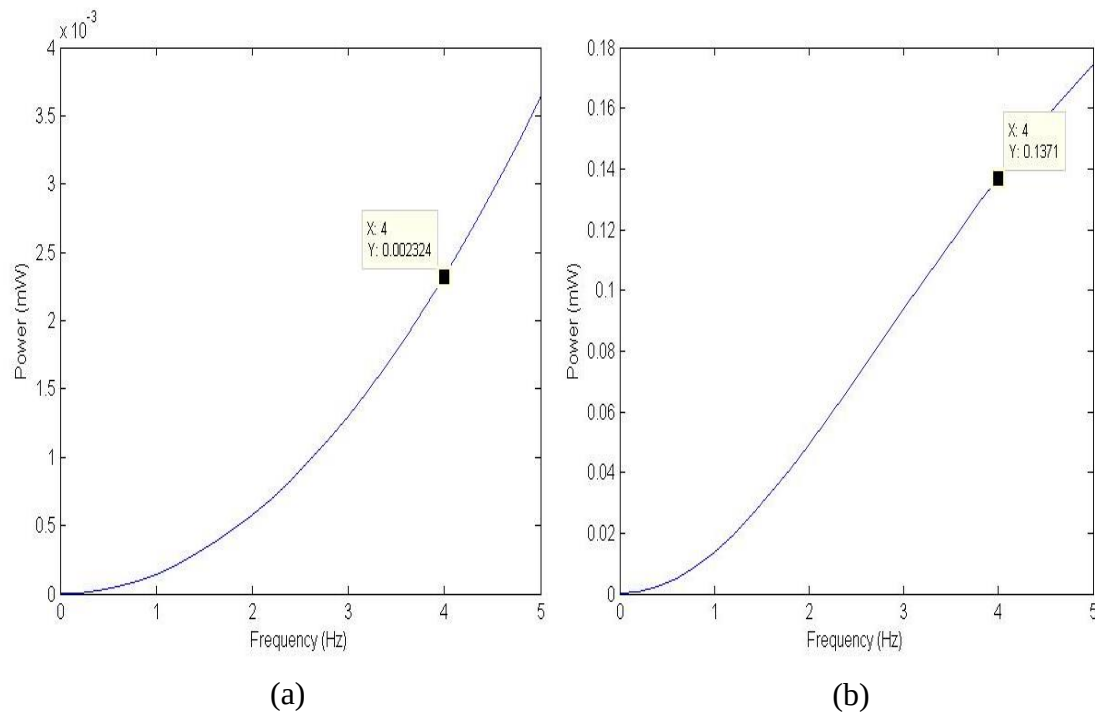


Figure 6: Power output of bimorph energy harvester at (a) 6 k Ω and (b) 600 k Ω load resistant.

The effect of changing the geometry of the bimorph energy harvester was also tested by using the power equation. For the simplicity of the task, the damping ratio of the bimorph energy harvester are assumed to be constant as the changes in geometry, mainly the length, width and thickness of the bimorph energy harvester are minimal (3 mm in length, 1.3 mm in width and 0.06 mm in thickness of the piezoelectric ceramic layer). Also, the capacitance of the bimorph energy harvester with altered geometry could be determined as the capacitance of the system is directly proportional to the volume of the effective piezoelectric ceramic layers. Load resistance of 600 k Ω was applied in the calculation as power output of the system will differ with different types of appliances connected to the system.

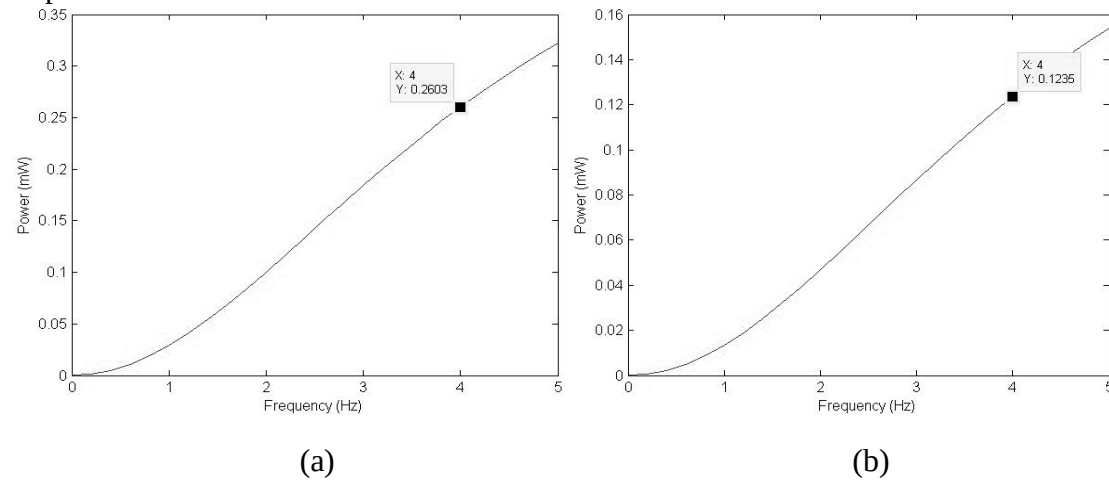


Figure 7: Bimorph energy harvester with altered (a) length = 26.5 mm, (b) width = 14 mm

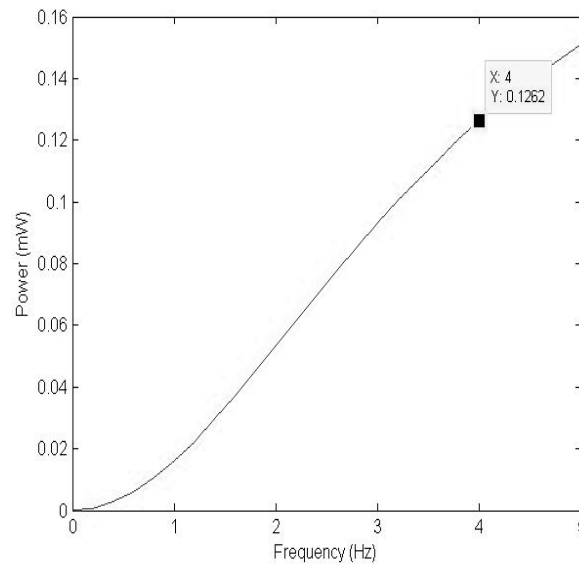


Figure 8: Bimorph energy harvester with piezoelectric layer thickness of 0.25 mm.

The power output of the system at 4 Hz is interested as it is the excitation frequency attainable by human in running motion. By comparing results shown in Figure 7 and 8 with Figure 6(b), it is observed that the power output of the bimorph energy harvester is directly proportional to the length of the bimorph, while the changes in the width and thickness of the piezoelectric ceramic layer causes slight reduction in power output. It is believed that this phenomenon occurred as the charge generated by the system is directly proportional to the mechanical strain formed in the piezoelectric ceramic layers. By increasing the effective length of the system, the amount of strain generated in each layers of piezoelectric ceramic will be greater due to the increment in bending moment, even when other parameters such as vibration magnitude and weight of tip mass remain unchanged. However, by increasing the width and thickness of the piezoelectric ceramic layers of the system, the amount of strain developed in the piezoelectric ceramic layer will decrease, which explains the slight reduction of the power output as shown in Figure 7(b), 8.

4. Conclusion and Recommendation

This project assesses the feasibility of harvesting energy from human vibration. Through proper review of 3 main transducers (electromagnetic, electrostatic and piezoelectric), it is found that piezoelectric transducer shows great promising result as it generally has higher power densities and able to generate high voltage output through direct piezoelectric effect, when compared to the two other transducers. While human body is capable of generating 1.8 Hz of excitation frequency in walking motion and 4.2 Hz of excitation frequency in running motion [10], through carrying out analytical analysis using Equation (1), (2), and (3), it is concluded that the Lead Zirconate Titanate (PZT) bimorph energy harvester, fabricated by Piezo System Inc (Model: T220-A4-303Y) shows satisfying power output of 0.04106 mW at 1.8 Hz (walking) and 0.1451 mW at 4.2 Hz (running), as shown in Figure 5(b). Discussions on the bimorph energy harvester were also presented in this paper. Increment in the effective length of the bimorph energy harvester will increase the mechanical strain developed in the piezoelectric ceramic layers of the system, thus increasing the power output of the system. However, increment in the width and the thickness of the piezoelectric ceramic layer will lower the mechanical strain developed in the piezoelectric ceramic layers, thus reducing the power output of the system.

Some of the parameters such as the damping ratio and the capacitance of the system in altered geometry were assumed in this project. Hence, for future recommendation, experimental testing of prototype could be carried out to measure the real value of the said parameters. By doing so, the accuracy of the result is easily attainable and the response of the system could be captured to provide solid evidence. Furthermore, the energy harvester could consist of multi-layer piezoelectric ceramics instead of limiting down to a bimorph structure. A multi-layer piezoelectric cantilever structure could be considered as it might show better power output and the model could be refined to smaller size to suits human application.

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Non-Contact Vibration Sensor for Rotating Machines

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Abstract

Engineers have been using condition monitoring system to observe physical condition of machineries, to avoid unexpected shutdown, financial loss and even fatal incidents. The industries have shown a trend of using rotating machines for elevated working load and speed and these rotating machines run at high speed and would lead to high vibration and unforeseen failure. The most commonly used vibrations sensors are accelerometers and optical sensors. For wind turbine industry, monitoring of power output of the wind turbines is used to predict the health condition of the machineries and other components. However, these techniques have limitation whereby they are not suitable to operate at high voltage and high speed condition. This study aims to discuss and verify effectiveness of a new monitoring technique, which is based on mechanical vibrators and Doppler Effect. The first prototype was clamped on to shaft which rotates by two different motors that operate at different RPM and noise. Sound wave collected from the mechanical sensor at motor running with and without whistle were recorded and analyzed. The current prototype has been unable to show distinguishable sound wave signal up to 1000 RPM. It is deduced that the circulation of air near mechanical sensor mouthpiece has form an air blockade, whereby drastically reduces the airflow and resulting in low intensity of sound wave generated. An improved mechanical vibration sensor is proposed and will be tested in the future.

Keywords: Condition monitoring, non-contact sensor, high voltage, high speed, frequency shift

1. Introduction

Condition monitoring system has been used by engineers to monitor the health of machinery, to avoid unexpected shutdown, monetary loss and even casualties of operators and people around. In practice, vibration of machineries, bearings condition, temperature of engine and other operating parameters are tracked and monitor to detect early sign of faulty components. If any signs are detected, engineers can plan preventive maintenance while the plant is still operational, hence reduces the shut-down time. This practice is exceptionally important as some machineries which are not easily accessible, for e.g. the nacelle of the offshore wind turbines are usually located 30 km away from the shore and 20 meters above the ground. In the other hand, extreme weathers like storms could hinder the repair work on offshore rigs and floating platoons for days. With an effective condition monitoring which can provide or predict the mean time between failure (MTBF) actually, it reduces the down time and cost of maintenance [1] for the operators.

Rotating machines are commonly used in the industries and have the trend of increasing working speed and load. The machine operates at rotating speed close to its critical speed would results in vibration on the equipment and leads to unexpected failures. Most of vibrations issues encountered are usually caused by misalignment of rotating shaft [2]. Other disadvantages include excessive noise that could affect people around and also reduces efficiency in term of power consumption [3]. Another common cause of vibration is imbalance rotating mass, or presence of mass eccentricity [4]. Excessive vibration can lead to failure of mechanical parts such as bearings and screws.

Most commonly used method to detect shaft misalignment is through vibration analysis. Accelerometers are commonly used to place on engine body to measure the rate of change of momentum during operation. These data is converted into the respective vibration amplitude and frequency. These signals are then analysed by various signal processing methods to detect any sign of faulty bearings [5].

Another form of vibration detection is using laser Doppler vibrometer. It is a non-contact acceleration/vibration sensor designed and used for detecting torsional and bending vibration in rotating shaft. Unlike other accelerometers, no attachment on surface of object is needed for laser Doppler vibrometer [6].

A condition monitoring technique based on generator output power was proposed by Wenxian Yang *et al.* [7]. By comparing power output with rotational speed of shaft, fault in shaft can be detected without using sensors and intensive computational analysis. This method is commonly used for wind turbines whereby other condition monitoring techniques being used cannot provide good monitoring in rapidly varying torque condition.

This study focuses on a new vibration detection technique for high voltage high speed rotary machines. The proposed method uses high pitch whistles which are commonly used to train animals. Noises from other sources can be disregarded as noises usually are located at lower frequency range. The prototype is a ring-like structure with two whistles integrated within. When it is clamped to rotating shaft, air will be directed into whistles and high pitch waves are generated. The sound samples

will be analysed and compared with validation data obtained from accelerometers. The relationships between vibration, frequency shift and intensity changes will be analysed and discussed to find out the effectiveness of this method.

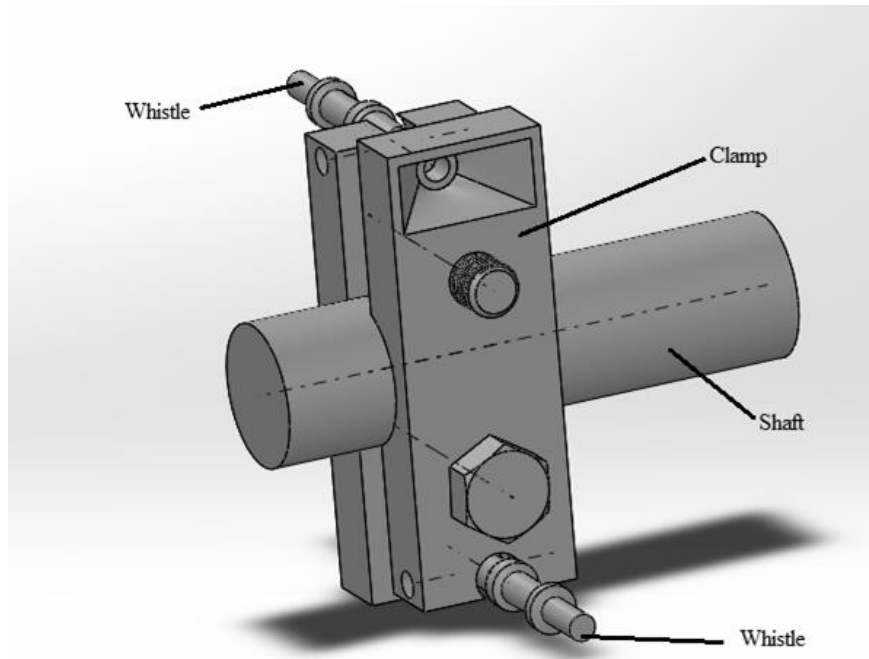


Figure 1. Design of testing equipment produced in SolidWorks.

2. Methodology



2.1 Design and Prototyping

The design criteria for the mechanical vibration sensor are:

- ability to withstand high RPM,
- provide sufficient airflow, (Please define your air flow rate required)
- light-weight and
- weight distributing.

As seen in Fig. 1, this mechanical vibration sensor equipment is designed to fit tightly on 26.5mm diameter shaft for experimenting purpose. Due to the gap in between the two blocks, it can also be used on shaft with minimum diameter of 16.5mm. Instead of using one available shaft size, this increase the flexibility of the experiments.

To lock this equipment onto shaft, two sets of 10mm bolts and nuts will be used. The gap allow tight locking and it has been successfully tested on 2000 RPM.

Information related to required airflow for the whistle was not known therefore an experiment was conducted to estimate the minimum air flow required to activate the whistle. A balloon was inflated in a known period of time and the flow rate of air from blowing was estimated. To achieve this, a cone-shaped cavity was designed for the mechanical vibration sensor, in order to drive more air into the mouthpiece of whistle. From equation (1), the minimum RPM of the shaft is 400 RPM.

$$\text{mass flow rate} = \rho v A \quad (1)$$

where ρ is density, v is velocity and A is area of cone-inlet,

On the other hand, mass of the entire mechanical vibration sensor must be distributed evenly to prevent vibration on its own. Imbalance mass or ‘heavy spot’ can create vibration especially at high RPM. Both blocks are identical to each other and two whistles are integrated within, where one is located at the exact opposite of other. This is important because non-vibrating base signal will be needed in order to compare with signal coming from a vibrating shaft. It is also because of this, the prototype size has been kept to minimum. The whistle used in this experiment is the most practical whistle available in market, giving highest frequency and ability to integrate with prototype used (due to its small size and slender shape).

Design of equipment and whistle was created and imported into ANSYS FLUENT in order to test its functionality. Due to complication of 3D meshing and simulation, a simplified 2D meshing (Fig 2) was used to observe air flow at different RPMs. 143389 nodes were used and further increasing the nodes yield insignificant changes in result. Since the length of prototype is 9cm, the total area used in this simulation is 90cm x 90cm. Simulation model used is standard K-omega and the outline of the prototype has been set to rotate about its centre at 400 RPM (42 rad/s). For momentum, turbulent kinetic energy and specific dissipation rate has been set to second order upwind to increase accuracy. All residuals converged at 0.001.

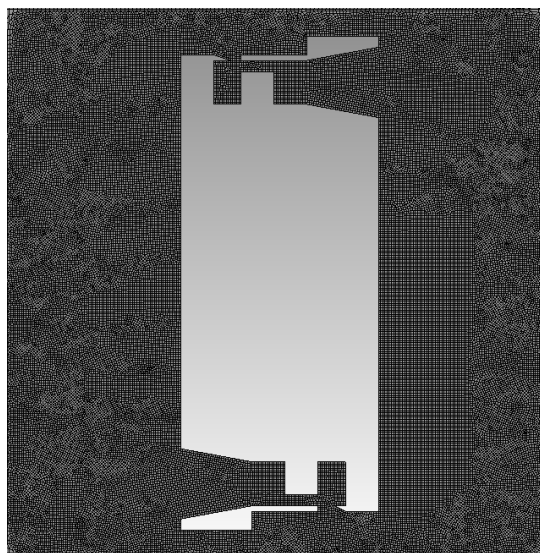


Figure 2. Focused view of simplified 2D meshing of prototype.

The result as shown in Fig. 3 and Fig. 4 show that air can efficiently enter the cavity at 400rpm, through the mouthpiece of whistle, circulating in resonance chamber and eventually leaves through the opening. In Fig.3, it can be seen that some of the air tends to recirculate before going into whistle. However, it must be noted that this is only estimation and can only provide an estimation of how air flows into the

whistle. The whistle was also modelled based on estimated dimensions. Simplifications of model was used to simplify meshing process.

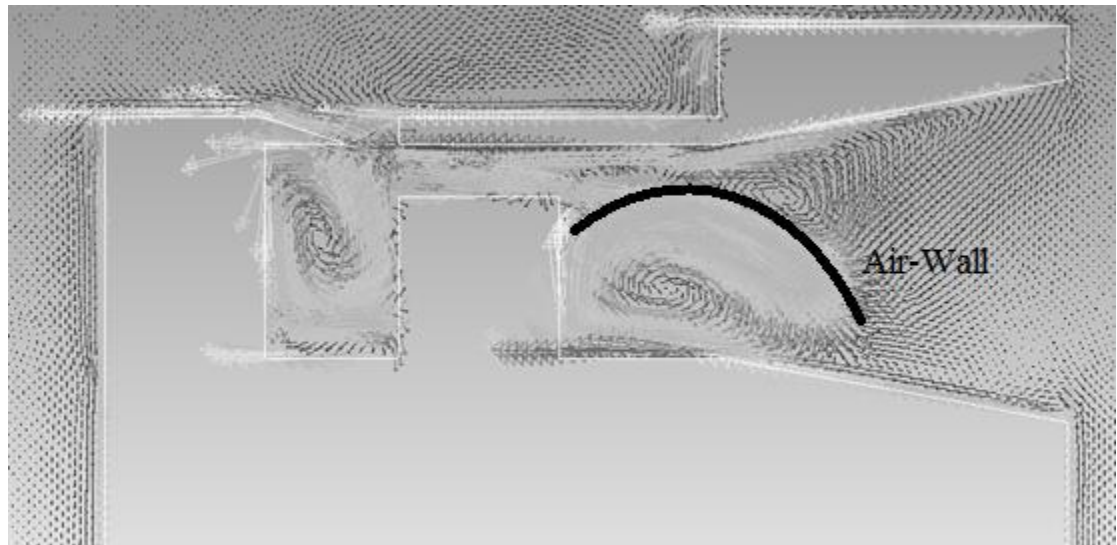


Figure 3. Velocity vectors of one end of the prototype.

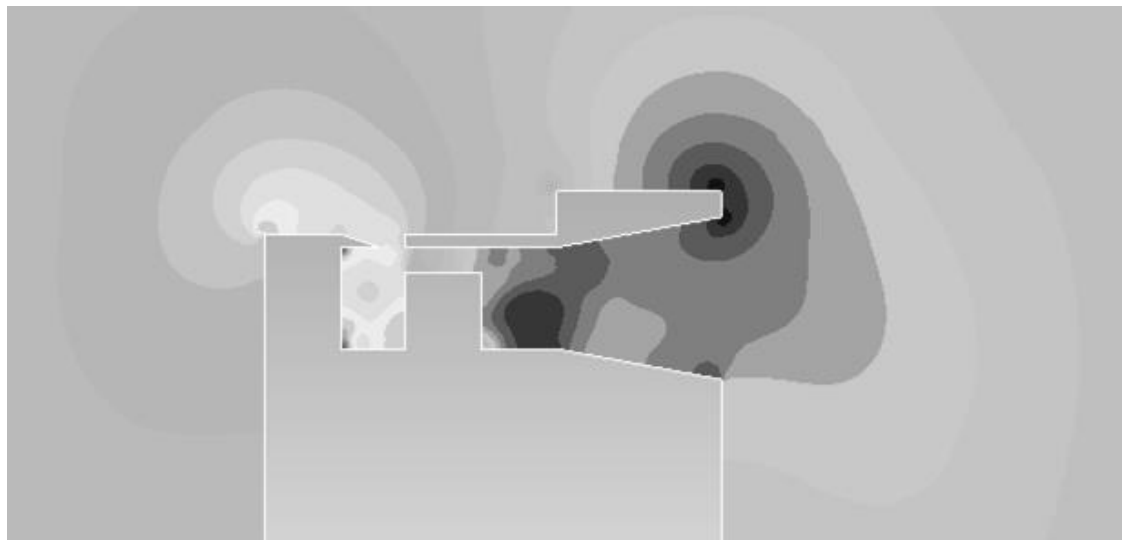


Figure 4. Static pressure contour of one end of the prototype where darker region indicates lower pressure region.

