

Rice Husk as a Fuel Source in Direct Carbon Fuel Cells

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Abstract

The increase in global energy demand and rising of the greenhouse gas emission from Southeast Asia drives developing nations such as Malaysia to use energy that is more sustainable with lower greenhouse gas emissions. In this research, rice husk is proposed to be used as a potential fuel source in direct carbon fuel cells. In this study, rice husk that was obtained from Sekinchan, Malaysia was initially dried for 24 hours at temperature of 105°C and milled into size of less than 2 mm. Subsequently, it was pyrolysed in a furnace at three sets of temperatures, which are 400, 500 and 600 °C with heating rate of 10 °C min⁻¹. Residence time of 1 hour and 2 hours were conducted for all samples. The biochars produced were analysed to determine the physicochemical properties and structural properties. The study revealed that biochar that has a higher fixed carbon content and surface area, low moisture and ash content is a favourable fuel for direct carbon fuel cells. From the proximate analysis, it was shown that biochar produced at 600 °C and 1 hour has the lowest mass loss at temperature between 25 and 600 °C. But the lower carbon content produced at 600°C and 1 hour, it was shown to contain lower sulphur content that is highly desired as solid oxide fuel cell fuel source. Pyrolysis treatment has improved the rice husk surface area from 1.4825 to 254.5275 m²/g. In summary, biochar produced at 600 °C and 1 hour show the most potential to be used as fuel for solid oxide direct carbon fuel cell.

Keywords: Biomass, Lignin, Pyrolysis, Biochar, Solid Oxide Direct Carbon Fuel Cell.

1. Introduction

Worldwide, energy demand had a drastic growth resulting from the rising number of industry and population. The 2013 reports on worldwide energy demand from Energy Information Administration (EIA) of United States have forecasted an increment of 43.64% within the next 5 years assuming that there are no changes in energy consumption policies[1]. Furthermore, due to the rise of greenhouse gas emission in Southeast Asia, it is essential for an Asian country such Malaysia to use energy that is sustainable and able to reduce emission of greenhouse gas. According to the Five Fuel Policy, biomass has been identified to be one of the potential renewable energy by Malaysian government as the production of biomass in Malaysia was found to be 168 million tonnes in year 2014. Agricultural wastes such as oil palm shell, rice straw, sugarcane bagasse, and rice husk are the main resources of biomass in Malaysia.

Direct carbon fuel cells (DCFC) has been identified as an efficient electricity generator that converts chemical energy in solid carbon into electrical energy directly. The expected electrical efficiency is above 70 % for DCFC, which is double of the electricity efficiency generated in coal-fired plants. Furthermore, DCFC releases 50 % less in CO₂ emission due to CO₂ will again be consumed by biomass [2]. In biomass, the useful carbon content can be measured by the percentage of lignin found within it. The higher the lignin percentage is, the higher the carbon content [2]. The technology available to convert biomass into fuel source such as biochar is known to be pyrolysis. Pyrolysis is a process which decomposes the biomass at high temperature without the presence of air [3]. The carbon rich solids termed as biochar which is produced from this process can be fed into the DCFC as the fuel source.

As a one of the producer and exporter of rice, the utilisation of rice crop residues, rice husk as a fuel source in a DCFC has the potential of reducing the CO₂ emission. However, most of the rice husk has been used to fertilise the farm field which resulted loss of energy to the atmosphere. There are only a few of researches performed to investigate the potential of carbon fuel derived by biomass as a fuel source in DCFC [4]. Moreover, the studies of sustainability of biochar derived from rice husk as a fuel source in DCFC has not been looked into. The performance (efficiency, stability and power output) of a DCFC is strongly dependent to the physicochemical properties of the biochar. A high carbon content and less contaminants of biochar provides more efficient and less failure in the operation of the DCFC. Crystal structure and surface area are the indication of the electrochemical reactivity of the biochar.

There is no research that has been performed so far to investigate the influences of physicochemical properties of biochar derived from rice husk to the performance in a DCFC. In addition, the development of the desired properties of biochar that fed into DCFC has not been optimised in terms of pyrolysis conditions such as temperature and residence time.

1.1 Objectives

1. To analyse the effect of pyrolysis process conditions (temperature and residence time) on the development of biochar properties produced from rice husk.
2. To study the effects of temperature and process duration on the yield of biochar.
3. To determine the physicochemical characteristic of the biochar produced and validate it with literature.

2. Methodology

The rice husks (rice scientific name: *oryza sativa*) was collected from Sekinchan, Malaysia. The biochars were prepared for pyrolysis process, after which they were analysed. A summary of the overall methodology is summarized in the flowchart in Figure 2-1.

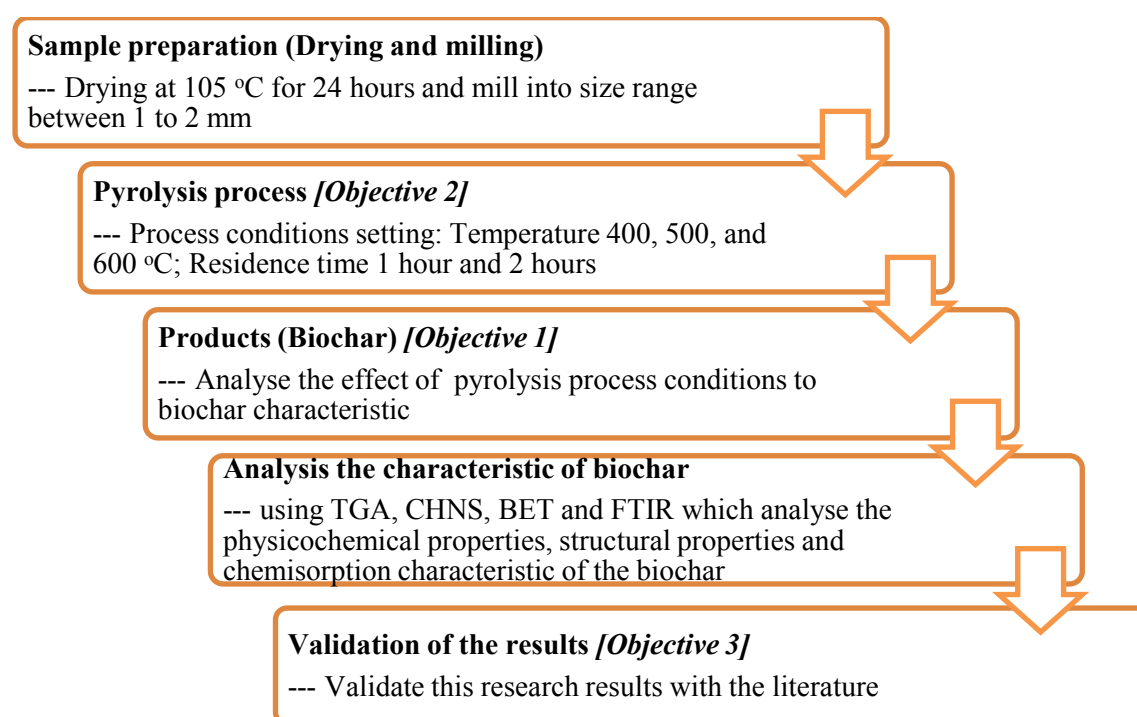


Figure 2-1: Methodology flowchart.

2.1 Sample Preparation

The rice husks were first dried in oven at 105 °C for 24 hours to remove the moisture content. It was then milled into a size between the ranges of 1 to 2 mm using a cutting mill with a 2 mm blade. After that, it was sieved with a Retch sieve shaker. The equipment used is Pulverisette14 variable speed rotor mill located at Monash University.

2.2 Pyrolysis process parameters

The pyrolysis of rice husk samples were carried out using furnace with nitrogen gas stream input to ensure oxygen free in the furnace. 20 g of each sample was placed into furnace and three set of temperatures was performed at 400, 500, and 600 °C with a heating rate of 10 °C min⁻¹. Residence time 1 hour and 2 hours was

conducted for all samples. Summary of pyrolysis process parameters used in this research for rice husk is shown in Table 2-1.

Table 2-1: Pyrolysis process parameters.