Because of the mass-distributing issue and the nature of this research, this testing equipment was created using computer numerical control (CNC) machining. It is able to create two identical blocks out of aluminium and effectively eliminates or at least minimize imbalance mass.

In the final product, two 3mm screws were used to secure each whistle on the right position. This is because since the equipment will be operating at high RPM, it must be ensured that every parts are secured firmly. The shaft should be made as short as possible to prevent unwanted and undesired vibration owing to imbalance mass.

Two Galton whistles, or commonly known as dog whistle as shown in Fig. 5, are used in this setup. It is noted that although they cannot produce ultrasound, their

frequencies can reach as high as 5 kHz, which is as high as any conventional whistle can go. By adjusting the length of resonance chamber, the frequency can be manipulated. To do that, screwing in the rod would shorten the chamber, hence giving higher pitch or frequency and vice versa.

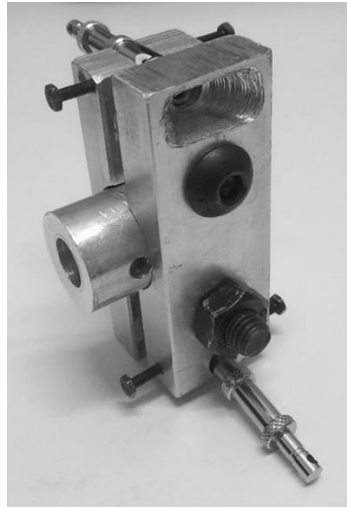


Figure 5. First prototype of testing equipment.

2.2 Experimental Procedure

Experiments can be carried out by using a motor or any machine to rotate a shaft is needed. Available options in the university includes an induction motor (Fig. 6) and lathe machine (Fig. 7). Lathe machine can hold the shaft easily and its RPM can be tuned from as low as 10 to maximum 2500 RPM. However, lathe machine tends to generate high pitch noise during operation. Therefore, the 3-phase induction motor was selected. Furthermore, induction motor, generally produces lesser noise and is located at an isolated quiet room.

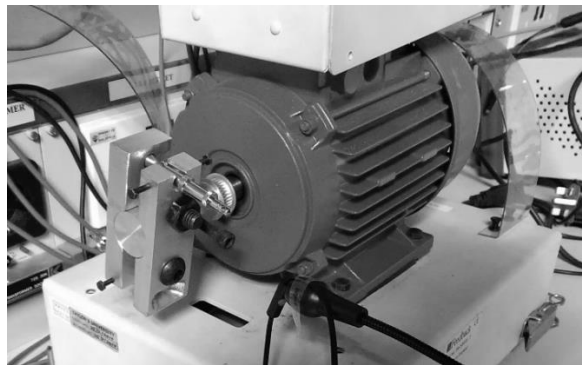


Figure 6. Prototype attached onto induction motor.



Figure 7. Lathe machine provides rotation speed up to 2500 RPM.

The microphone that is being used comes from an original HTC One m7 headset which is able to receive crisp and clear sound signal. It is also unidirectional, which helps to reduce surrounding noise when pointed at the equipment. Using an ASUS laptop as recording device, Windows operation systems often come with dedicated audio enhancement such as DC offset cancellation and noise suppression. All enhancements are turned off before recording as they often suppress recurring frequencies. This would badly affect the result and analysis. Since all frequencies of interest are below ultrasound, a sampling rate of 44100 kHz would suffice.

Experimental procedure is as follow:

1. Place microphone at a distance of 15cm away from the centre of shaft.
2. Start the motor and record the sound for 5 seconds.
3. Turn off the motor, attach and secure testing equipment (without whistles) onto motor shaft.
4. Start the motor and record for 5 seconds, and then turn off.
5. Attach both whistles and secure them firmly.
6. Start the motor and record for 5 seconds

Location of microphone is remained at the same location throughout the recording session, to ensure all recording data are comparable. It was placed 15cm away to prevent the air movement. All three sound recording can be used to determine the base signal, signal with equipment and lastly signal with whistle. This helps to identify the correct frequency range for analysing purpose later on.

The next step is to create the excitation vibration by adding imbalance mass on the equipment. By attaching a small mass on one end of the block, controlled vibration can be induced. After that, attach the equipment back to the motor and run it. The sound will be recorded and compared with previously recorded sound.

2.3 Analysing Result

Recording and analysing data will be done through Audacity software. It is a dedicated recording software and provide frequency analysis. Due to the limitation of recording devices and sound card used by ASUS laptop, the maximum sampling rate is set at 44100 Hz. At 400 RPM, vibrating frequency is 6.67Hz. According to Doppler Effect, sound wave generated by the whistles should have different peak frequencies at different time. When whistles are moving towards the microphone, frequency would be higher than when they are moving away. This phenomenon is often experienced when an ambulance travelling towards an observer. Observer would hear a higher pitch and right after ambulance travels past the observer, the pitch immediately becomes lower.

However, the complication comes into play as the whistles themselves are also rotating about the axis of shaft. Therefore there will be two movements involved, rotation and vibration as shown in Fig. 8. The frequency and decibels recorded at the microphone vary due to the rotation movement only. However, the recorded sound waves may change when external vibration is induced on the shaft.

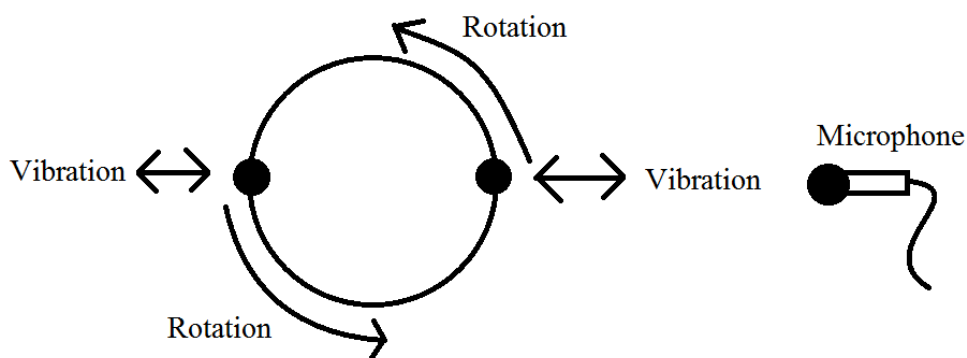


Figure 8. Movement of whistle during experiments.

Audacity, or any other similar software, plot spectrogram by using a group of data and perform Fast Fourier Transform to convert the recorded data to frequency domain. Data blocks are split into 0.0375second a block due to the rotational frequency, i.e. it would take $1/6.67$ second (or 0.15s) to complete a cycle and it requires 4 points to detect the sound wave at each cycle (Fig. 9).

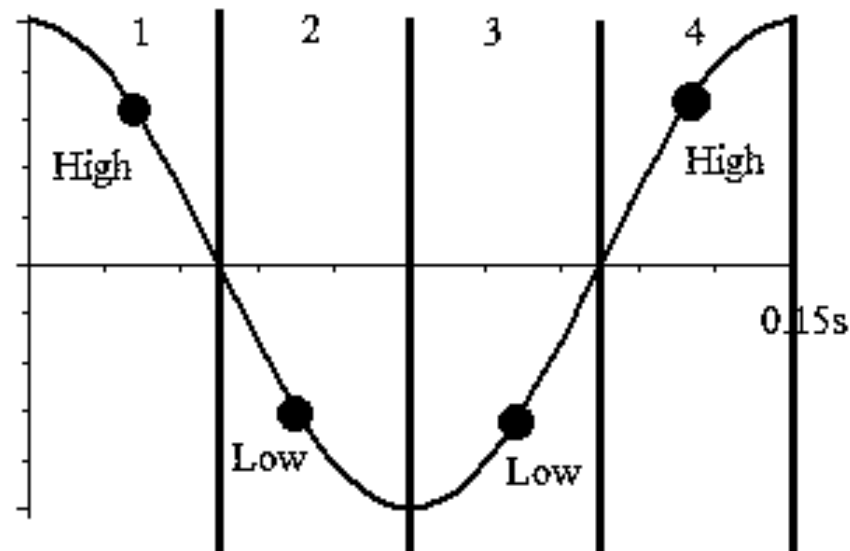


Figure 9. Four data blocks of 0.0375s each can be used to represent changing parameters.

By using this method, frequency and dB changes could be observed using frequency spectrogram. Frequency would change due to Doppler Effect and dB would change due to changing distance relative to microphone. The physical formulas that govern both changes are:

$$f_{apparent} = \frac{v}{v+v_s} f_{source} \quad (2)$$

where v denotes velocity of sound and v_s denotes velocity of moving sound source,
and

$$sound\ intensity\ at\ surface\ of\ sphere, I = \frac{P}{4\pi r^2} \quad (3)$$

where P denotes acoustic power and r denotes distance from the sound source.

Validation of result will be done by using accelerometers placed on either bearing or engine mounting. Real acceleration and displacement can be determined from accelerometer and be used to validate experiment results. However, since accelerometer cannot be placed on shaft itself, there will be some deviation from true results.

3.0 Result and Discussion

Results

Table 1. Frequency analysis of results using induction motor at 400 RPM.

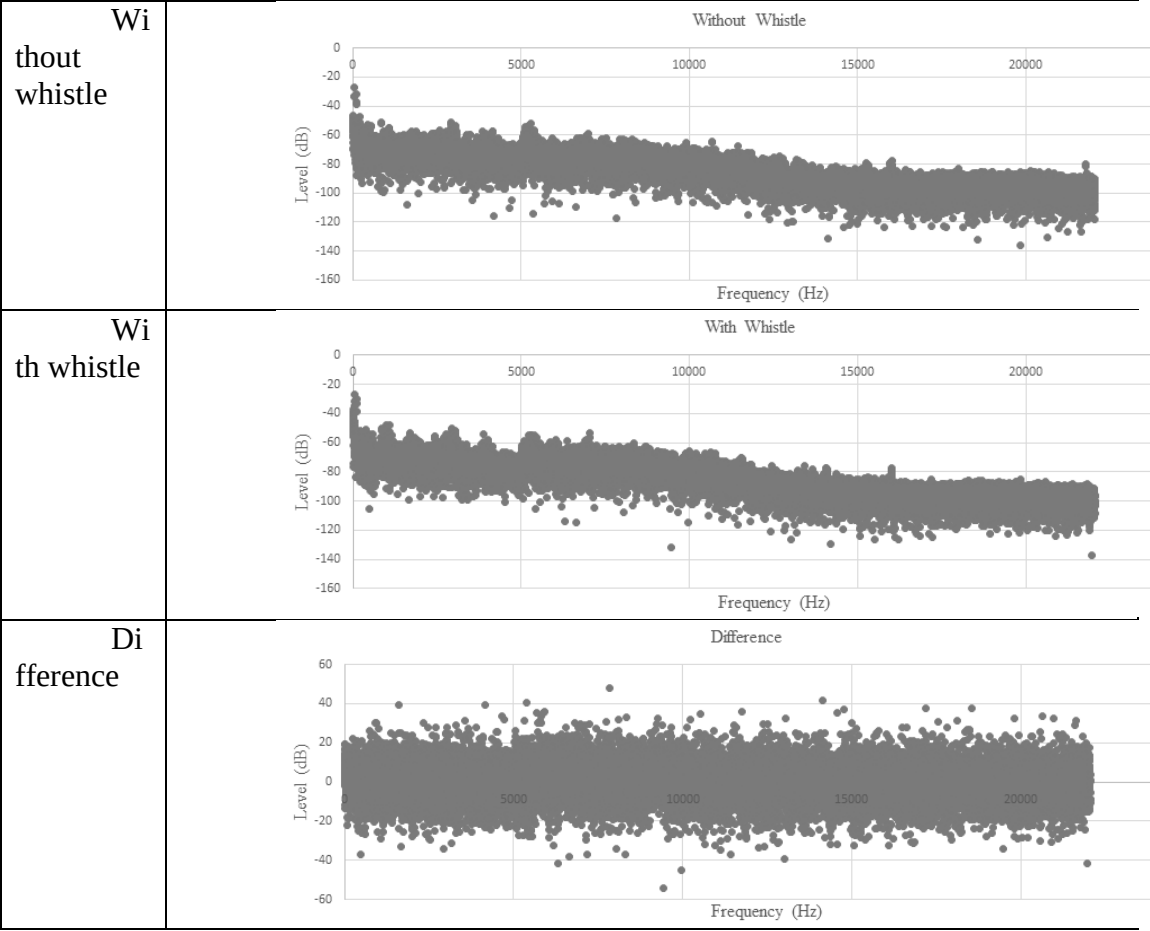
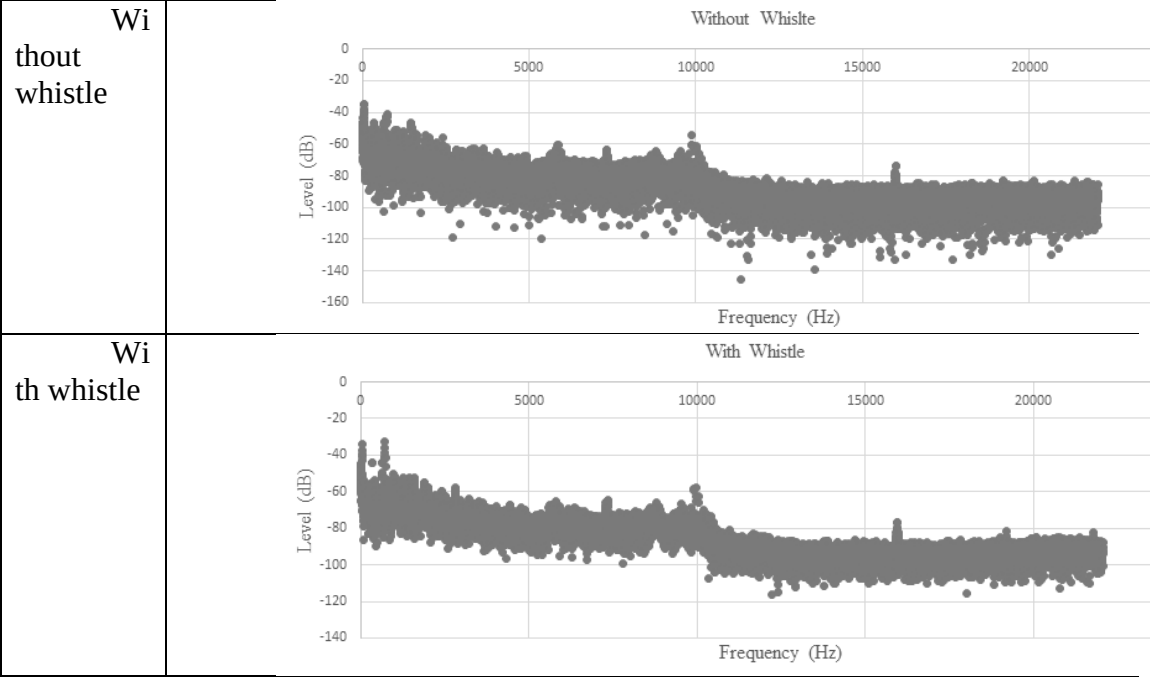
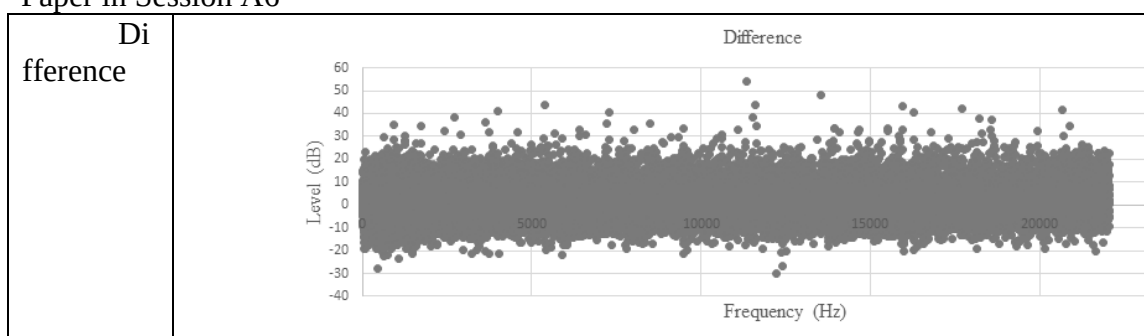


Table 2. Frequency analysis of results using lathe machine at 1000RPM.





Discussion

Based on early results, the first prototype of testing equipment has failed to generate distinguishable frequency plots. Experiments were carried out with both induction motor and lathe machine at various RPM. Although testing environments are not sound proof and absolutely quiet, recordings were done with as little background noise as possible. All other equipment, including air-conditioning and exhaust fan, were closed to eliminate possible unwanted noise being picked up by microphone.

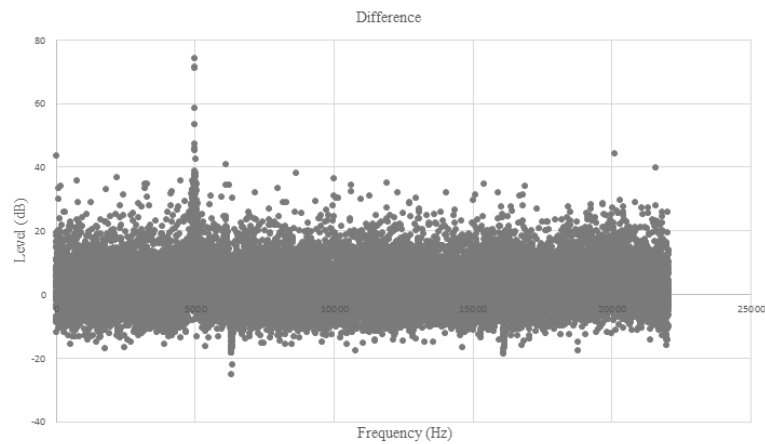
Results were taken from both induction motor and lathe machine for several reasons, i.e. although lathe machine generates more noise, it can be controlled to operate at higher RPM in order to drive more air in to the mechanical vibration sensor. Another reason is to make sure the whistle signal is not masked by either of the machines used. Nevertheless, if both samples cannot show distinguishable whistle signal, there is no way to tell if the whistle signal is there at all. Unfortunately, using this prototype has so far unable to generate distinguishable frequency spike at around whistle frequency, which is between 4 kHz to 5 kHz. All recordings were repeated twice to ensure the results are constant and repeatable. Table 1 uses induction motor which has lower noise, whereas table uses lathe machine which can run at higher speed but with louder noise.

Difference graph was created by subtracting the level (dB) of noise without whistle, from level (dB) of noise with whistle under the same frequency band. It can be used to eliminate frequencies generated by the same source, i.e. motor and background noise which theoretically have same intensity at specific frequency band. This would leave only frequencies that are only present in either sample. In this experiment, remaining frequency would be the one generated by whistle. This helps to make analysing sample much simpler since many of the similar and useless data are eliminated after subtraction.

As seen in the difference graph, there is no distinguishable frequency peak at around 4.5 kHz. Motor noises in both samples would cancel each other out during subtraction. The other differences, mainly at 20dB, are most probably due to white noise as these recordings were not carried out in completely silent room. Intuitively speaking, since white noise is present at both samples, zero difference is expected when white noise sample is subtracted by another white noise sample. However, by definition, white noise has average amplitude in *all* frequency bands. Using frequency spectrogram on longer sound sample would ‘average’ these readings and obtain values with much smaller range, i.e. longer sound sample gives smaller difference in power of white noise. In these data, the recordings are only 2 seconds long and hence

have very random values in each frequency band in each sample. This explains the large range of differences when one is subtracted from other.

To put these graphs into perspective, a pure tone of 5 kHz was generated by smartphone and recorded. Another sample was recorded under same condition, but without the tone. Frequency plot of second sample was deducted from first sample (with tone). The difference (Graph 1) shows a clear peak at 5 kHz, which proved that the graphs previously discussed could not show whistle sound in distinguishable manner, if not at all.



Graph 1. Frequency-level plot of sample with 5 kHz tone subtracted by sample without tone.

In real-life hearing application, the loudness is measured by

$$\text{decibels, } \beta = 10 \log \frac{\text{Intensity} \left(\frac{\text{Watts}}{\text{m}^2} \right)}{10^{-12} \frac{\text{Watts}}{\text{m}^2}} \quad (4)$$

where 10^{-12} W/m^2 is the threshold of human hearing. However, in digital recording, the common bit depths (similar to human hearing threshold) are 0, making log invalid. To establish a measuring system, highest possible sample value is used as reference instead. Hence,

$$\text{decibel full scale, dBfs} = 20 \log \frac{\text{sample value}}{\text{highest possible sample value}} \quad (5)$$

would always generate values equal or smaller than 0. For 32-bit recording used throughout this experiment, highest possible sample value is 2^{32} or 4,294,967,296.

It is suspected that whistle is not generating distinguishable sound is because of insufficient air flow. From 2-D CFD analysis as shown in Fig 3, the circulation of air at whistle mouthpiece could have form an “air wall” that blocks air from going in further. This has probably allowed lesser air than previously calculated into whistle, generating sound at very low intensity. Since both motor and lathe are not noise-free machines, these noises could have easily masked whistle sound. Limitation of

experiment is reached because maximum frequency of whistle is around 4.7 kHz and both machines have noise within 5 kHz range. To get distinguishable whistle sound, its intensity must be higher by increasing airflow, which leads to development of second prototype.