Materials	Sample weight (g)	Sample size (mm)	Temperature (°C)	Heating rate (°C/min)	Residence time (hours)
Rice Husk	20.0	Range 1.0 - 2.0	400, 500 and 600	10	1 and 2

2.3 Experiment Setup

Pyrolysis was done by using furnace (model: MTI KSL-1100X) (Figure 2-2) located in process laboratory in Taylor's University. The furnace is heating by using coils and it had N₂ gas input to provide free oxygen atmospheric conditions. The temperature limit of the furnace is 700 °C, thus the experiment was ensured to be conduct at lower than this temperature. Furthermore, the flowrate of N₂ gas was unable to measure due to the unsatisfied range of the flowrate gauge and thus the N₂ gas was allowed to flow in an approximate flowrate during the experiment conducted.

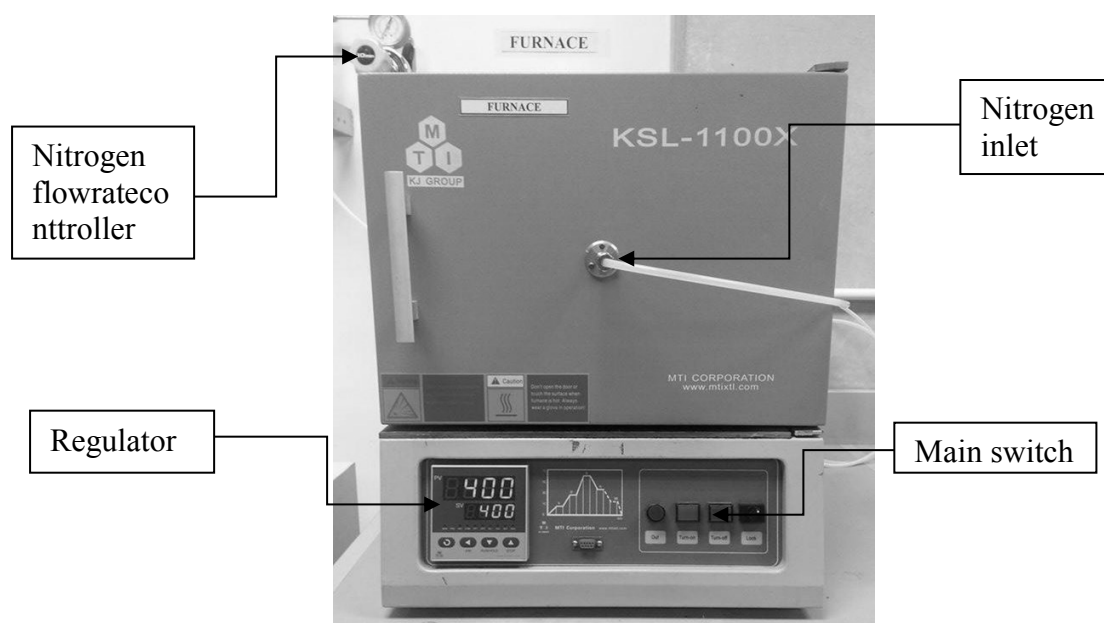


Figure 2-2: Furnace (MTI KSL-1100X).

2.3.1 Experimental Procedure

20 g of samples were stuffed into crucible and covered by aluminum foil. Crucible was then put into furnace and nitrogen gas started introduce in. Regulator was set into desired temperature (400, 500 and 600 °C) and residence time (1 and 2 hours).Run button was pressed and hold to start the timer and the main switch is then turned on to start heating. Cool down of the samples were allowed after the process. The nitrogen input and the electrical power was then turned off.

2.4 Biochar characteristic

Analysis such as TGA, BET, FTIR, and CHNS was performed to obtain the characteristic of biochar.

2.4.1 Thermogravimetric Analysis (TGA)

TGA was used to determine the physical properties of fixed carbon, ash, volatile matter and moisture of biochar. The equipment used was Thermogravimetric analyser (Settaram TGA92) located at Monash University, Malaysia. The procedure was: 0.1 g of the biochar sample was heated to 110 °C with N₂ inert gas, and held for 20 minutes to eliminate moisture content entirely. After that, increase the temperature from 110 °C to 950 °C, held it for 30 minutes inerting with N₂ gas to remove volatiles matters completely. At the temperature of 950 °C, inert gas supply will be cut off, and switched to air and held for 20 more minutes, by allowing combustion of carbon to occur, leaving only the ash. The analysis is carried out at heating rate of 10 °Cmin⁻¹.

2.4.2 Brunauer-Emmett-Teller (BET)

BET was used to determine the specific surface area and porosity of the biochar. The equipment used is Micrometrics 3Flex Surface Characterisation Analyser located at LabAlliance, Malaysia. The procedure was: 0.5 g of biochar samples was degassed at 90 °C for first 60 minutes followed by 300 °C for the next 480 minutes. CO₂ was used as adsorption gas and the adsorption was studied at 0 °C under circulating water bath.

2.4.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was used to obtain the infrared spectrum of adsorption of the biochar. The chemical bonds and functional groups of the biochar can be determined. The analysis was done in Monash University using the Thermo Scientific FT-IR. The graph was plotted into software named OMNIC. The procedure was: 0.1 g of biochar was put on top of the scope then enclosed it with the clamping above. Run the software and data was recorded in the wavelength of 525 to 4000 cm⁻¹.

2.4.4 Elemental Analysis (CHNS)

CHNS was used to determine the carbon, hydrogen and nitrogen contents of biochar. The equipment used is Ultimate analysis (Euro EA3000 series, Elemental Analyser). Samples were sent to University of Malaysia Pahang for this analysis. The procedure was: 0.5 g of biochar sample was combusted in a crucible with the presence of vanadium pentoxide catalyst, and then purified electrolytic copper and copper oxide in a packed reactor. The gas mixture containing nitrogen, carbon dioxide, water, and sulphur dioxide flows into the chromatographic column, where separation takes place. Eluted gases were sent to the thermal conductivity detector (TCD) where electrical signals processed by the Eager 300 software provide percentages of nitrogen, carbon, hydrogen, and sulfur contained in the sample.

3. Results and Discussion

3.1 Thermogravimetricanalysis of biochar

Thermogravimetric analysis was carried out for every sample to observe the losses of mass (TG) proportional to the thermal effect (DTA) which occurred during operation of SOFC. The results from this analysis are compared with carbon black that fed in as fuel source in SOFC. Figure 3-1 shows the curve of TG and DTA for biochar derived at 400 °C and 1 hour (Sample 1), 500 °C and 1 hour (Sample 2), 600 °C and 1 hour (Sample 3), 400 °C and 2 hours (Sample 4), 500 °C and 2 hours (Sample 5), and 600 °C and 2 hours (Sample 6) respectively using N₂ as shield gas.