The prototype being developed will be based on the first prototype. An external cone will be manufacture to drive more air in. This external cone can be attached on to existing prototype to enlarge the intake area, hence making more air to go into whistle. This also helps to reduce manufacturing time and complexity. This should allow the whistle to generate frequency at intensity high enough to be distinguishable during data analysis.

4.0 Conclusion

Based on the result and analysis, said prototype has failed to generate any detectable difference as of submission of this paper. It is suspected that circulation of air near the whistle mouth piece has choked the air flow from going into whistle, which causes sound intensity to be very low. Nevertheless, this result may not apply to a rotating shaft which has no noise, e.g. motor located far away or isolated in sound-proof wall.

These early findings have likely reflect the efficiency and limitation of this method to detect shaft vibration. For example, two identical sound samples could have enough differences that causes misjudgement. The whistle frequency must be either higher than motor/engine operating frequencies or have distinguishable high intensity that it stands out from nearby frequency bands.

Experiments results can be improved by conducting the experiment in a silent room. Although real life applications have noises in all frequency range, effectiveness of new method must be carried out first in controlled environment. An external vane can be manufactured and attach to existing equipment to drive more air into whistle to get higher sound intensity. Sound sample can be then analysed for its effectiveness in detecting vibration.

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Development of an Optimisation Methodology for Air Conditioner Copper Tube Designs

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Abstract

Safety and reliability are the main concern in structural designing in order to meet the needs of the end user. Confidential reports had claimed that copper tubes inside packaged outdoor air conditioner unit during transportation via shipping are very prone to failure due to random horizontal vibration. One of the critical positioning of copper tube in the outdoor air conditioner unit is suction tube; which has a rigid attachment to the accumulator of a compressor on one end and four way valve on the other end. The resonance phenomenon occurs when the natural frequency of the suction tube coincides with the excitation frequency. At resonance, suction tube tends to vibrate at maximum displacement resulting in fatigue failure. Sources of excitation frequency to the suction tube are identified to be random horizontal vibration input from unit transportation and also compressor excitation during unit operation. In order to mitigate the vibration issues of suction tube, dynamic behaviour of suction tube was studied using finite element (FE) modal analysis and experimental modal analysis (EMA). Variations of natural frequency within the allowable range of 5% validate the accuracy of FE modal analysis. However, on diagonal coefficient in MAC plot lesser than 0.8 indicates the presence of human error occurring due to high number of excitation points with irregularities excitations. Usage of insufficient sensors to distinguish two different mode shapes lead to off diagonal value in the MAC plot to be higher than 0.2. The design of suction tube was optimised using shape optimisation in order to have lower manufacturing cost and improved performance due to reduced mass participation in horizontal vibration. Although there were many methods to control vibration in pipelines such as addition of mass, design optimisation has high market value as due to its exceptional advantages compared to other methods. The high end of the project is to develop a mathematical model to determine the natural frequencies of suction tube at different loop length reduction; which will assist the air conditioner design engineers for future design optimisation work.

Keywords: Design optimisation, modal analysis, mathematical modelling, suction tube, morphing.

1. Introduction

In engineering field, pipelines often experience two types of phenomena; namely the flow-induced vibration and structural failures [1]. Pipe flow inducing vibration is due to the disturbance that present in the system itself such as pump, fittings and valves. On the other hand, structural failures of pipes can be closely linked to vibration problems [2]. Vibration problems can lead to broken pipe lines and cause leakage of fluid in the system. In order to prevent pipe failures, vibration analysis on the pipe structures had to be performed to maximize the reliability of pipeline. This is because pipe failures could be costly in terms of maintenance and loss in production [3]. One of the engineering systems that use an extensive low pressure pipeline for fluid transportation is air conditioning system.

Copper tubes are used to transport fluid from one place to another in an air conditioner system and a segment of the copper tube is called the suction tube; which has a rigid attachment to the accumulator of compressor at one end and the other is connected to a four way valve. This research focuses on optimising the design of suction tube by studying its dynamic behaviour due to excitation from air conditioner unit transportation and compressor vibration. The design parameters that affect suction tube vibration can be identified by interpreting its vibration behaviour; which can be analysed through modal analysis. Modal properties of a structure can be determined in experimental modal analysis (EMA); which is a method used to validate the accuracy of finite element (FE) modal analysis. Design optimisation was performed later on to improve the design of a structure. Design optimisation is a method to acquire the optimum design solutions by concerning mathematics and operations [4]. Vast growth of technology has made optimisation to be a part of computer aided engineering (CAE). The purpose of optimisation is not only to produce a feasible design but to achieve the design objectives; which are closely related to minimising the manufacturing cost and increasing the performance of the design.

In the current practice of design optimisation, there is topology optimisation, topography optimisation, shape optimisation and size optimisation. Topology optimisation determines the features in a structure such as number, location and design of holes [5]. Then, it performs iterations to find the optimal design for the structure based on a confined design space. On the other hand, topography optimisation determines the best shape sequence for thin walled structures [6]. The difference between topology and topography optimisation is that topology optimisation uses density variable whereas topography optimisation utilises shape variable. Morphing is an advanced technology used in shape optimisation to alter the dimensions by selection of nodes. This feature changes the dimension of the design without the need for re-meshing. The meshes produced have the ability to adapt to a new geometry. Quality of meshes produced is not affected by the alteration of geometry. This in turn reduces the engineering costs and time for design optimisation.

The significance of the project was highlighted by addressing the gap between previous works conducted by researchers in comparison with the current work. In the past studies on determining dynamic behaviour of structure, Trebun'ahas et.al have conducted experimental modal analysis (EMA) on two different turbo compressors to determine the natural frequency and mode shapes with the use of Brüel & Kjær

PULSE Reflex software [7]. 12 excitation points and 1 accelerometer position was used for the first turbo compressor whereas 8 excitation points and 1 accelerometer position was set for second turbo compressor. In reality, more excitation points and less accelerometer should be used in EMA. This is to produce much more accurate experiment results by analysing response at different excitation points; which was believed to excite the mode of vibration. This study incorporated high number of excitation points with less accelerometer usage to overcome this limitation.

Besides that, the knowledge on FE modal analysis and EMA was applied in the past on suction tube as well to determine the vibration properties. Loh et al. conducted EMA and FE modal analysis on an air conditioner suction tube. The mode shapes of both analysis was correlated and the results show that the maximum percentage difference of natural frequency is 8.5% [8]. This study uses a fixed-base boundary condition; which is not appropriate to study the vibrational behaviour. This is because of the presence of coupling between the fixture and the suction tube [9]. The use of free-free boundary condition in this study was much suitable to determine the natural behaviour of suction tube.

Without the use of design optimisation to improve the performance or efficiency of a structure, some researchers have studied and patented design as a solution to overcome vibration in pipe systems. The pipe vibration reducer, a component patented by Kucera uses a resilient cantilever arm for attaching a vibration dynamic mass to a pipe [10]. This invention is capable to reduce pipe vibrations to frequencies up to 500 Hz.

Besides that, Uselton proposed to mitigate pipe vibrations in air conditioning system by adding strips of rubber around the refrigerant line, which reduces vibration due to added mass on the line and by frictional damping [11]. Length of each rubber strip preferably to be a quarter of the standing wave vibration wavelength. The rubber strips are attached at the outdoor air conditioner unit; at where the condenser and compressor are situated.

Another invention was made by Cooksey; who patented a design of suction accumulator for refrigeration system; which includes a storage vessel, a tube within the storage vessel and a flexible yieldable support [12]. The purpose of his design is to overcome transmission of vibration and noise from compressor to suction accumulators. Flexible yield support was fixed between the accumulator casing and internal suction tube; which has the ability to damp the vibration and noise transmission through the suction accumulator. Addition of mass in the pipe design had shown improved result in reduction of vibration. Addition of mass results in higher manufacturing cost due to increase in material. Due to advanced technology growth in the field of design optimisation, the suction tube was optimised at its best geometry for better performance in terms of vibration.

Design optimisation had been widely used in various field including dentistry field. Chang et al. optimised the design of dental threaded implant using topology optimisation; which removes unwanted material from the implant [13]. The secondary purpose of their study was to increase the space for new bone ingrowth. ANSYS 11.0 software was utilised for topology optimisation whereby the possible parameters for elasticity, stress and strain was determined in a confined space. Density variable was varied between 0 to 1; which means that density variable close to 0 indicates the

removal of material whereas density variable close to 1 indicates the material that must be retained. At the end of their work, it was estimated that about 17.9% of the total volume from the dental implant can be removed without affecting its biomechanical performances. This allows more new bone ingrowth and bone graft fusion into the bone. The only disadvantage from their work is that the optimised dental implant experienced higher stress level compared to the original implant. In this study, a shape optimisation was much preferred than topology optimisation as the suction tube geometry has only one design parameter that can be optimised, which is the loop length. The utilisation of shape optimisation with aid of mesh morphing was a much appropriate technique to optimise the design of suction tube.

Besides that, Kilian et al. used Altair OptiStruct to optimise suspension of hard disk drive, in which combined topology and topography optimisation were used to generate the result [14]. Topology optimisation uses a confined design space whereas topography optimisation uses the beads pattern to optimise a design. From the research, it is concluded that optimisation software should be used in the design stage where the design can be still altered. In this research, combined topology and topography optimisation will not be used. This is because suction tube has a thin rough thickness ranging from 0.7mm to 0.8mm. Any removal of copper element from suction tube using topology optimisation will affect the feasibility of the design. In contrast, topography optimisation adds material such as bead stiffeners to the existing structure to improve the performance. Optimisation through shape optimisation for suction tube were determined to be the best technique for optimisation as great material reduction takes place; which in turn reduce the manufacturing cost and improve the performance of the structure.

In air conditioning industry, Manekshaw et al. optimised layout of air conditioner copper tube using shape optimisation [15]. The purpose of their study was to increase the natural frequency of copper tube in order to avoid resonance caused by the compressor excitation. A free-free modal analysis was conducted in Altair Hypermesh to determine the natural frequency of copper tube at the first mode. The objective was set to maximize the natural frequency and the constraints were applied to maintain the dimension of copper tube diameter and thickness throughout the optimisation process. From their research, the optimised design of copper tube layout was found to be when the loop length was reduced by 90mm. However, the study conducted by them was not justified in terms of performance. The optimised design of the copper tube was to have a higher natural frequency compared to the existing design. Modal analysis conducted in Altair was not validated with EMA testing. These gaps in their research were addressed in this research study as EMA on suction tube was conducted to validate the accuracy of FE software in predicting dynamic behaviour. Besides that, the performance of the optimised design of suction tube was compared with the original design in terms of vibration reduction.

In this project, the dynamic behaviour of suction tube was studied by FE modal analysis and EMA. During EMA and FE modal analysis, a “free-free” boundary condition was set for the suction tube. In a “free-free” boundary condition, the suction tube does not experience any constraints on it. The correlation was obtained to validate the accuracy of FE modal analysis in predicting the mode shapes of suction tube. In order to reduce vibration of suction tube, the design will be optimised through

shape optimisation comprising of advanced morphing technology since material reduction by reducing loop length have higher significance in cost savings. The novelty of the project is to develop a mathematical model to compute the natural frequencies of suction tube under controlled factors using factorial design studies.

2. Research Methodology

2.1 Finite Element (FE) Modal Analysis

2.1.1 Geometry and Meshing

The suction tube were exported from SolidWorks as a Parasolid file. Parasolid file is the universal file format; which is readable by NX Nastran. The geometry of suction tube is shown in Figure 1.

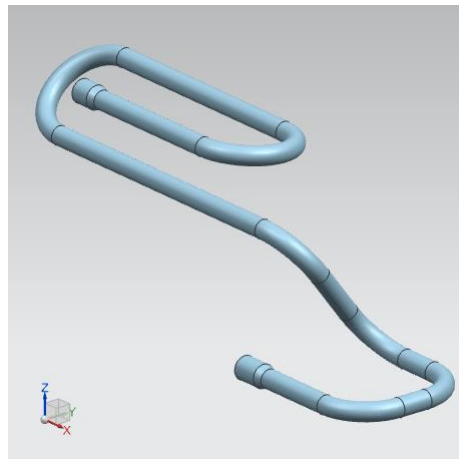


Figure 1. Geometry of suction tube

The geometry of suction tube was then offset to 0.35 mm inwards; which is half of the original thickness of suction tube and the mid surface was utilised for further analysis. A two dimensional (2D) mesh of 3mm element size, shown in Figure 2, was preferred over a three dimensional mesh (3D) due its faster computation time and less complexity [16]. An element size of 3mm was used to mesh the geometry to reduce time taken to mesh and evaluate the mesh significance on the result.

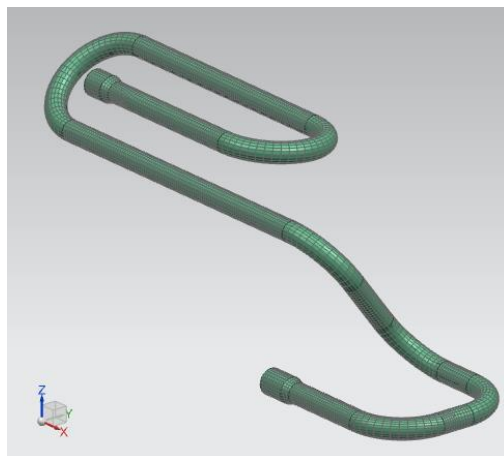


Figure 2. Meshing of suction tube

After meshing, two important parameters were set; which is C10100 copper alloy as the type

of material and 0.7mm as the original thickness of the suction tube. This is the material and properties setting of the suction tube in NX Nastran.

In FE modal analysis, the SOL 103 Real Eigenvalues solver was used to conduct the analysis together with Lanczos method for extraction of data. Lanczos method were preferred due it is high efficiency in extracting eigenvalues and eigenvectors; which enables natural frequency and mode shapes computation at each vibration modes. The results of the FE modal analysis were stored for the purpose of correlation later on with EMA results. Displacement, stress and strain were set as the result output of the FE modal analysis for further viewing later on. The range of frequency were set to 1 Hz to 300 Hz; which is set based on ASTM D 4728 – 01 Standard Test Method for Random Vibration Testing of Shipping Containers [17]. The results obtained are in terms of mode shapes of the suction tube at each vibration mode and it is further discussed in the results and discussion segment of this paper.

2.2 Experimental Modal Analysis (EMA)

2.2.1 Pre-test Planning

Pre-test planning is the early stage of EMA that produces a test analysis model (TAM). TAM is the selection of nodes for impact and sensor points from NX Nastran. Proper selection of impact points and sensor points is crucial as these points will be used in the experiment to capture all the natural frequencies with its corresponding mode shapes within the desired frequency range. The sensors are located at the position of suction tube that undergoes maximum displacement during each vibration mode. Impact points are selected based on random selection and are evaluated based on pre-test modal assurance criterion. Figure 3 depicts the MAC plot for pre-test planning of suction tube.

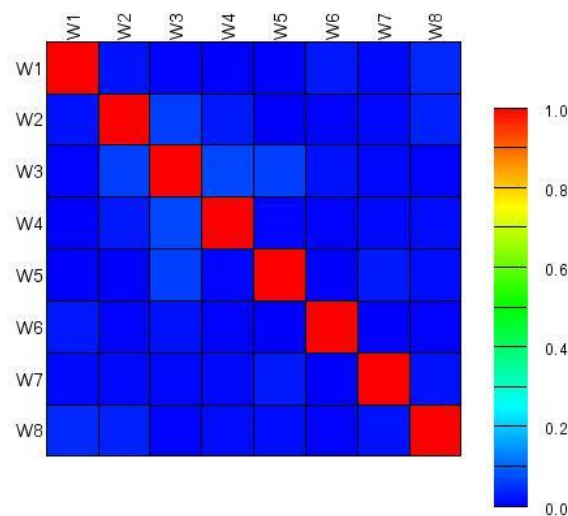


Figure 3. Pre-test MAC for sensor and excitation points

In this experiment, 4 sensor points and 49 excitation point including the sensor points was selected. The method of excitation is impact hammer as it requires less hardware to perform the test and measurements can be completed within shorter time [18]. The selected nodes in TAM are then exported PULSE Reflex for geometry decimation. In geometry decimation, all the nodes are selected and trace lines are formed to connect all the selected nodes in pre-test. This trace line depicts a geometry based on the selected nodes which will be useful during the EMA. Figure 4 shows the nodes and trace line formed in PULSE Reflex based on TAM.

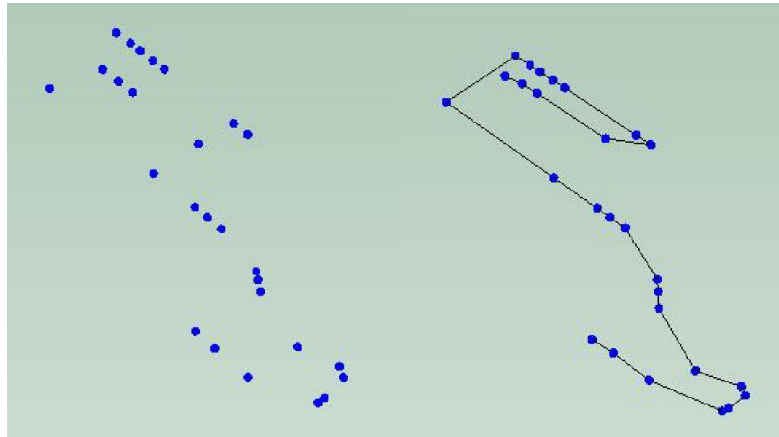


Figure 4. Nodes and trace lines formed in PULSE Reflex

2.2.2 Experiment Set-Up

EMA of suction tube was conducted by setting up the suction tube on the test rig. Figure 5 shows the experiment set-up of the suction tube and the insulated test rig.



Figure 5. Experiment set-up of suction tube (left) and insulated test rig (right)

In this experiment, 4 Brüel & Kjær accelerometer type 4517 and a Brüel & Kjær miniature impact hammer type 8204 was utilized to capture the mode shapes at each vibration mode. Each accelerometer has a mass of 0.65g and the selection of number of accelerometer should not be more than 5% of the total mass of the structure in order to avoid mass loading. The mass of suction tube is 217g hence the usage of 4 accelerometer were practical. Brüel & Kjær Fast Fourier Transform (FFT) analyser with 12 channel input was utilized to convert transient signal from time domain to frequency domain. MTC Hammer is the software provided by Brüel & Kjær for EMA and used throughout the measurement process. The suction tube was attached to the test rig with elastic chord where else the 4 accelerometers are attached to the suction tube using beeswax. The test rig is well insulated with foam pads to ensure that the test is conducted in a free-free boundary condition and there is no ground vibration that exerts external force to the structure. An average of 3 readings are taken for each impact points and the frequency response function (FRF) graph together with coherence

graph were observed to finalise each measurement. FRF displays all the modes resulting from the impact in MTC Hammer. The consistency of each impact were measured based on the coherence graph; in which if the coherence graph is close to 1 after three impacts on each point, the measurement will be a valid data. The results obtained from EMA are further discussed in the results and discussion segment of this paper.

2.3 Design Optimisation

2.3.1 Meshing

The process of suction tube optimisation was started by meshing the structure of suction tube in Altair HyperWorks. Figure 6 shows the setup menu of meshing in Altair HyperWorks. The geometry of suction tube is imported from NX Nastran to Altair HyperWorks as an IGS file. Two dimensional (2D) auto meshing was utilized to mesh the geometry of the suction tube into elements. In the meshing setup, it was ensured that the entire suction tube is selected before meshing. An element size of 3mm was used to reduce computation time during meshing and mixed mesh of quadrilaterals and tetrahedrons was utilized in Altair HyperWorks.

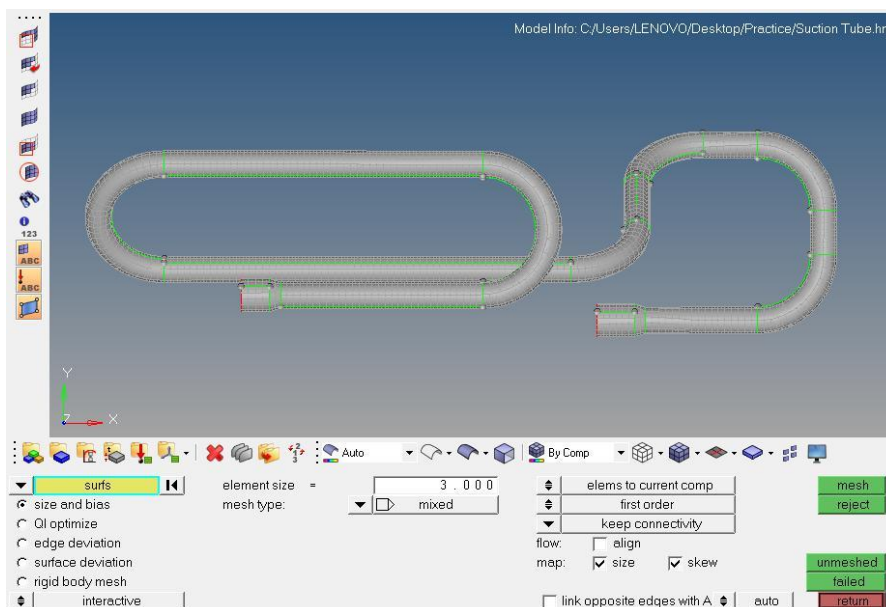


Figure 6. Meshing setup of suction tube

2.3.2 Material Setting

In the material setting, the material information of suction tube was inputted before any further analysis. Figure 7 shows the setup menu for suction tube material setting.