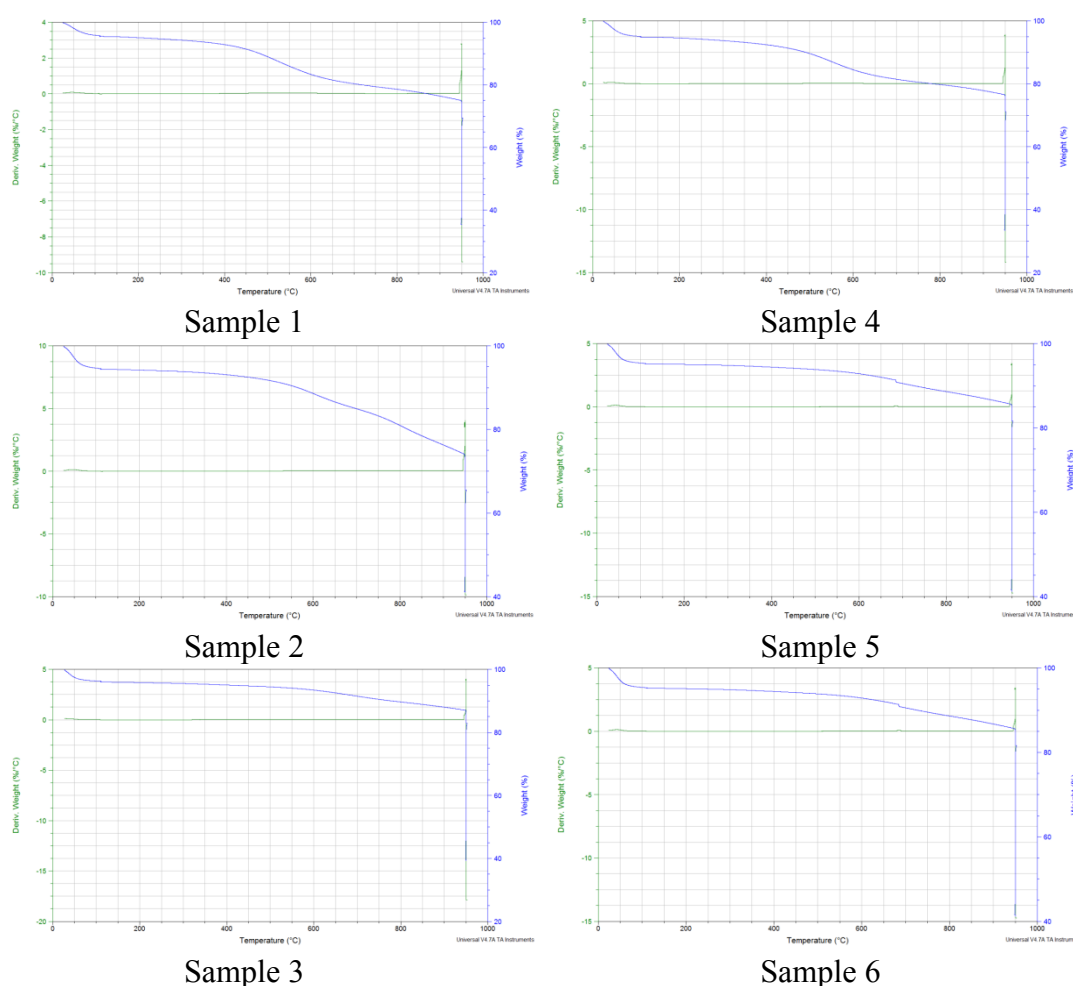


Figure 3-1: Curve of TG and DTA for biochar derived at various pyrolysis conditions.

Highest mass loss between the temperature ranges of 25 to 1000 °C was observed from Sample 1, 26 wt%, followed by Sample 2, 25 wt%, Sample 4, 23 wt%, Sample 5, 16 wt%, Sample 6, 15 wt% and Sample 3, 13 wt%. Summary of the results is recorded in Table 3-1.

Table 3-1: Mass loss of the biochar samples on TGA analysis.

Sample	Pyrolysis conditions	Mass loss (wt %)
1	400°C, 1 Hour	26
2	500 °C, 1 Hour	25
3	600 °C, 1 Hour	13
4	400 °C, 2 Hours	23
5	500 °C, 2 Hours	16
6	600°C, 2 Hours	15

It is determined that the biochar produced does not have a mass loss which similar to activated carbon (mass loss up to 20 %) between the temperature ranges of 25 to 600 °C which is favourable to use as fuel source in SOFC as there would be a reduction of the duration and efficiency of the fuel if there is a mass loss below SOFC operating temperature (700 to 1000 °C)[4].

3.2 Elemental analysis of biochar

According to Salman & associates [5], raw rice husk has a carbon content of 42.78 wt%. Results obtained from this research shows that the carbon content increases when the pyrolysis temperature increases which it is agree with many other research. Besides, sulphur content is lower than 1 wt% which is definitely suitable to become a fuel source of SOFC as the sulphur is a poison to SOFC constituents. The highest carbon content of 51.99 wt% was recorded for biochar produced at 500 °C and residence time of 1 hour while the lowest sulphur content of 0.054 wt% was recorded for biochar produced at 500 °C and residence time of 2 hours. To be potential to become the SOFC fuel source, high carbon content and low sulphur content was required. Thus, the biochar that produced at 600 °C and 1 hour have the most potential among the samples as it has the second high carbon content of 49.17 wt% and relatively low sulphur content. But it is still lower than carbon black carbon content (>90 wt %) that usually tested on SOFC. Compared it to raw rice husk, the carbon content has increased by 6.39 wt%, this is because the vaporisation of major volatile compound in lignocellulosic biomass starts at temperature 600 °C. Table 3-2 lists the elemental analysis results for biochar.

Table 3-2: Elemental analysis results.

Sample No.	Pyrolysis conditions	N (wt %)	C (wt %)	H (wt %)	S (wt %)
1	400°C, 10 °C min ⁻¹ , 1 Hour	1.02	48.56	3.025	0.759
2	500 °C, 10 °C min ⁻¹ , 1 Hour	0.97	51.99	2.341	0.591
3	600 °C, 10 °C min ⁻¹ , 1 Hour	0.83	49.17	2.107	0.295
4	400 °C, 10 °C min ⁻¹ , 2 Hour	0.92	47.89	2.799	0.068
5	500 °C, 10 °C min ⁻¹ , 2 Hour	0.84	48.33	2.153	0.054
6	600°C, 10 °C min ⁻¹ , 2 Hour	0.66	33.91	2.712	0.113

It was found that the fixed carbon will have highest yield when at high temperature and shorter residence time [6]. However residence time does not make a huge change in element composition of biochar claimed by Mengie [7]. As observed from graph (Figure 3-2), the percentage of fixed carbon produced having a direct proportional relationship to the temperature and an inverse proportional relationship

to the residence time. This is because the fully decomposed of rice husk happened before residence time of 2 hours.

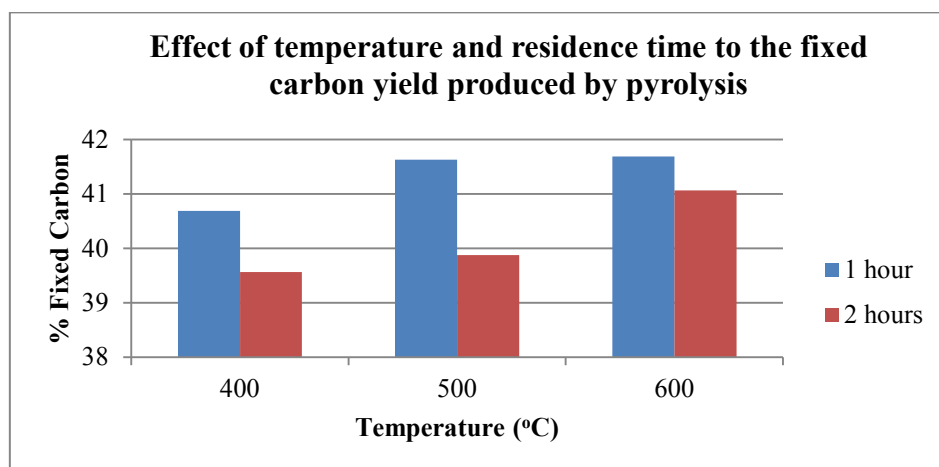


Figure 3-2: Effect of temperature and residence time to the fixed carbon yield of biochar.

3.3 Surface and porosity of biochar

Pyrolysis enhanced rice husk surface area and porosity. It will be further enhanced when it treated at higher temperature. The results obtained from BET analysis shows in Table 5-3. Rice husk has a surface area of $1.4825 \text{ m}^2/\text{g}$ and biochar has a surface area of $254.5275 \text{ m}^2/\text{g}$, it proven that pyrolysis has improved the surface area of rice husk by almost 200 times as the biochar produced in temperature 600°C and residence time 1 hour. Besides, the pore size also has a greatly improved from rice husk to biochar. Total area and total volume of the pore were greatly improved as well. As mentioned in literature, larger surface area and porosity of solid carbon fuel used in SOFC has a huge effect to its performance. Results shows biochar derived from rice husk has potential to become fuel source in SOFC as it has high surface area and a pore size larger than 50 nm .

Table 3-3: BET analysis results.