The material of suction tube is C10100 copper alloy. The Young's Modulus (E), Poisson's ratio (NU) and density (RHO) of C10100 copper alloy were inputted in

Altair HyperWorks for further processing. The material properties of C10100 copper alloy is obtained from NX Nastran and showed in Table 1.

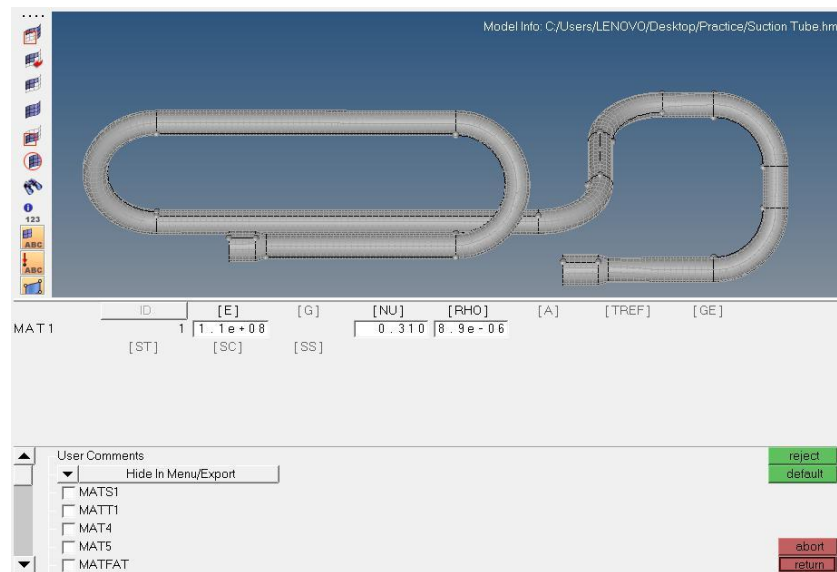


Figure 7. Material setting setup of suction tube

Table 1. Material properties of C10100 copper alloy

Young's Modulus (kPa)	Poisson's Ratio	Density (kg/mm^3)
1.14×10^8	0.31	8.92×10^{-6}

2.3.3 Properties Setting

Figure 8 below shows the properties setup menu of suction tube in Altair HyperWorks.

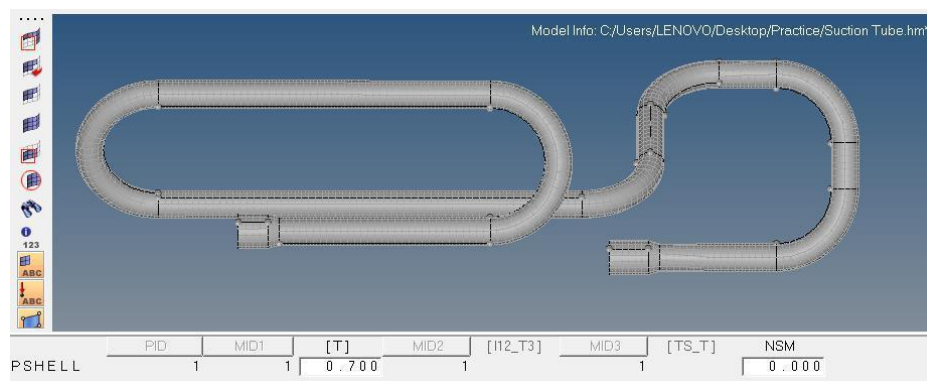


Figure 8. Properties setup of suction tube

In properties setup, the PSHELL card image and 2D type were selected to indicate that the geometry is 2D shell tube geometry and not a solid geometry. The thickness of suction tube; which is 0.7 mm was inputted as well in the property setup.

2.3.4 Load Collector

Figure 9 shows the load collector setup of suction tube in Altair HyperWorks. In load collector setup, the lower limit and upper limit of the frequency range were set. The lower limit were set as 1 Hz where else the upper limit were set as 300 Hz. This is to indicate the software to extract natural frequencies that lies within these frequency ranges. The lower limit frequency was set as low as 1 Hz to avoid rigid body modes between 0 Hz to 1 Hz. The

card image was set to EIGRL; which indicates the solver type will be real eigenvalues in extracting the natural frequencies with it respective modes.

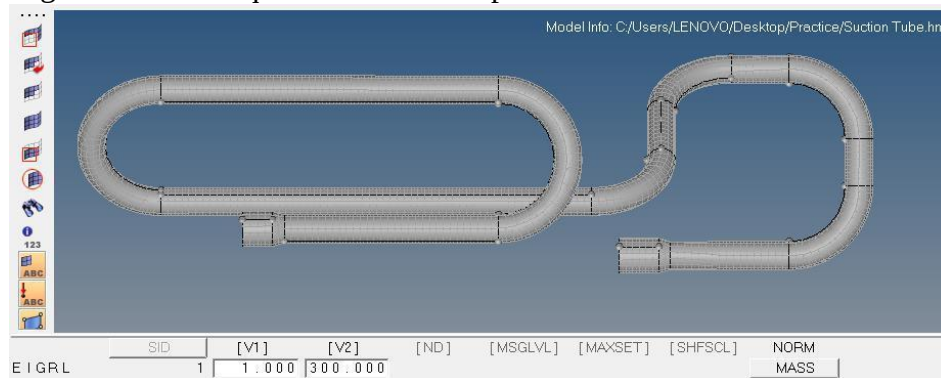


Figure 9. Load collector setup of suction tube

2.3.5 Load Steps

Figure 10 shows the load steps setup menu of suction tube in Altair HyperWorks.

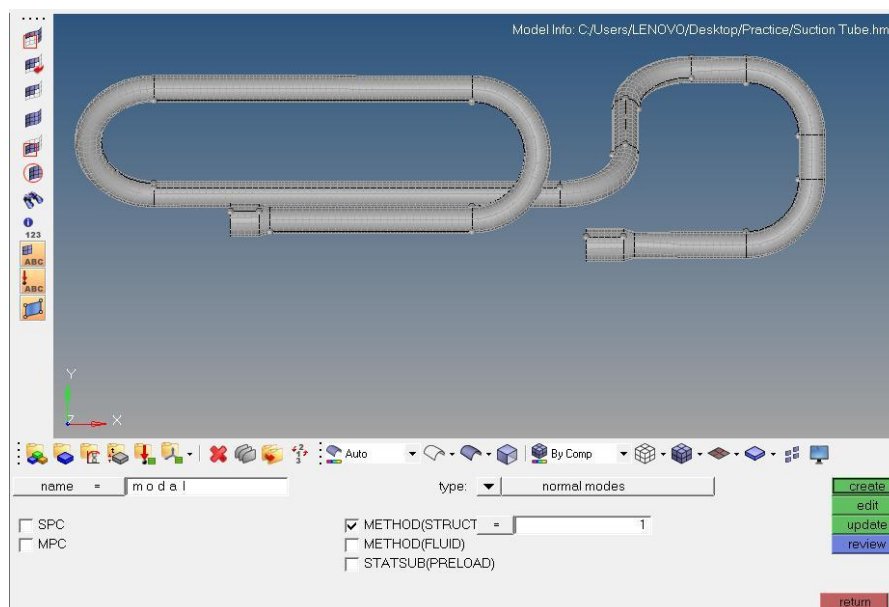


Figure 10. Load steps setup of suction tube

In load steps, the type of output result was set to normal modes; which indicates HyperWorks to extract natural frequency of normal modes and not complex modes. The method was set to structural as the analysis subject is based on suction tube structure. The process of meshing to load steps is the modal analysis setup in Altair HyperWorks. The result of the modal analysis can be later reviewed after load steps before morphing and optimising the design of suction tube.

2.3.6 Morphing and Shape Optimisation

Morphing is a shape optimisation technique use to change a dimension of a structure without affecting the mesh quality and produces minimal element distortion. After performing the modal analysis of suction tube in HyperWorks, the design space of suction tube was defined by morphing technique. The objective of the optimisation was set to maximize the natural frequency of suction tube compared to the original design. The constraints were set to maintain the diameter of suction tube together with its thickness for a uniform optimisation. The response was set to results of modal analysis of original suction

tube; in which the objective will react upon the response set. Morph constraints were applied at the free ends of the suction tube since both free ends has rigid attachment.

3. Results and Discussions

3.1 Modal Analysis

Modal analysis can be either performed by finite element simulation or through an experiment. In this study, both methods had been utilized to study the dynamic behaviour of suction tube. The primary goal of correlation is to validate the accuracy and precision of finite element (FE) modal analysis with experimental modal analysis (EMA). Correlation is done by comparing the mode shapes of suction tube obtained from FE modal analysis and EMA. Mode shapes is the shape of the geometry at each vibration mode; which means at each natural frequency, the mode shape of the structure will be different. Figure 11 to 18 below shows the mode shapes of suction tube acquired through FE modal analysis and EMA.

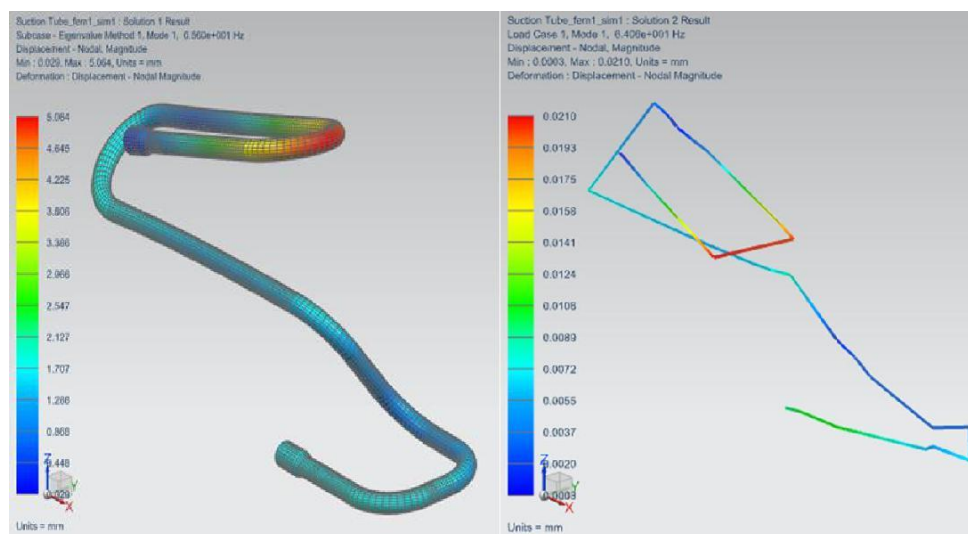


Figure 11. Mode shape in FE modal analysis (left) and EMA (right) at mode 1

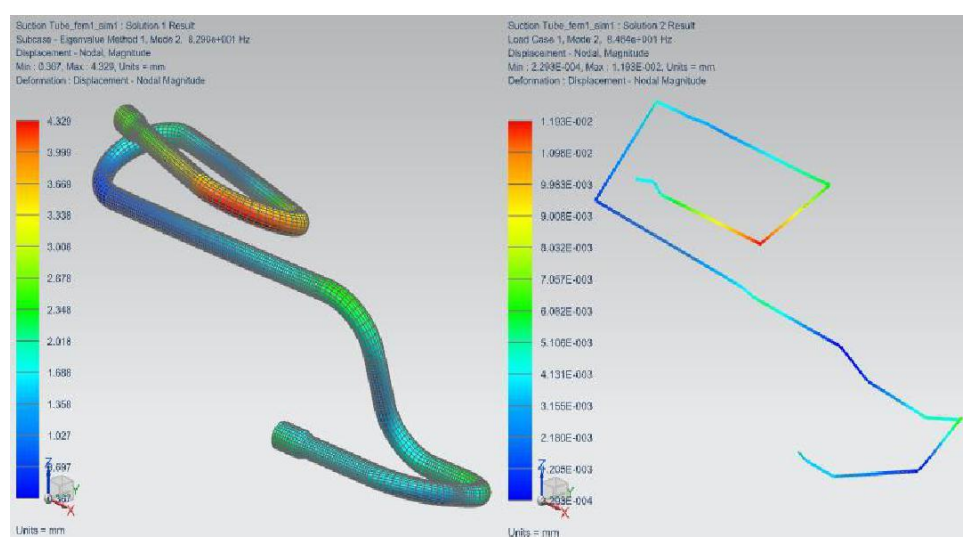


Figure 12. Mode shape in FE modal analysis (left) and EMA (right) at mode 2

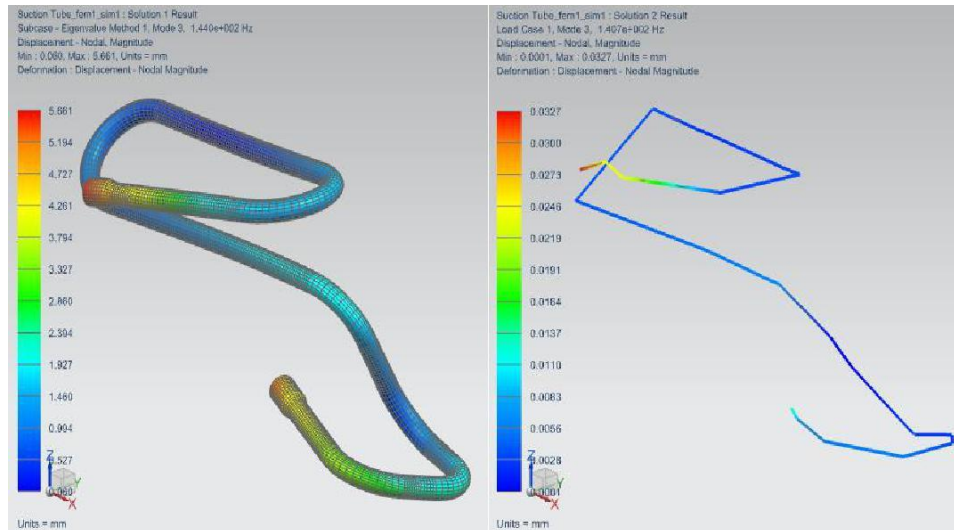


Figure 13. Mode shape in FE modal analysis (left) and EMA (right) at mode 3

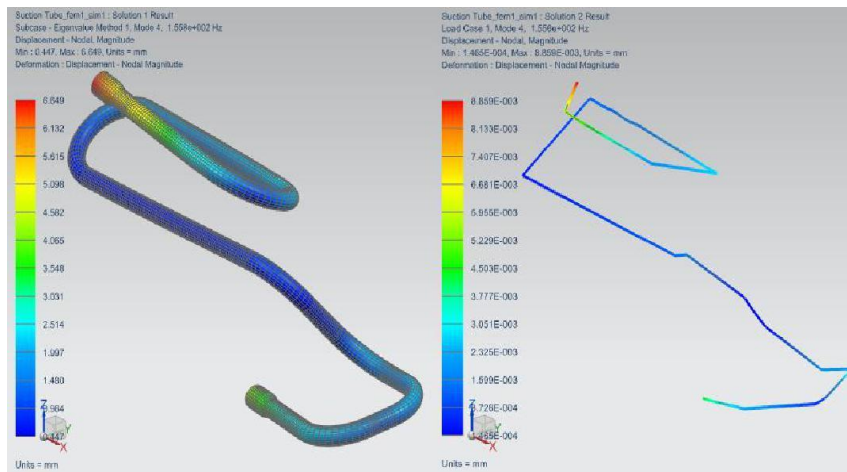


Figure 14. Mode shape in FE modal analysis (left) and EMA (right) at mode 4

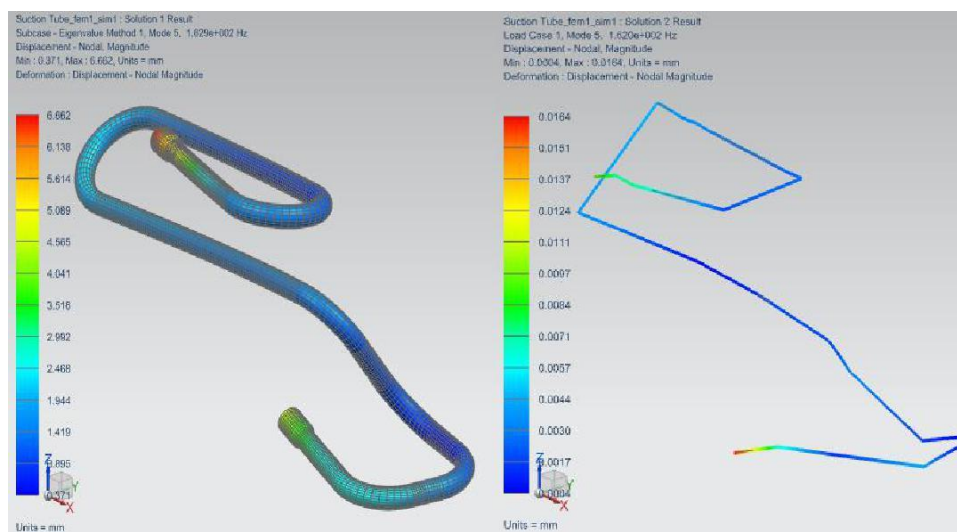


Figure 15. Mode shape in FE modal analysis (left) and EMA (right) at mode 5

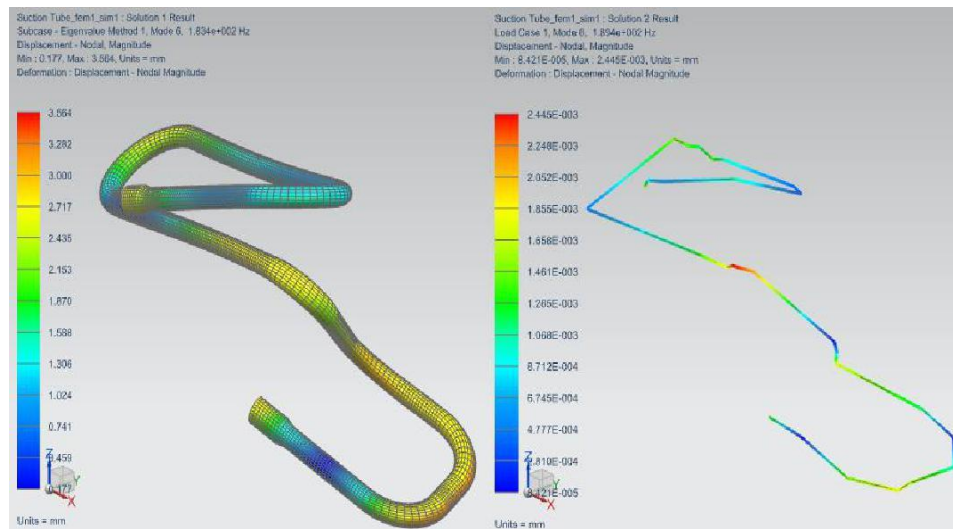


Figure 16. Mode shape in FE modal analysis (left) and EMA (right) at mode 6

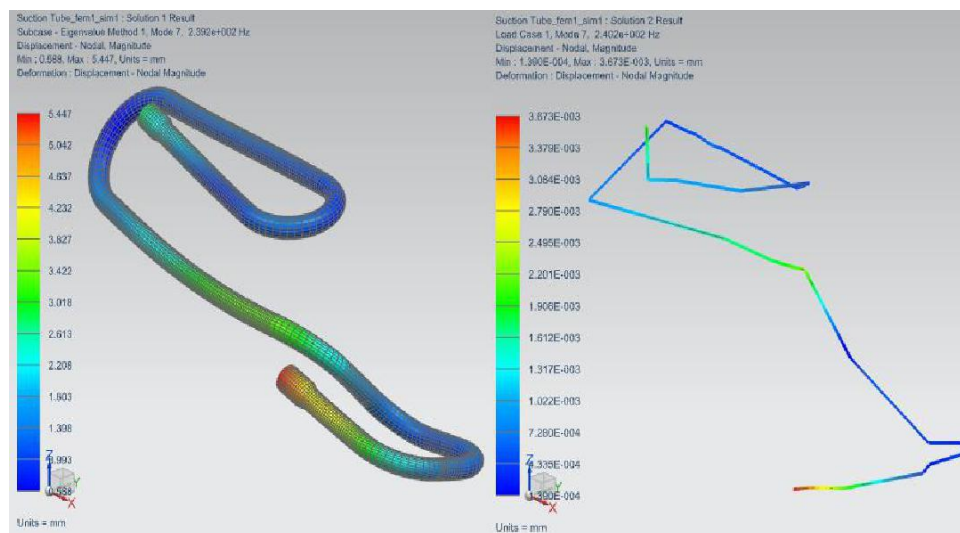


Figure 17. Mode shape in FE modal analysis (left) and EMA (right) at mode 7

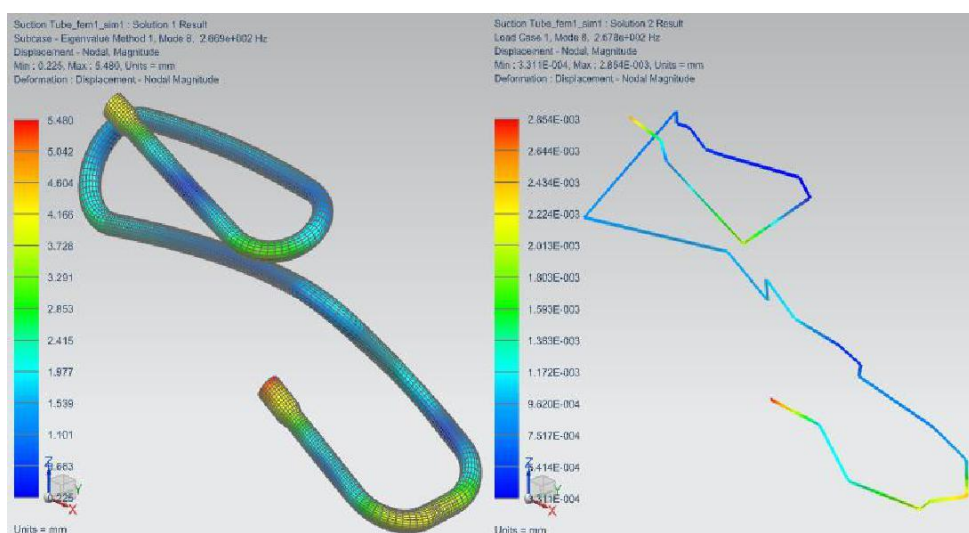


Figure 18. Mode shape in FE modal analysis (left) and EMA (right) at mode 8

Based on the observation of mode shapes of Figure 11 to Figure 18, it can be concluded that the mode shapes of suction tube at each vibration mode possess similarity as the maximum and minimum displacement at each vibration mode is identical. Hence, the FE modal analysis is well validated with EMA in the study of dynamic behaviour of suction tube. In future works, the modal analysis of suction tube can be performed via FE modal analysis to reduce analysis time compared to EMA; which requires longer time period and increases complexity in extracting dynamic behaviour of suction tube such as natural frequency and mode shapes.

During the post processing of suction tube modal analysis, it is noticed that there are variations between the natural frequency obtained from FE modal analysis and EMA. The comparison of these natural frequencies is shown in Table 2.

Table 2. Natural frequency comparison between FE modal analysis and EMA

Mode	Natural frequency (Hz)		Frequency Difference (%)
	FE Modal Analysis	EMA	
1	65.60	64.06	2.40
2	82.90	84.64	-2.05
3	143.98	140.66	2.36
4	155.82	155.55	0.18
5	162.87	161.97	0.55
6	183.41	189.38	-3.15
7	239.20	240.20	-0.42
8	266.93	267.81	-0.33

It was observed that the percentage difference of natural frequencies obtained from FE modal analysis compared to EMA is within 5%. In engineering, variation of data within 5% is considered as an acceptable data. Hence, these little variations indicate that the quality of the FE modal analysis and EMA was assured.

After performing the EMA of suction tube, the dynamic properties of the suction tube is extracted from the Brüel & Kjær PULSE Reflex and exported to NX Nastran for correlation. The correlation of FE modal analysis and EMA is expressed in terms of modal assurance criterion (MAC) plot. The MAC plot of suction tube in this study is shown in Figure 19 and the numerical value of each MAC is shown in Table 3. Practically, in a MAC plot, a value of 1.0 is obtained when the experimental and theoretical mode shapes relate to each other where else a value of 0.0 is observed for the case where the two sets of mode shape does not relate at all [19]. However, in general practice, a good MAC plot value of more than 0.8 is acceptable to relate two mode shapes where else a value of 0.2 is acceptable to indicate there are no relations between the mode shapes. From table 2, it can be observed that mode shapes at mode 1, 2 and 6 are well correlated since values of more than 0.8 are obtained. Mode shapes at mode 3 and 4 are observed to be close to obtaining a good correlation as the values differ from an acceptable value by 0.02 and 0.09 respectively. Mode shapes at mode 5, 7 and 8 indicates a poor correlation with a MAC value of 0.60, 0.60 and 0.65 respectively. The reason for the on diagonal values to be less than unity is due to the presence of human error resulting from number of excitation points

and irregular knocking.

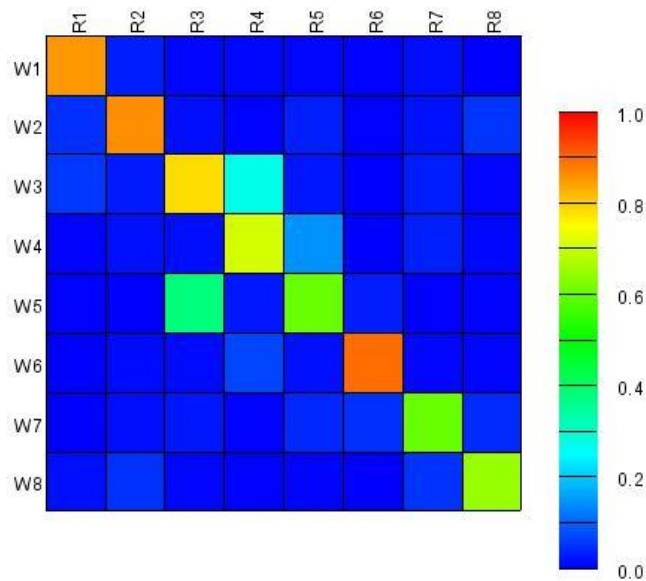


Figure 19. MAC plot of FE modal analysis against EMA

Table 3. MAC plot of FE modal analysis against EMA

	EMA 1	EMA 2	EMA 3	EMA 4	EMA 5	EMA 6	EMA 7	EMA 8
FE 1	0.85	0.03	0.01	0.01	0.01	0.00	0.01	0.00
FE 2	0.05	0.86	0.01	0.00	0.03	0.00	0.02	0.05
FE 3	0.06	0.03	0.78	0.27	0.02	0.00	0.03	0.01
FE 4	0.00	0.02	0.01	0.71	0.14	0.00	0.03	0.01
FE 5	0.00	0.00	0.38	0.02	0.60	0.03	0.00	0.00
FE 6	0.00	0.01	0.01	0.07	0.01	0.89	0.01	0.00
FE 7	0.00	0.01	0.02	0.00	0.04	0.05	0.60	0.04
FE 8	0.01	0.05	0.01	0.00	0.00	0.00	0.05	0.65

In MAC plot, consideration should be given to the off diagonal values as well and based on the plot, a MAC value of 0.38 was observed between FE mode 5 and EMA mode 3 where else a value of 0.27 was observed between FE mode 3 and EMA mode 4. These high off diagonal values of more than 0.2 could be resulting from insufficient usage of sensors to distinguish two different modes.

3.2 Design Optimisation

The optimised design of suction tube through shape optimisation was as shown in Figure 20. In the shape optimisation technique, the morphing technique was utilised to reduce the loop length of the suction tube. The reduction of tube length by 44mm results in manufacturing cost savings together with improved efficiency; which is aligned with the goals of optimisation. The performance of the suction was improved by reducing the effective modal mass participation in horizontal direction due to unit transportation and the natural frequencies of the optimised suction tube is away from the compressor excitation; which indicates the design is reliable during unit operation.

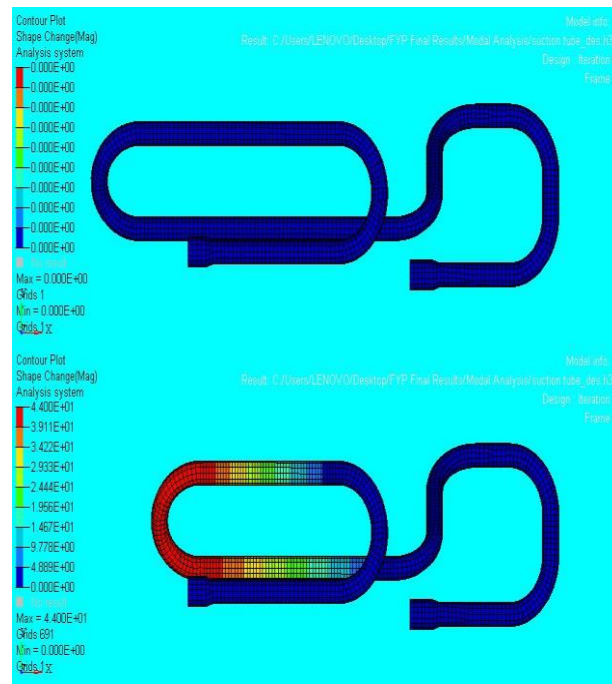


Figure 20. Original design (top) and optimised design (bottom)

4. Conclusions

The significance of this project was to optimise the design of suction tube reduce manufacturing cost and improve the performance of structure in terms of resisting horizontal random vibration due to transportation. In general, suction tube in an outdoor air conditioner is subjected to vibration due to unit transportation and compressor vibration during operation. Two different modal analysis approaches was conducted to study the dynamic behaviour of suction tube; FE modal analysis and EMA. The accuracy of FE modal analysis results of suction tube was validated with EMA results. The maximum variation of natural frequency of 3.15% indicates both FE modal analysis and EMA was conducted well in extracting natural frequency of suction tube. However, 5 mode shapes between FE modal analysis and EMA was not well correlated due human error. In the off diagonal, two MAC coefficients was found to be higher than the acceptable value due to insufficient use of sensors to distinguish the mode shapes. Modal analysis was carried out in Altair HyperWorks before shape optimisation of suction tube, in which the optimum design of suction tube was found at loop length reduction of 44mm. In the end of the project, mathematical modelling were developed to determine the natural frequencies with different dimensions under controlled factors; which will serve as a helpful tool for air conditioner engineers in future design optimisation work.

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Optimization of a Gamma Type Stirling Engine

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Abstract

Stirling engines are external combustion engines, which are powered by external heat sources such as biomass or solar energy. Unlike internal combustion engine, it has low noise levels and can be powered by heat. Stirling engine produces power from cyclic compression and expansion of working fluids inside the engine. A power piston generates power from the working fluids, while a displacer controls the movement of the working fluid between the expansion and compression chambers. A regenerator connects the working fluid between power piston and displacer and absorbs and releases heat to the working fluid. A simplified 2D axisymmetric gamma type Stirling engine CFD model with 12440 nodes and 11735 elements was optimized by using ANSYS FLUENT 15.0, where SST k – ω turbulence model was applied with 500 time steps per cycle, or with a time step size of 3.5823×10^{-4} second. Dynamic mesh technique was used to model the fluid flow and heat transfer inside the engine, to account for the movement of the piston. The CFD code was validated and shown good agreement with the exact adiabatic P – V relation when the engine was set to operate at 60 rpm. 3 different configurations of the gamma Stirling engine were tested under the same boundary conditions to predict the engine performance. Simulation results revealed that concave piston profile improves the Stirling engine performance. The engine with concave profile on both the power piston and displacer generated 370 N force output, and increases the engine performance by 27.6 %. Larger swirling flow created on the concave surface promotes better heat transfer and mixing between the cold and hot working fluids, hence improving the engine performance.

Keywords: Gamma type Stirling engine, Computational Fluid Dynamics (CFD), User Defined Function (UDF), Dynamic meshing technique, Concave profile.

1. Introduction

The Stirling engine was first developed and patented by a Scottish minister, Rev. Dr. Robert Stirling in year 1816. This Stirling engine is a mechanical device that principally functions on the Stirling cycle, and produces output power by repeatedly heating and cooling of a constant volume of working fluid concealed inside the engine. The common working fluids used for Stirling engine are pressurised hydrogen, helium, air, nitrogen and vapours. Stirling engine is first brought into commercial use to provide auxiliary power for manufacturing and mining [1]. However, in the early 1900s, the development of Stirling engine was slow due to the rapid development of the internal combustion engine. In a nutshell, internal combustion engine provides a better power to weight ratio and have quick speed responses, which makes it is a better option than the Stirling engine, which normally has slower response time and lower power output [1].

In recent years, global warming issue has become one of the prominent topics and there is a need for clean and sustainable alternative energy for the future. Many researches and studies have been conducted to utilize renewable energy or waste energy and other potential technologies to minimize the demand on electricity. Lately, Stirling engines have become great interest to the industry as well as to the academicians due to their effectiveness in using energy. Since Stirling engines are external combustion engines, they can be powered by heat generated from biomass, fossil fuels, solar radiation, and other energy sources. Unlike internal combustion engines, Stirling engines provide clean combustion and remarkably quiet, which allow specialized application such as submarines and space where a silent approach required [1].

Generally, there are three configurations of Stirling engine, namely the alpha, beta and gamma types as seen in Figure 1 [2]. Each type operates on a closed regenerative thermodynamics cycle i.e. the Stirling cycle, but has different configurations of the working spaces and the kind of mechanical piston control. This cycle offers a constant volume and isothermal process during compression and expansion. The compression and expansion processes occur in the power cylinder, where the power piston converts the linear motion into rotary motion on the flywheel that is connected to a crankshaft which produces torque. A displacer functions to control the movement of the working fluid without affecting the pressure in the cylinder. The loosely fit displacer is designed to have a smaller diameter than the cylinder, to ensure transfer of the working fluid between the hot and cold regions without generating any work. A regenerator is usually positioned between the cold and hot regions of the cylinder. It acts as the thermal storage, where it absorbs and releases heat to the working fluid. The Stirling cycle represents the idealized closed regenerative thermodynamic cycle, which consists of 4 main processes as shown below in Figure 2 [2].

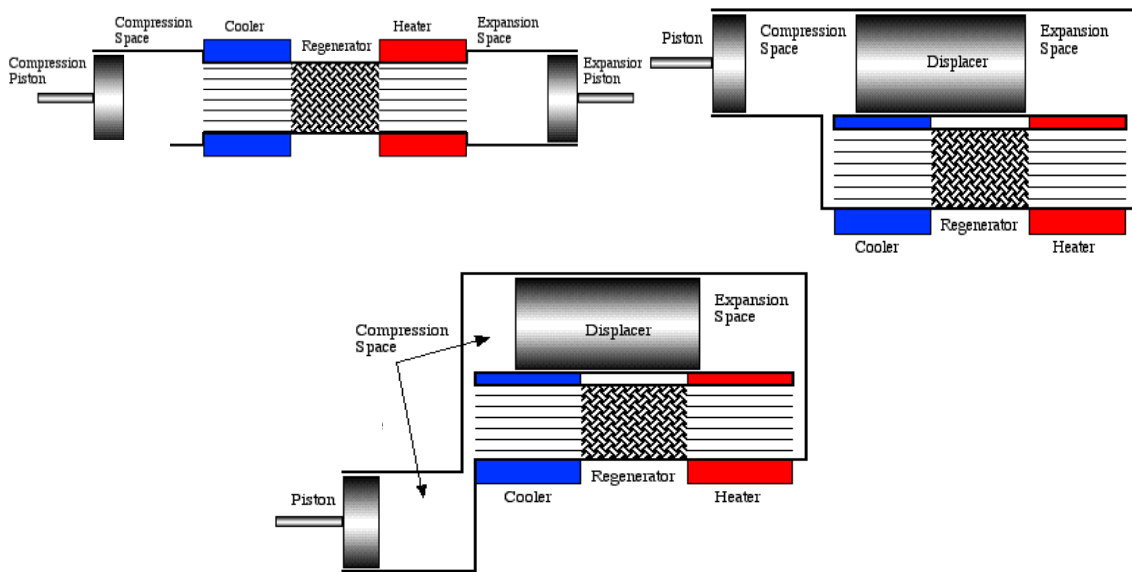


Figure 1. Three configurations of Stirling engine (a) alpha, (b) beta and (c) gamma.

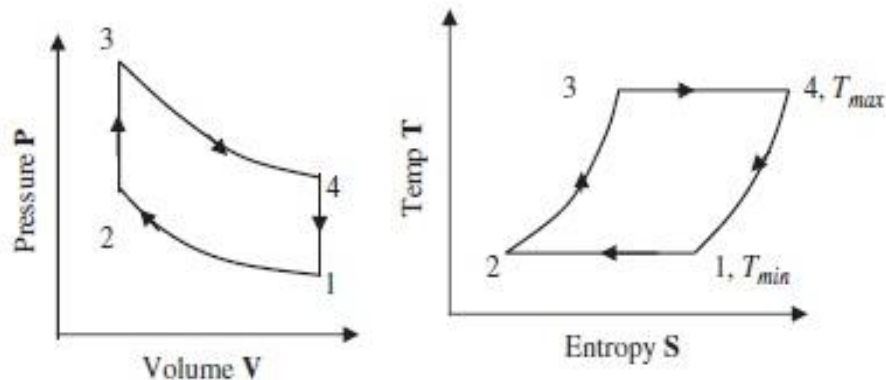


Figure 2. The P – V diagram and T – S diagram for ideal Stirling cycle.

Among the three configurations of the Stirling engine, the gamma type Stirling engines is mostly considered due to its simplicity and suitability to operate with low temperature ratios, which makes the material required for fabrication less demanding and more economical. In the gamma Stirling engine, the regenerator, heater and cooler are connected in series. The power piston of the engine is placed in complete separation with the displacer cylinder and the heat exchanger, which means the working fluid can simultaneously flow between them. Since both power piston and displacer are not aligned in a single cylinder, the size of the power piston is not restricted by the size of the displacer. Also, the gamma type Stirling engines have larger dead volume, which result in lower power output from the system. Cheng and Yang [3] has shown that alpha Stirling engine generates the greatest shaft power while gamma engine has the lowest. However, gamma type Stirling engines are the most appropriate for LTD application as the dimensionless shaft work of alpha Stirling engine vanishes at higher temperature ratios.

Designing or optimizing a Stirling engine is a very sophisticated process as it requires consideration of the multiple components and parameters involved in the system such as power of the piston and displacer and regenerator performance of which the geometrical effects cannot be neglected. Besides, the heat and mass transfer that takes place during the expansion and compression processes in the Stirling engine are also crucial in predicting the overall engine performance. Therefore, computational fluid dynamics (CFD) became an important numerical tool to simulate the complex processes that take place in the Stirling engine and predict the overall engine performance. With this approach, the effect of the geometry of the components can be easily identified and to be implemented on the experiment. Chen et. al. [4] showed that CFD simulation of the moving regenerator on the two-dimensional alpha type Stirling engine model has good impact on improving the engine power output and efficiency, despite the pressure drop in the regenerative channel. However, limited studies have been conducted on the geometrical effect of the power piston and displacer design on the Stirling engine performance. Therefore, the objective of this research is to improve the gamma type Stirling engine performance by optimising the design of the power piston and displacer by using computational fluid dynamics (CFD) simulation.

2. Research Methodology

The overall approach for this project was to construct a simplified 2D axisymmetric gamma type Stirling engine computational model and simulate it by using ANSYS FLUENT 15.0. The simulation was conducted with $k - \omega$ turbulence models at 500 time steps per cycle, which corresponding to the time step size of 3.5823×10^{-4} second. The generated results were verified with the results reported in other published journals. As the gamma Stirling engine consists of two moving parts, i.e. power piston and displacers, dynamic mesh technique was used to simulate the volume of the working fluid domain which changes with time during the compression and expansion processes. Dynamic mesh modelling allowed mesh layers to be added or removed when the volume of the computational domain changes as the boundary wall move relative to the adjacent boundary wall. This mesh layers can be created based on height layer of each moving wall as specified by the user. In order to define this dynamic mesh feature, a User Defined Function (UDF) written in C is used which is linked to the ANSYS FLUENT 15.0 solver. Before applying the dynamic meshing, the slicing method was used to create two separate bodies during the simulation, i.e. inner wall of the displacer cylinder and the displacer wall. These two bodies were coupled with a mesh interface zone to ensure the working fluid able to flow between the expansion and compression chambers, without interfering the mesh layers between the displacer and inner wall of the displacer as indicated in Figure 3. This also means that only the top and bottom mesh layers will be created or removed when the displacer moves, but the mesh layers between the displacer and inner wall of the displacer will remain the same throughout the cyclic motion.

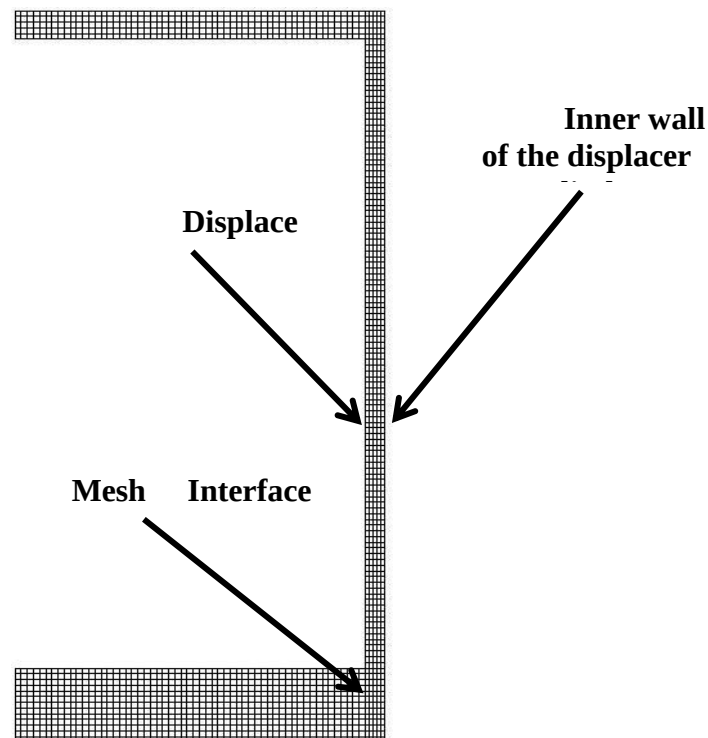


Figure 3. Mesh interface zone for the dynamic mesh on the computational mesh.

Meshing plays a significant role in the CFD simulation as it affects the accuracy of the simulation results. The finer the meshing size of the geometry, the more accurate the results will be obtained. However, longer computational time is required to complete the simulation. Therefore, it is important to conduct mesh independency study to determine the optimum element size that is suitable for simulation, and reduce the computational time and cost. Initially, mapped face meshing was applied on the entire geometry of the simplified 2D axisymmetric gamma type Stirling engine computational model. Edge sizing was then applied on each edge by defining the mesh into a number of divisions of the mesh. An initial meshing size of 12440 nodes and 11735 elements was created in the model. Then, the simulation was run by defining the working fluid as ideal gas. The simulation was then repeated under the same boundary conditions but with different meshing sizes. Based on the simulation results, an optimum meshing size was selected and used in the simulation method for the entire simulation analysis.

3 different configurations were designed and tested to predict the force output of the engine. The first configuration consists of both flat surfaces for power piston and displacer, while configuration 2 consists of a concave design displacer with flat surface power piston. Lastly, the configuration 3 consists of both concave design on both the power piston and displacer. Numerical results generated during the simulation were then compiled to measure the force output and justification was made to select the best configuration for the gamma Stirling engine. Figure 4 shows the three different configurations of the gamma type Stirling engine and the outline of the research methodology is shown in Figure 5.

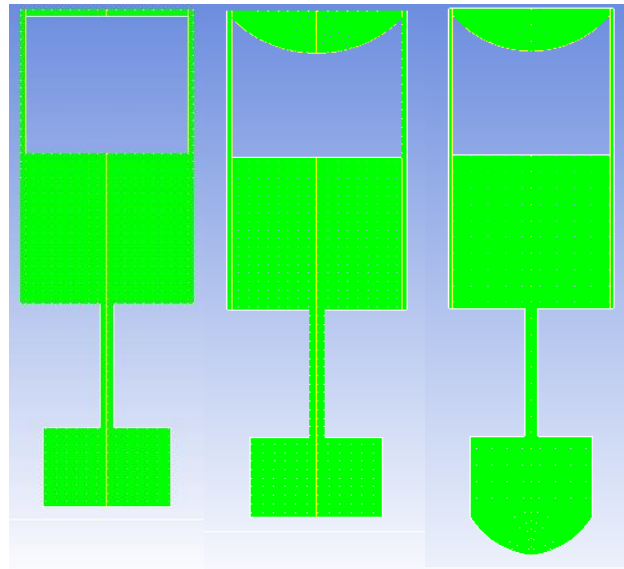


Figure 4. Three configuration of the gamma type Stirling engine
(a) flat – flat (b) concave – flat and (c) concave – concave.

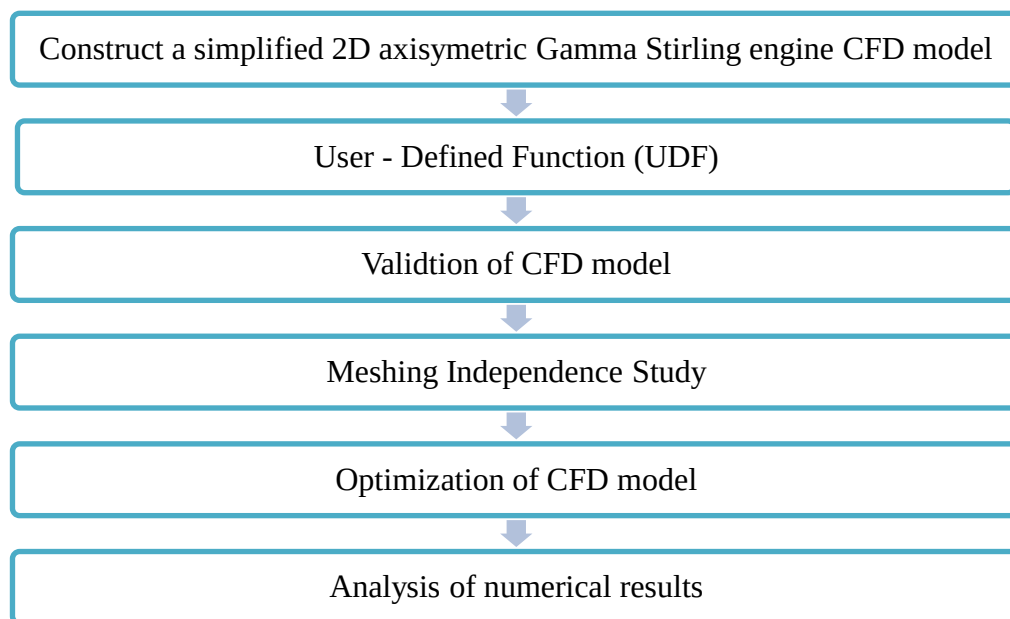


Figure 5. Overall flow chart of this project research methodology.

2.1 Setting of boundary condition

The computational domain of the gamma Stirling engine shown in Figure 6 is in axisymmetric, which allows a two dimensional mathematical model to be constructed. The small gap between the displacer and inner wall of the displacer cylinder will also act as the regenerator, which promotes heat transfer in the working fluids in both compression and expansion chambers. In the CFD simulation, the computational model was simulated with transient SST $k-\omega$ turbulence model using ideal gas as working fluid. The convection heat transfer coefficient for the regenerator wall and cold cylinder was set at $48 \text{ W/m}^2\text{k}$, while the

hot cylinder side bottom set at approximately $1000 \text{ W/m}^2\text{K}$ due to the free convective heat transfer of water. The free stream temperature of the regenerator wall, cold cylinder and hot cylinder side bottom was set at 300K . Heat flux of 900 W/m^2 was applied to the hot cylinder top and hot cylinder side top. The engine speed was then simulated under 335 rpm with amplitude of 0.0575 m . The velocities of the power piston and displacer are:

$$V_p = A\omega \sin(-\frac{\pi}{2} + \omega t) \quad \text{----- (1)}$$

$$V_d = A\omega \sin(\omega t) \quad \text{----- (2)}$$

Since the working fluid used was an ideal gas, which the mechanical and heat losses could be neglected. Therefore, the governing equations for the fluid flow as follow:

Continuity Equation

$$\frac{\partial(\rho)}{\partial t} + \nabla \cdot (\rho V) = 0 \quad \text{----- (3)}$$

Momentum Conservation

$$\frac{\partial \rho u}{\partial t} + \nabla \cdot (\rho u V) = -\frac{\partial P}{\partial x} + \nabla \cdot (\mu \nabla u) + S_{m,x} \quad \text{----- (4)}$$

Energy Equation

$$\frac{\partial \rho e}{\partial t} + \nabla \cdot (\rho e U) = -p \nabla \cdot U + \nabla \cdot (k \nabla T) + \xi + S_i \quad \text{----- (5)}$$

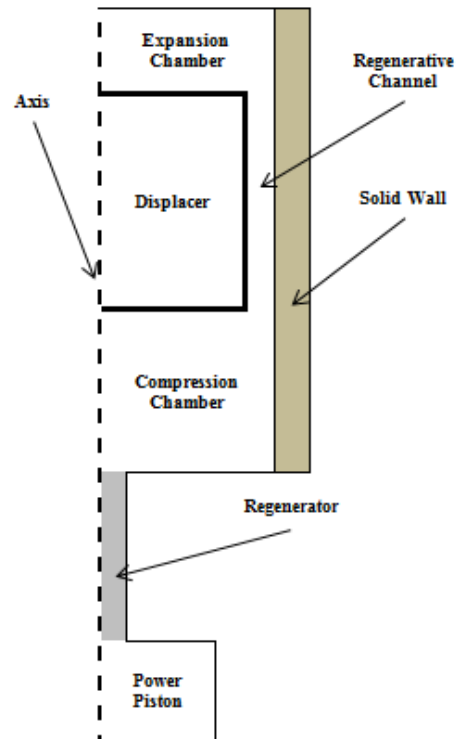


Figure 6. Axisymmetric 2D computational domain for Gamma Stirling engine.

3.0 Results and Discussions

3.1 Mesh Independence Study

Firstly, 3 simulation cases were conducted based on different number of meshing elements, i.e. 10799, 11735 and 12671 elements. These three mesh grid sizes were simulated with 500 time steps per cycle, which correspond to 3.5823×10^{-4} time step size. The mesh was concentrated towards the regenerative channel for better heat transfer flow between the expansion and compression chambers. About 10 cycles were required for the solution to become periodical in each simulation case. According to Figure 7, the results revealed that a better output power was obtained with more meshing elements being used. Chen et al. [5] mentioned that the values of the maximum velocity, heat input, or force output within a cycle with less than 0.5 % in difference are served as the benchmark in judging the mesh grid sizes. As the differences among the different mesh grid sizes were only 0.5%, 11735 mesh elements at 500 time steps per cycle was chosen for the rest of the entire simulation methods in order to reduce the computational time and cost [5].

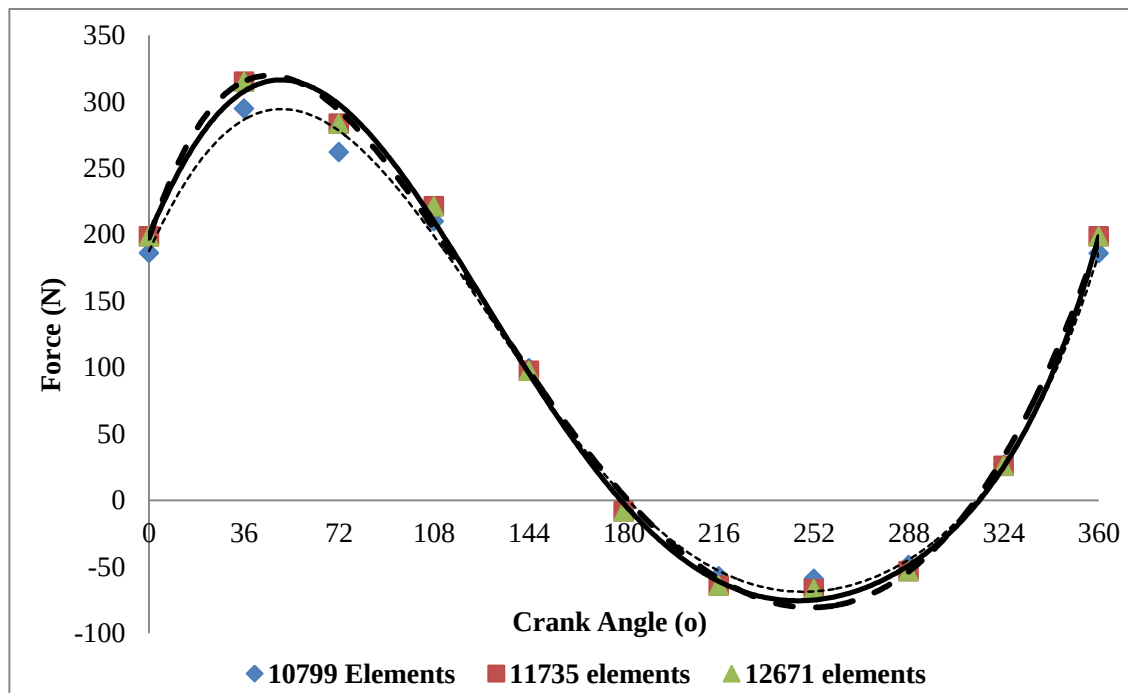


Figure 7. Force generated against crank angles for configuration 1 with different meshing sizes.

Total volume, expansion chamber volume and compression chamber volume of the gamma Stirling engine at different crank angles are plotted, as shown in Figure 8. The minimum and maximum of the total volume occurred at the crank angle of 90° and 270° respectively. This corresponds to a minimum volume of 0.00157 m^3 and the maximum volume of 0.00229 m^3 , which give a compression ratio of 1.459.

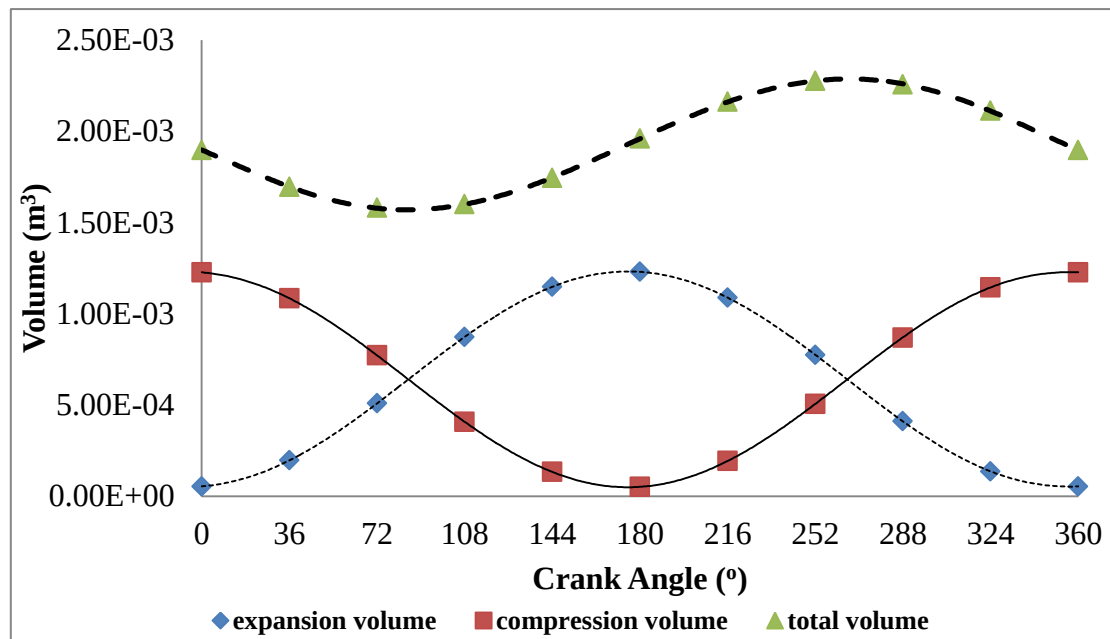


Figure 8. Variations of total volume, expansion chamber volume and compression volume at different crank angles.

3.2 Validation of CFD model

In order to simulate the compressible flow inside the engine, the CFD code used has to be validated. Chen et al. [6 - 8] mentioned that the engine with low speed of 60 rpm is still considered under adiabatic condition, which would be near to an ideal reversible adiabatic cycle. Since the CFD code does not considered any frictional losses, the exact $pV^{1.4} = \text{constant}$ will be used by obtaining from the equation of state. As shown in the Figure 9, the CFD simulation shows a good agreement with the exact adiabatic P - V relation when the engine operating at 60 rpm. Therefore, the CFD code used for the simulation was correct and hence validated.

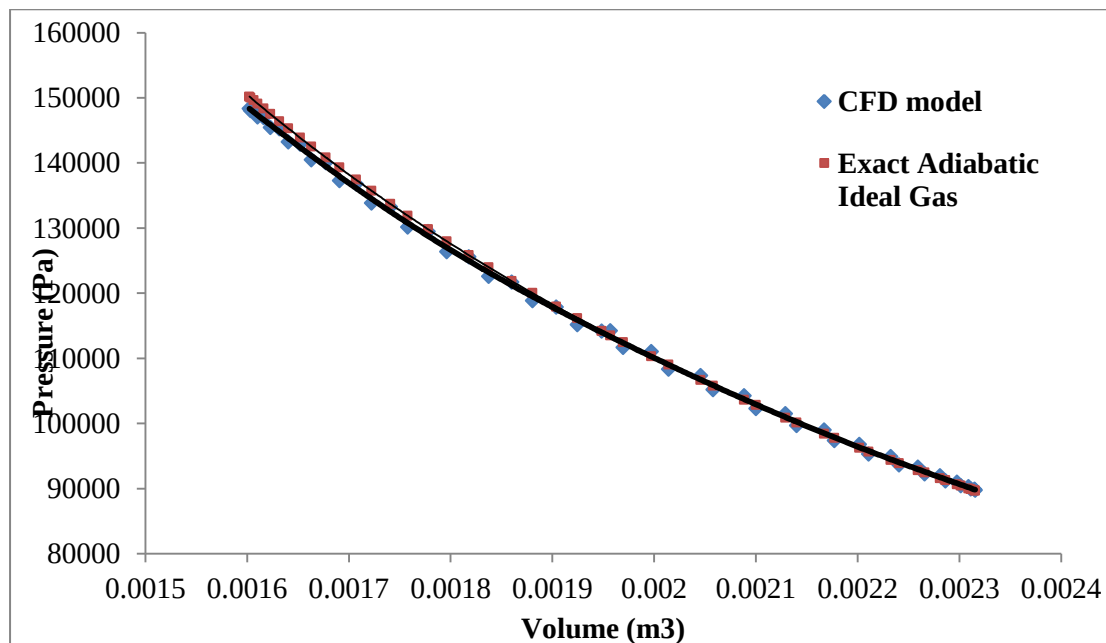


Figure 9. Code validation of the P - V relations between exact and present values in an adiabatic cycle.

3.3 Geometrical effect of Gamma Stirling Engine Configuration

As mentioned earlier in the Research Methodology, several 2D computational models were designed and simulated with ANSYS FLUENT 15.0 in order to select an optimize gamma Stirling engine configuration that will increase the efficiency and performance of the engine. All simulations were conducted under the optimum simulation methods and the results and discussion on each configuration are explained in the following sub- sections.

3.3.1 Flat – flat configuration

As observed from the graphical representation in Figure 10, the power piston generated a peak force of 290 N on the first half of the cycle, and then followed by negative 70 N peak force on the other half of the cycle. The positive values represent the power piston undergoing compression where work is done on the working fluid in the engine. The negative values represent the power piston undergoing expansion where the work is done by the working fluid on the power piston. As seen from the trend of the graph, higher magnitude of force was required by the power piston to push the displacer to the top dead centre (TDC) position between the crank angles of 180° to 310° . The loosely fit displacer was designed to have smaller diameter than the cylinder, allowing good heat transfer in the working fluid between hot and cold region without generating any work. Hence, the force generated by the displacer was extremely low as compared to the power piston.

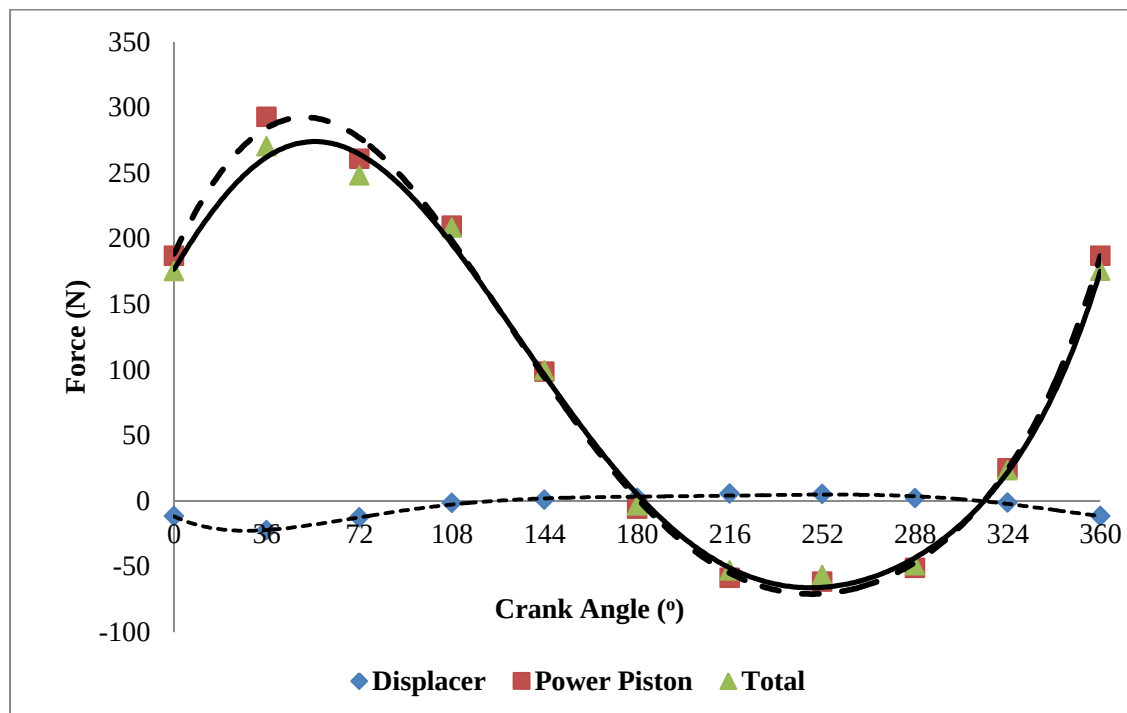


Figure 10. Force generated against crank angles for the flat – flat configuration Gamma Stirling engine.

3.3.2 Concave - flat configuration

In the concave – flat configuration, the power piston produced a peak force of 310 N on the first half of the cycle, and then followed by negative peak force of 60 N on the other half of the cycle. Comparing with the flat – flat configuration, the peak force generated by the power piston was increased by 6.9 %. In spite of the theoretical expectation that the displacer only functions to move the working fluid, the concave design on the displacer has also contributed to the force generated by the system. Large force output from the displacer was observed due to the swirling effect occurred on the top of the concave surface that will be further explained in the following section. The force generated versus the crank angle for the concave – flat configuration Gamma Stirling engine represented in Figure 11.

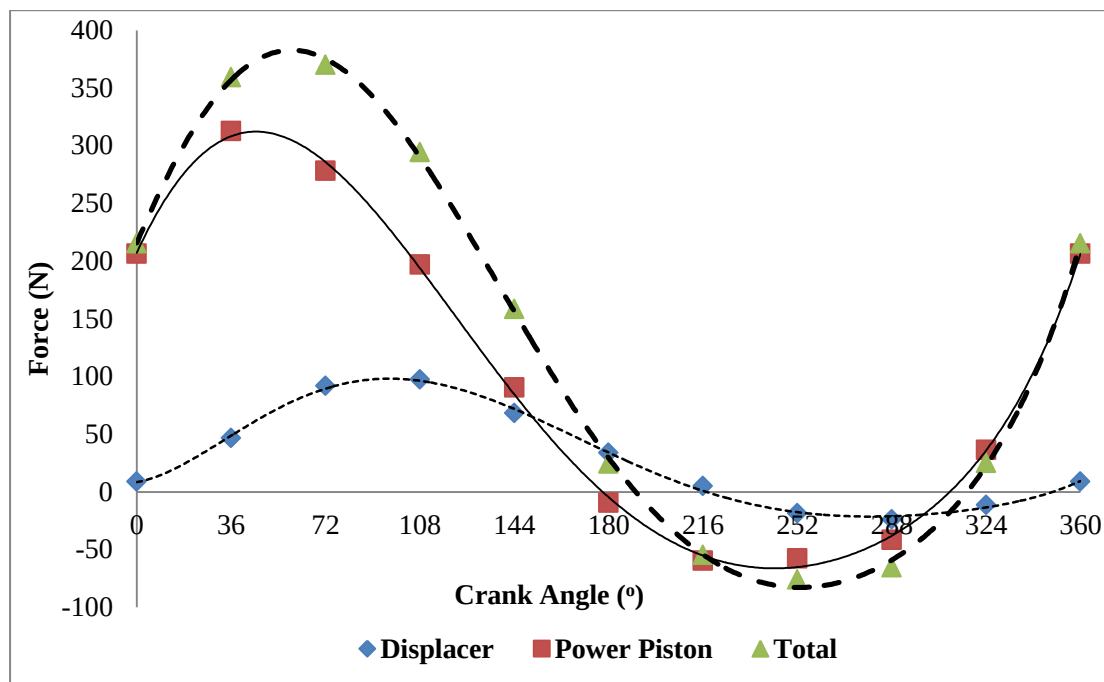


Figure 11. Force generated against crank angles for the concave – flat configuration Gamma Stirling engine.

3.3.3 Concave - concave configuration

Similarly, the results for the concave – concave configuration is shown in Figure 12, which indicated better performance with this profile. The highest force generated from the power piston was 370 N, which is higher by 27.6% than the output force of the flat – flat configuration Gamma Stirling engine. In contrary, there is no obvious increment on the highest force generated from the displacer as compared to the concave – flat configuration. Change of the concave surface on the power piston has no further effect to the force output generated by the displacer, but only on the power piston itself. It can be concluded that concave profile had a positive impact on improving the gamma Stirling engine performance.

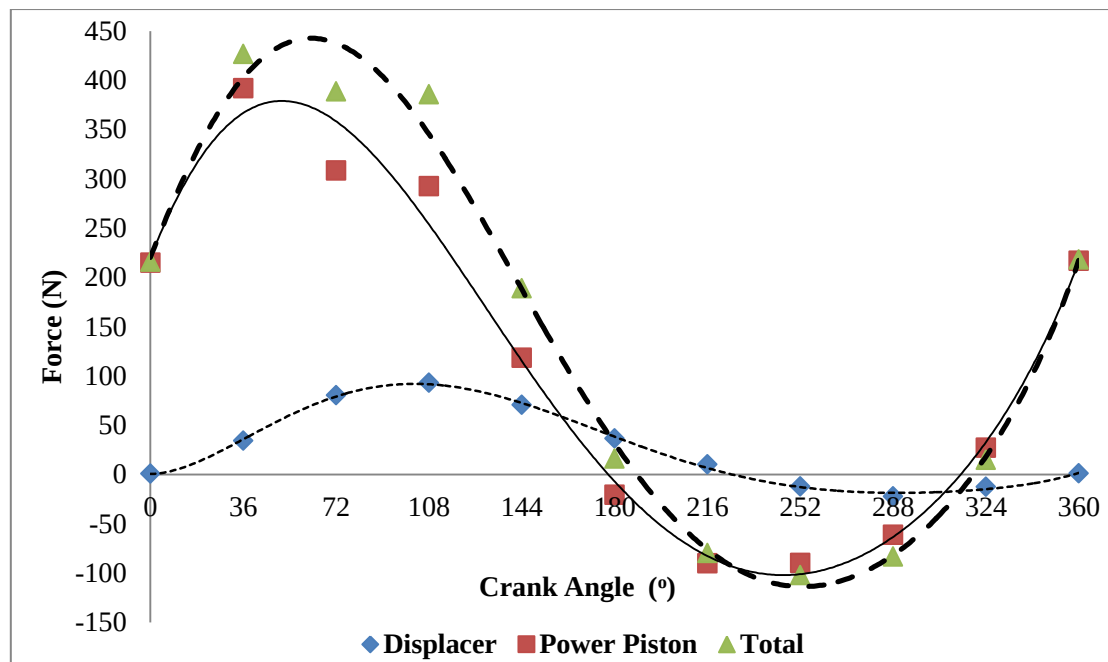


Figure 12. Force generated against crank angles for the concave - concave gamma Stirling engine.

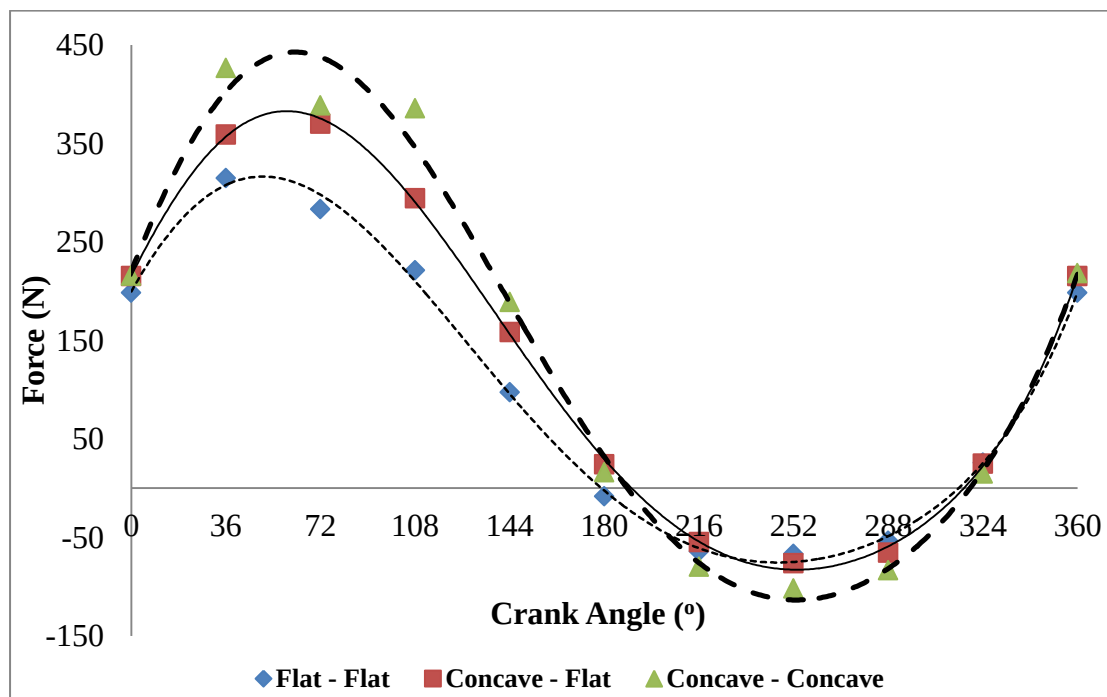


Figure 13. Comparison of the total force generated against crank angles for the all configurations Gamma Stirling engine.

In order to compare the temperature variation within the engine, the temperature contour of the gamma Stirling engine at crank angle of 288° was selected from each configuration, as seen in Figure 14. It was observed that larger swirling flow was created on the concave surface, which tends to draw in more working fluid into the expansion chamber. This phenomenon allowed better heat transfer and mixing of the cold and hot working fluid, therefore lesser time was needed for the working fluid to be heated up [7]. Besides that, this swirling effect also has significant effect in spark ignition engines, where the combustion duration can be shorten and able to operate at higher speeds and produce higher engine outputs [9]. The figure also revealed that the temperature difference between displacer and power piston regions in the flat – flat configuration was the highest. Kontragool and Wongwises [10] have proved that by increasing the solar intensity input to the displacer cylinder, the greater will be the generated output power and thermal efficiency of the Stirling engine. Further numerical research by Cheng and Yang [11] has also shown that power output can be increased by increasing the temperature ratio of the hot and cold regions. However, this is contrary to the simulation result presented for concave-concave configuration and convex-convex configuration, which have the highest force output. Therefore, this suggests that it is not only the temperature ratio between the hot and cold regions which determines the power output. The swirling effect generated within the expansion and compression chambers should also be taken into consideration to improve the engine performance.

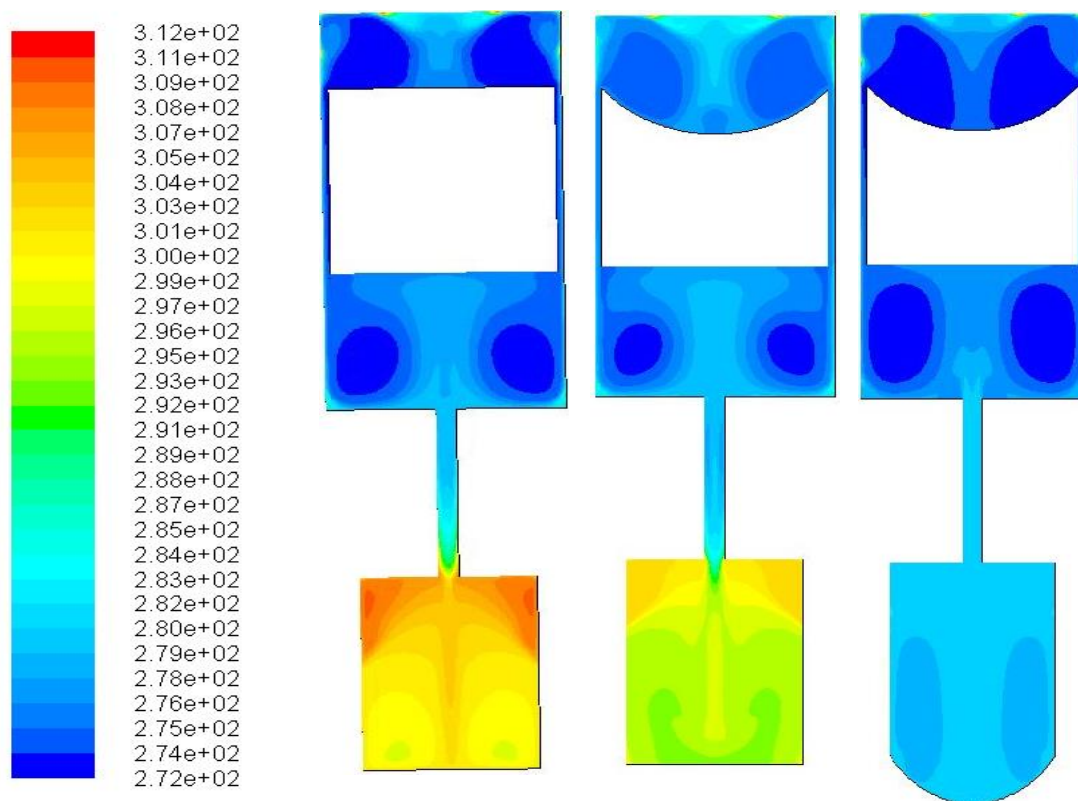


Figure 14. Temperature contour of the engine at crank angle of 288° for three different configurations (a) flat - flat (b) concave - flat (c) concave - concave.

4.0 Conclusions

In conclusion, a simplified 2D gamma Stirling engine CFD model was constructed and simulated by using ANSYS FLUENT 15.0. An optimum meshing size with 12440 nodes and 11735 elements was chosen for the simulation model, and each simulation case was conducted under SST $k - \omega$ turbulence model at 500 time steps per cycle, which corresponds to time step size of 3.5823×10^{-4} second. Dynamic mesh technique was used to allow mesh layers to be added or removed when the volume of the computational domain changed as the boundary wall move relative to the adjacent boundary wall. The CFD code is validated and shown good agreement with the exact adiabatic $P - V$ relation when the engine was set to operate at 60 rpm. Three different configurations of the gamma Stirling engine were tested under the same boundary conditions to predict the engine performance. Simulation results revealed that the concave profile on the power piston and displacer has improved the Stirling engine performance. Concave – flat configuration was able to improve the output force by 6.9 % as compared to flat – flat configuration. The Gamma Stirling engine with both concave profile on power piston and displacer generated 370 N of output force, which was the highest among the three configurations. The greater swirling effect created on the concave surface promotes better heat transfer and mixing of the cold and hot regions of the working fluid, hence improving the engine performance.

For future work, irreversibility factors such as mechanical losses, heat and friction losses should be taken into consideration in the CFD simulation. Studies on more configurations should be carried out on the 2D axisymmetric computational model to identify the best configuration to further improve the output force and efficiency of the gamma Stirling engine. It is also known that the regeneration channel plays an important role in transporting the working fluid between the expansion and compression chambers. Therefore, the gap between the displacer wall and the displacer cylinder wall should be investigated to ensure optimum heat transfer effectiveness to be achieved. Last but not least, a Gamma Stirling engine test rig is in progress of fabrication which will be used to validate the experimental results with the numerical results

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Parametric Study of a Bias Two-Wheel Tire

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Abstract

The objective of this study is to develop a computational model for bias two-wheel tire through finite element analysis (FEA) method. An 80/90-17 bias two-wheel tire was adopted as the subject of study. The bias two-wheel tire is made up of four major layers which consists of rubber compound with different material properties. Mooney-Rivlin hyperelastic model was applied to represent the behaviour of incompressible rubber compound. This paper presents the uniaxial tensile testing on the materials of the tire to investigate the material property of rubber and rebar model for the reinforcement material. Curve fitting was executed to obtain the Mooney-Rivlin material constants for each layer of the tire. A 3D tire model was built for structural static finite element analysis. Inflation and footprint tests analysis were conducted for validation purposes. Experimental tire was inflated at various pressures and the geometry between numerical and experimental tire were compared. Then, the FEA tire model is compared with the experimental tire, on the footprint shape under various vertical loadings. Structural static finite element analysis method is suitable for evaluation of the tire design and improvement of the tire behaviour to desired performance. In this paper, only the inflated tire geometry and footprint shape were compared between the numerical and experimental tire. There are good agreements between numerical simulation model and the experiment results. This indicates that the simulation model can be applied to the bias two-wheel tire design in order to predict the tire behaviour and improve its mechanical characteristics.

Keywords: Bias tire, Finite Element Analysis, Footprint test.

1. Introduction

Tire is a component which allows interaction between a road surface and a vehicle. Its main function is to allow steering control for the vehicle to travel to intended destination and to support load of vehicle and passenger. Bias two-wheel tire is commonly used for underbone motorcycles in Malaysia and its construction consists of multiple layers (Fig. 1). Bias two-wheel tire consists of 4 major components which are the tread, tread base, cord-rubber plies, and inner liner. The cord-rubber plies which are made up of twisted Nylon-6 cord and rubber compound are arranged on bias at an angle within the range of 25° to 40° [1]. Bias tire provides smoother ride on rough and uneven surfaces as the construction structure is strong and has stiffer sidewall with softer tread which can be flexed easily.

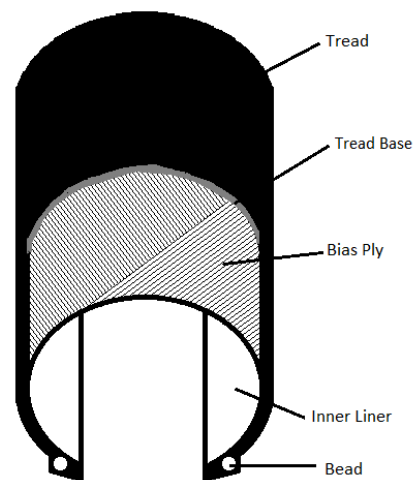


Figure 1. Components of Bias Tire.

Tire is inflated to a standard pressure allocated based on the load and speed rating of the tire. An 80/90-17 bias two-wheel tire with load index of 44 and speed rating of P is the subject of this study. This tire should be inflated to a pressure of 230 kPa as this is the basic inflation pressure for this type of tire [2]. Measurements on the tire geometry will be conducted after inflation to check on the dimension of the tire as compared to its intended design. Footprint test can then be carried out on the inflated tire. Contact areas at various loads are investigated for the bias two-wheel tire.

Experimental tires can be manufactured based on various parameters to observe the effect on the tire geometry after inflation and footprint test. However, to reduce the experimental cost and time, computer simulation is opted. In this study, the main objective is to develop a computational tire model for finite element analysis (FEA) which can predict the behavior of the bias two-wheel tire under different condition of load and pressure during footprint test. This computational tire model is expected to be further continued for other tire testing such as plunger test and dynamic testing which are not described in this paper.

This paper focused on static loading on bias two-wheel tire and its effects on the geometry of the tire; before and after inflation, as well as the footprint shape of the tire. As described by Korunovic et al. [3], axisymmetric tire model is enough to show good correlation between the analysis results with the experimental results.

Mohsenimanesh et al.[4] reported that the computational modelling of axisymmetric tire models on the inflation pressure has higher effect on the contact area of the tire compared to the load on a rigid surface. These tire models are focused on car and truck tires but little research is carried out for bias two-wheel tire for the motorcycles.

FEA is a common alternative to the expensive and time-consuming physical prototyping for new tire designs. Thus, detailed modelling of the tire structure is necessary to allow higher accuracy in predicting the behavior of the future tire. One of the major criteria is to describe the material behavior of structural tire components accurately. The Mooney-Rivlin hyperelastic material model is applied in this study to represent the material properties of rubber compound of the bias two-wheel tire. The Mooney-Rivlin model is employed due to the material model stability and it is commonly used for other researchers which have proven to yield results with minor discrepancies. Korunovic et al. [3], Watanabe and Kadjian [5], and Cheng et al. [6] have managed to model tires by adopting incompressible Mooney-Rivlin material model and have generated FEA tire model with results that are comparable to the experimental tires. In addition, Mooney-Rivlin hyperelastic model is suitable as deformations in tire rarely reaches 40% during its service, as mentioned by Tönük [7]. Therefore, this method is applied for the modelling of two-wheel bias tire.

Static analysis is primarily applied in this study to check the validity of the FEA bias two-wheel tire model. In the following sections, the detailed modelling of the tire are presented.

2. Methodology

An 80/90-17 bias two-wheel tire is taken as the subject in this study. The tire is a composite material consists of mainly four layers which are the tread, tread base, cord-rubber plies, and inner liner. The cord-rubber plies are made up of high modulus cord and low modulus rubber; with twisting threads of Nylon-6 made up the cord.

Each layer of the tire is made up of rubber compound with different material properties. Hence, determination of the material properties of the rubber compound is important to ensure proper settings for the FEA simulations.

In the following sections, the methods to estimate the material properties of each layer are described. The modelling of tire model through FEA software is also explained in detail.

2.1 Determination of Mooney-Rivlin Constants

Mooney-Rivlin is a hyperelastic model which is commonly used to represent the material properties of rubber compound. In this study, the rubber compounds that made up the bias ply two-wheel tire are assumed to be incompressible. The strain-energy density function for hyperelastic materials can be represented in Eq. (1).

$$W = \sum_{i,j=0}^N C_{ij}(\bar{I}_1 - 3)^i(\bar{I}_2 - 3)^j + \sum_{k=1}^N d_k (J - 1)^{2k} \quad (1)$$

where C_{ij} is the constants for distortional response, d is the volumetric response constant, and J is the ratio of compressed volume to uncompressed volume. In the case of incompressibility, the J value is 1. Parameters i, j , and k represents the direction of the material response in three different directions within the three-dimensional space.

From Eq. (1), the strain energy density function, W is expressed in terms of strain invariant I , where I_1 and I_2 are the first and second deviatoric strain invariants. Strain invariant I can be represented in terms of stretch ratio, λ as shown in Eq. (2). The relation between $\bar{I}_1$ and $\bar{I}_2$ with J are shown in Eq. (3) and (4).

$$\begin{cases} I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \\ I_2 = (\lambda_1\lambda_2)^2 + (\lambda_2\lambda_3)^2 + (\lambda_1\lambda_3)^2 \\ I_3 = (\lambda_1\lambda_2\lambda_3)^2 \end{cases} \quad (2)$$

$$\bar{I}_1 = J^{-2/3} I_1 \quad (3)$$

$$\bar{I}_2 = J^{-4/3} I_2 \quad (4)$$

Polynomial form of the strain energy function Eq. (1) for hyperelastic model is the general form for Mooney-Rivlin model. In this study, 5-parameters Mooney-Rivlin model is applied. It is a better representation of the stress-strain response at larger values of stretch compared to 2-parameters or 3-parameters Mooney-Rivlin hyperelastic model [8].

Extending Eq. (1) to the second order term where $N=2$ leads to the 5-parameters Mooney-Rivlin model strain energy density function as shown in Eq. (5).

$$W = C_{10}(I_1 - 3) + C_{01}(I_2 - 3) + C_{20}(I_1 - 3)^2 + C_{11}(I_1 - 3)(I_2 - 3) + C_{02}(I_2 - 3)^2 \quad (5)$$

Where C_{10} and C_{01} terms described the shear behavior of the material. C_{20} , C_{11} , and C_{02} were the additional higher order terms to provide good curve fit for the Mooney-Rivlin strain energy function in the Eq. (5). The strain energy equation is a representation of the stress-strain relationship of a rubber compound. Various types of experiment such as the uniaxial tensile testing, biaxial test, planar or pure shear test, and volumetric test can be executed to estimate the rubber material properties through the Mooney-Rivlin hyperelastic model.

In this study, uniaxial tension testing was carried out to determine the stress-strain behavior of rubber compound for different layers of the bias two-wheel tire.

2.1.1 Uniaxial Tension Test

Uniaxial tension test is executed to determine the material properties of each layer of rubber compound for the bias two-wheel tire. The rubber compounds were cured into standard ring shape with diameter of 44 mm and external diameter of 53 mm, at a thickness of 6 mm. The rubber ring was positioned on the tensiometer

pulleys and pulled until rupture. The equipment used in this test was a tensile testing device with pulleys for mounting the test specimen (Fig. 2).

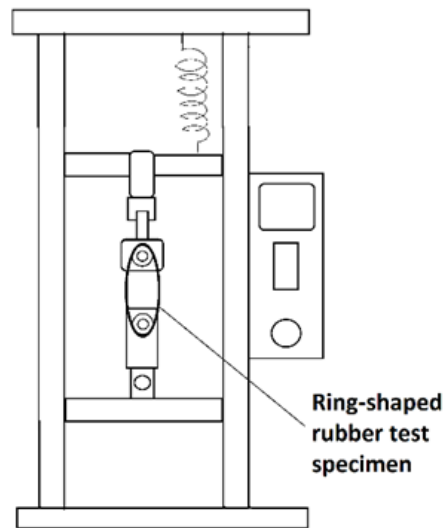


Figure 2. Ring Testing Device.

The uniaxial tension testing is carried out at surrounding temperature of 23°C, no earlier than 16 hours after vulcanization. The driven pulley made one revolution for every 50 mm linear motion of the tensioning head. One side of the pulley is driven while the other is free-wheeling. The speed of the pulley was 500 mm/min and three rings were tested for each layer of the rubber compound of the bias two-wheel tire. The test machine is under remote computer control to record the testing results.

Strain invariants of each layer of the rubber compound can then be determined based on the testing results. Material constants for the Mooney-Rivlin hyperelastic model were then predicted through curve fitting using ANSYS Workbench. Experimental stress-strain data were fit according to the hyperelastic model to estimate the material constants of C_{10} , C_{01} , C_{20} , C_{11} , and C_{02} .

Similar technique was applied to gather Mooney-Rivlin constants for the tread base, cord-rubber ply, and inner liner. The material constants obtained from the curve fitting were tabulated (Table 1).

Table 1. Hyperelastic Material Constants.

Rubber Material (Compounds)	Material Constants of Mooney-Rivlin Strain Energy Potential (MPa)				
	C_{10}	C_{01}	C_{20}	C_{11}	C_{02}
Tread	-3.65	5.53	0.01350	0.0452	1.270
Tread Base	-5.54	9.16	-0.35900	1.9900	0.106
Ply	-1.84	3.32	0.01690	0.1330	0.582
Inner Liner	-3.37	5.23	0.00494	0.1010	1.190
Cord-Rubber Ply	-1.84	3.32	0.01690	0.1330	0.582

2.2 Cord-Rubber Layer Rebar Model

Tire has complex characteristics as it is a product of composite materials. The cord-rubber plies that are made up of rubber compound and reinforced with twisting threads of Nylon-6 were modelled using rebar model to estimate the material properties at these layers. The rebar model (Fig. 3) was setup for uniaxial tensile testing simulations.

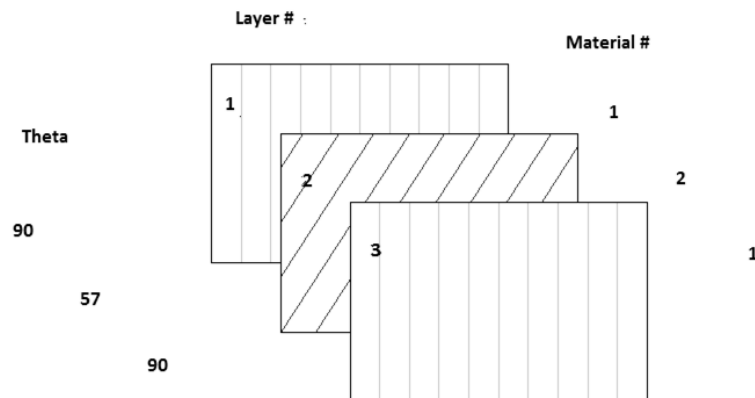


Figure 3. Rebar model for uniaxial tensile testing.

Shell181 was applied in the simulation for the element of the rebar model, followed by orientation angle setting of 90° for rubber compound layer and 57° for the cord layer. Then, forces were applied in the vertical x-direction to the rebar model (Fig. 4).

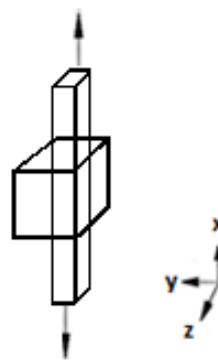


Figure 4. Uniaxial tension testing.

Stress and strain values generated from the simulations were used to determine the Mooney-Rivlin material constants for the cord-rubber ply (Table 1).

2.3 Tire Model

A 3D model of the bias two-wheel tire (Fig. 5(a)) was generated for the FEA simulation based on the geometry of the tire cross-section (Fig. 5(b)).

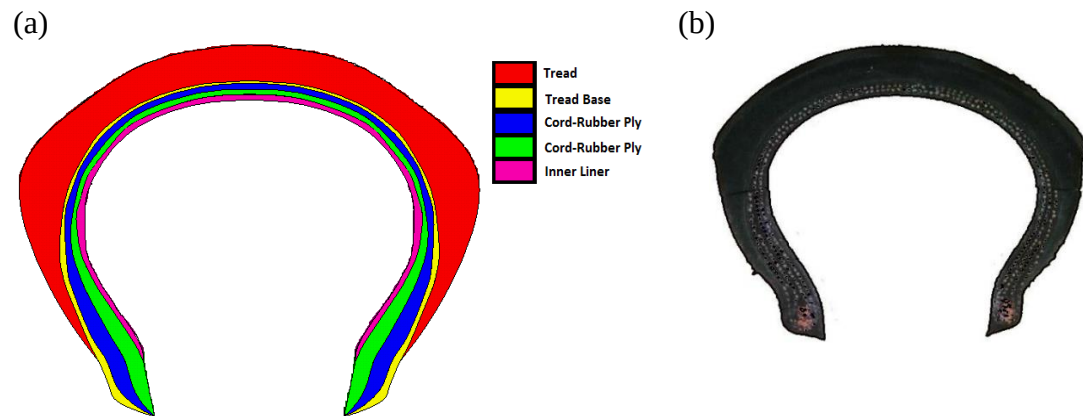


Figure 5. (a) 3D model for the bias two-wheel tire. (b) Cross section for 80/90-17 bias two-wheel tire.

The tire 3-D model of whole tire is constructed according to the cross section geometry and tire specifications for the 80/90-17 bias ply two-wheel tire. Each individual layer was set to be SOLID186 which is a 20-node solid element that is suitable for incompressible hyperelastic materials. The tire is modelled first in 360-degree (Fig. 6(a)) and further reduced to 20-degree to reduce computational time by decreasing the number of elements and nodes. The bias two-wheel tire 3D model is assumed to be symmetrical along its neutral axis and inflation pressure was set to simulate inflation process similar to the real inflation process on experimental tire. Fixed displacement was set on the area of the tire where it was mounted on the rim. The boundary conditions were set for the 3D tire model to represent inflation process and footprint test (Fig. 6(b)). Plane displacement was set to represent ground surface moving towards the tire, resulting in resultant load acting on the tire and the contact area can be observed under various vertical loadings.

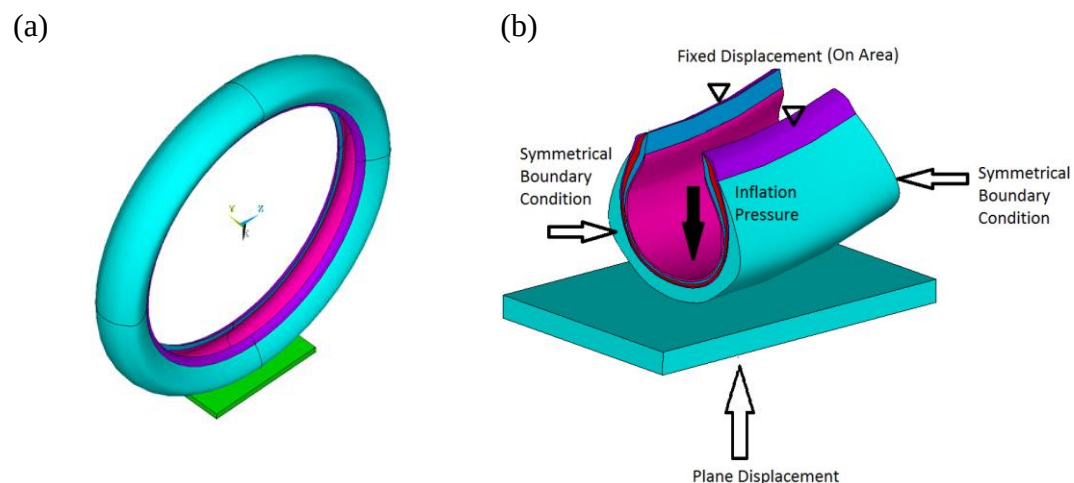


Figure 6. (a) 360-degree 3D tire model. (b) 20-degree 3D tire model with boundary condition settings.

Meshing of the 3D bias ply two-wheel tire was done through hexahedral meshing with element size of 1 mm. For the inflation test, tire model (Fig. 7(a)) was

applied for simulation. Footprint test however, requires a plane to act as solid ground to resemble the real footprint experiment using experimental bias two-wheel tire. CONTA174 is used to represent the contact surface while TARGE170 is used to represent the target surface. The tire model with its hexahedral 1 mm mesh elements (Fig. 7(b)) was then applied for the footprint test simulation.

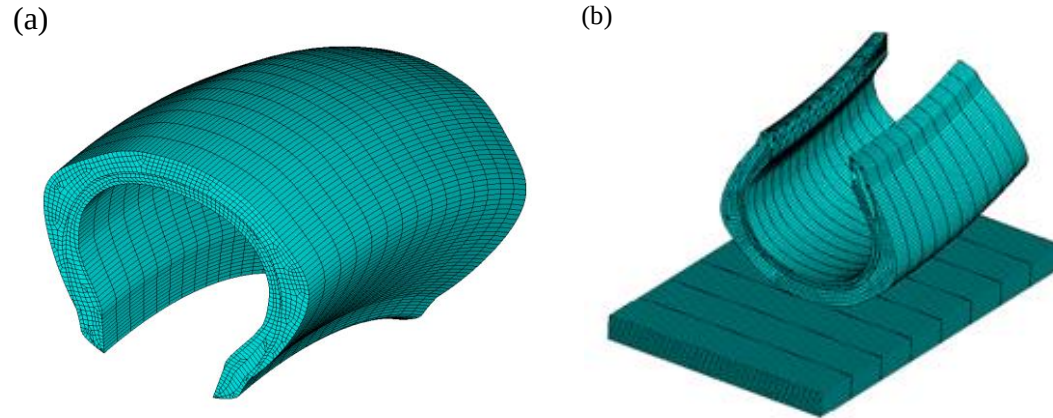


Figure 7. Tire model for (a) inflation test and (b) footprint test.

3. Results and Discussions

The FEA tire models described in previous section were used to generate simulation results which could be compared to the results obtained from the experimental bias two-wheel tire. Inflation test and footprint test results are compared and analyzed. Analyses of the results are shown and commented in the following sections.

3.1 Inflation Test

Validation on the FEA tire model was carried out through inflation test. Experimental bias two-wheel tire was mounted on a tire rim and inflated to the standard inflation pressure of 230 kPa, in accordance to the speed rating at the maximum load of the tire. Measurements were carried out on the mounted tire after the tire was conditioned to room temperature of 27°C for 3 hours. This was the standard procedure carried out by the tire manufacturer.

The diameter of the FEA tire model was calculated based on the results of section height for the tire model. Deformation of the FEA tire model under inflation pressure of 190 kPa, 210 kPa, 230 kPa (Fig. 8), 250 kPa, and 270 kPa were obtained. The increments in section height for the FEA tire model in the x-direction were analysed. The diameter of the FEA tire model was calculated based on the diameter when the tire was not inflated. Thus, at 230 kPa, FEA tire model diameter can be calculated using Eq. (6). The simulation results were then compared to the results of the experimental bias two-wheel tire (Fig. 9).

$$D_{FEA} = D_{P=0} + 2d_x \quad (6)$$

where D_{FEA} is the FEA tire model diameter; $D_{P=0}$ is the tire diameter before inflation; and d_x is the displacement deformation in x-direction.

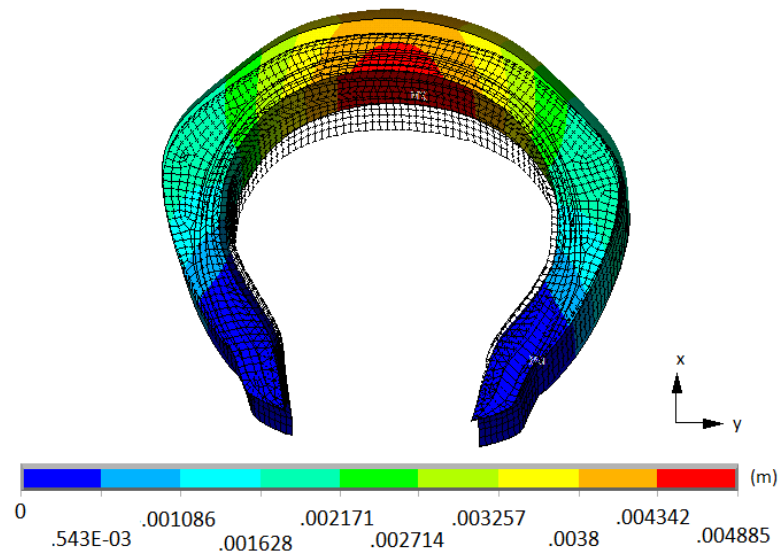


Figure 8. Vertical displacement deformation (x-direction): initial deformation (wire frame) and final deformation at pressure 230 kPa.

Experimental Tire against Numerical (FEA) Tire Diameter at Various Inflation Pressure

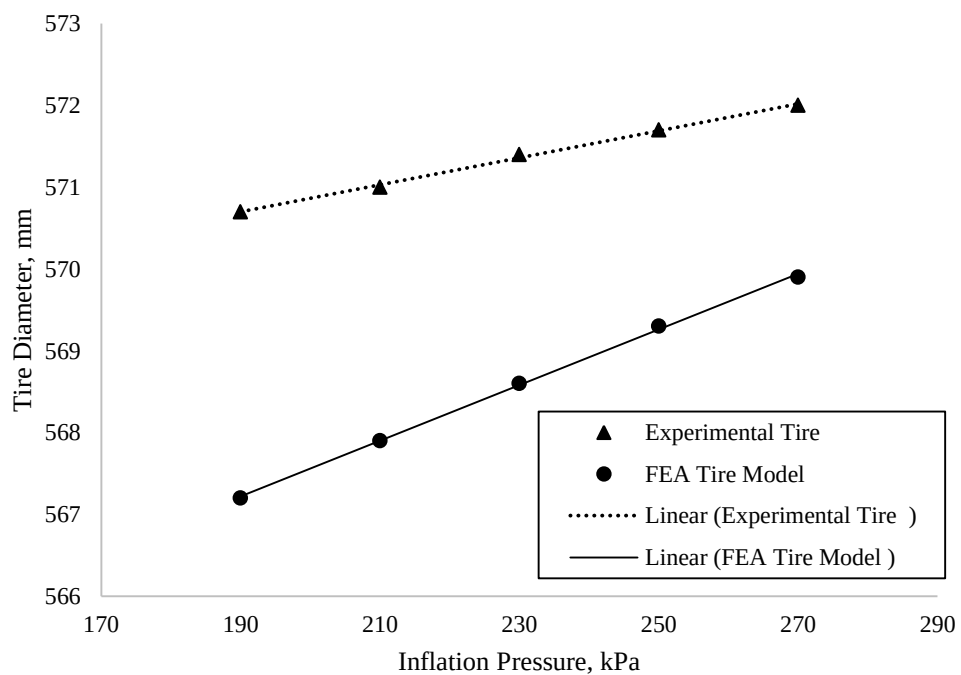


Figure 9. Comparisons of experimental tire and simulation results.

As the inflation pressure increased, the diameter of the tire increased for both experimental bias two-wheel tire and the FEA tire model. This could be expected as the elements used for the cord-rubber layer are assumed to be a uniform layer with constant behavior. In the experimental tire, each Nylon-6 cord integrated in the cord-

rubber layer changed its position with respect to the deformation of tire at different direction. The exact orientation of the cord is not the focus in this study. Thus, the analysis results are considered to be in a good correlation between the experimental tires and simulation model which is approximately differ by 0.36% to 0.62%.

3.2 Footprint Test

In addition, the comparisons of tire footprints were carried out as to further validate the FEA model. The footprint contact area and its measurements of length and width (Fig. 10) were analyzed. In the FEA tire model, plane displacement was set to represent ground surface moving towards the tire, resulting in resultant force acting on the tire and the contact area can be observed under various vertical loadings. The comparison of tire footprints when the tire is inflated at pressure of 230 kPa, while load intensity from the plane varied from 805 N to 1885 N are illustrated (Figs. 11 and 12). Similar comparisons were made and tabulated (Table 2).

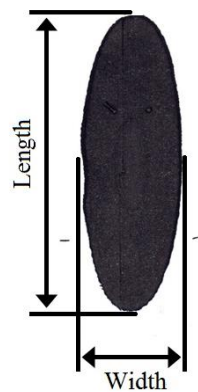


Figure 10. Length and width of a footprint shape.

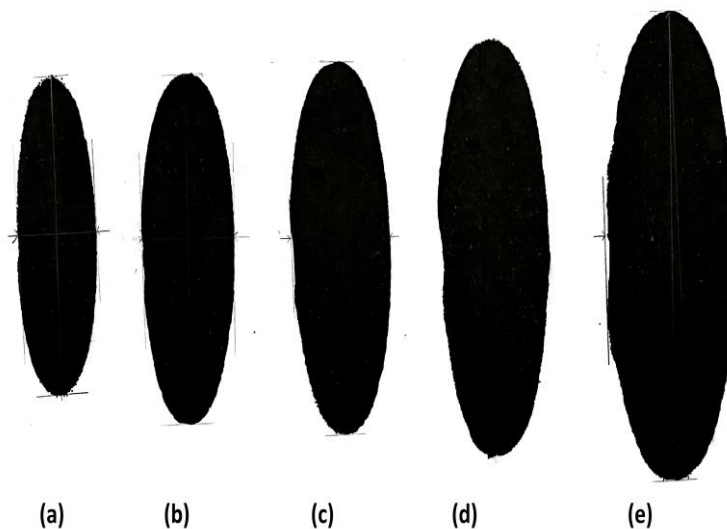


Figure 11. Footprint shape for experimental tire: (a) under-loaded at 805 N; (b) under-loaded at 1005 N; (c) at load of 1256 N; (d) normally loaded at 1570 N; and (e) overloaded at 1885 N.

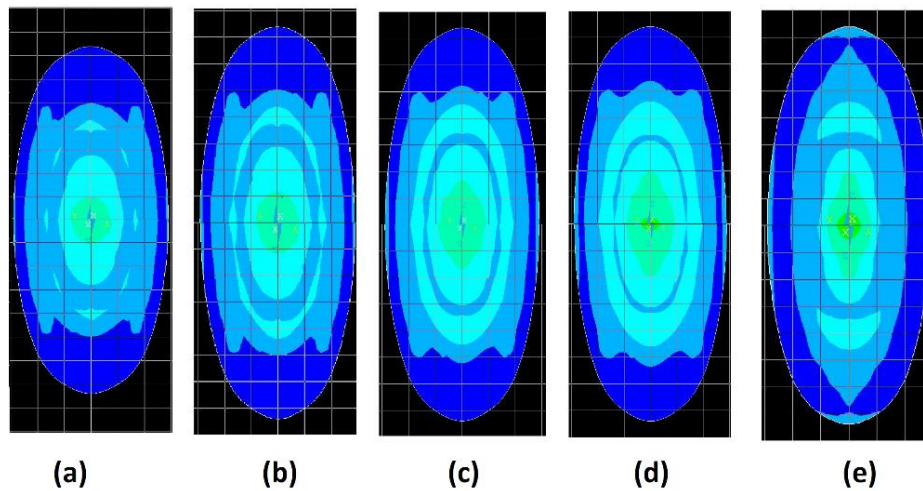


Figure 12. Footprint shape for FEA tire model: (a) under-loaded at 805 N; (b) under-loaded at 1005 N; (c) at load of 1256 N; (d) normally loaded at 1570 N; (e) overloaded at 1885 N.

There were slight differences in the contact area in terms of length and width (Table 2), but the same trend in changes of shape for the footprint depicts that the results are in good agreement. The contour shape of the footprint between the numerical and experimental tire are similar. In reference to the FEA simulated footprint results, as the load amount increased, the tire footprint area increased. These match with the experimental bias two-wheel tire during footprint test.

Table 2. Comparisons of tire footprints obtained numerically and experimentally at various loadings when inflated at a pressure of 230 kPa.

	Experimental Tire		FEA Tire Model		% Difference	
Load (N)	Length (mm)	Width (mm)	Length (mm)	Width (mm)	Length	Width
805	105	34	100	40	5.00	17.6
1005	115	39	100	44	13.0	15.4
1256	125	43	104	48	8.80	11.6
1570	138	47	106	50	23.2	6.38
1885	148	52	134	60	9.46	15.4

The discrepancies in the length and width of footprint shape between the experimental tire and FEA tire model are expected as in the simulation, plane displacement is set to represent the vertical loadings on the tire. The plane displacement was estimated from the load-deflection curve based on the experimental tire. There will be some slight differences as the plane displacement set in the simulation might not represent the same amount of load with respect to the load on experimental tire.

4. Conclusions

The geometry of the tire during the inflation process are compatible between the real experimental tire and the FEA tire model of bias two-wheel tire. Although there are minor discrepancies for both the inflation process and footprint test, similar trends were observed when different inflation pressure and vertical loads were applied on the tire. The results of static loading on the FEA tire model shown in this paper indicate that this tire model is successfully developed in order to predict the bias two-wheel tire behavior during inflation process and footprint tests. FEA method is important as it reduces the cost and time required for designer to explore on a variety of designs.

On top of that, the FEA tire model can be used to tune and optimize the current performance of the tire. It is also possible to observe and evaluate possible effects on tire durability. Extension to the footprint contact area is the analysis of the contact pressure distribution. The extension is already performed and will be reported in a separate paper.

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