Sample	Surface Area (m^2/g)	Pore Size (nm)	Total Area (m^2/g)	Total Volume (cm^3/g)
Rice Husk	1.4825	18.7807	0.78	0.00181
Biochar (600°C , 1 hour)	254.5275	55.603	5.996	0.10869

3.4 Chemisorptions of biochar

From the infrared spectrum showed in Figure 3-4, it is observed that every sample has a major peak in the range of wavenumbers from 900 to 1300 cm^{-1} . The peak located from this range is subjected to the aliphatic ether C-O and alcohol C-O stretching. It confirms that the chemical bonds are mainly C-O. Salman[6] stated that raw rice husk spectrum has a major band of peak at 3500 cm^{-1} wavenumber and peak at range of 866 cm^{-1} to 1044 cm^{-1} , which the main peak is found to be characteristics of generic oxygenated hydrocarbon due to the biomass is dominated by cellulosic fraction. Follow by the peak at range 866 cm^{-1} to 1044 cm^{-1} , it is indicated that the presence aromatic structures. The results that Salman[6] obtained also showed that

pyrolysis eliminated the major peak at 3500 cm^{-1} and remain the peak on 866 cm^{-1} to 1044 cm^{-1} after the rice husk has been pyrolysed. Compared to the result that obtained in this research, it has similar findings with Salman as the peak was normalised at 1100 cm^{-1} .

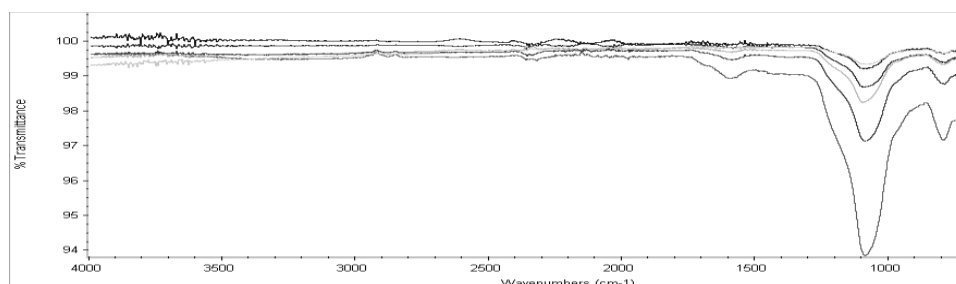


Figure 3-4: FTIR results.

4. Conclusions

In conclusion, biochar produced from pyrolysis of rice husk at $600\text{ }^{\circ}\text{C}$ and 1 hour shows best potential as carbon fuel for solid oxide fuel cells. This is due to its low mass loss when subjected to heating up to $600\text{ }^{\circ}\text{C}$, high carbon content of 49.17 wt%, low sulphur content (2 wt %) when compared to other biochars produced in this study. The surface area of biochar produced at this condition was $254.5275\text{ m}^2/\text{g}$ which is 100 times higher than the untreated rice husk ($1.4825\text{ m}^2/\text{g}$). For future work, it is recommended to optimise the pyrolysis process condition in order to produce better quality of biochar that can be applied to SOFC. In addition, the objectives may include the testing of the biochar produced in SOFC in order to investigate the cell performance and power output. The study on pre-and post-treatment techniques can be included to further improve the development of desired biochar properties such as higher carbon content in biochar, larger surface area and pore diameter, and higher degree of disorder of graphite structure.

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Investigate the Common Factor in Poisoning Herbs

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Abstract

Herbs had been long used as a medicine to cure many illnesses and diseases. The *Aconitum napellus* (Aconite), *Actaea spicata* (Baneberry), *Nicotiana tabacum* (Tobacco), *Datura stramonium* (Jimson weed), *Lonicera xylosteum* (Fly honeysuckle), and *Cannabis sativa* (Marijuana) were chosen as the research subjects of this project. These herbs are known to have poisoning effects. Six herbs were chosen and then categorized into three groups as high, medium and low poisoning level. This research was to determine if there is a common factor between herbs of same poisoning level or amongst all herbs. The chemical constituents and the physical properties of each poisoning herb are investigated to find the common factor between these six poisoning herbs. The chemical constituents are determined by using journal papers and other sources available. The physical properties of each poisoning herbs would also be determined by obtaining details published in journal papers, herb dictionaries, and observation through reliable pictures from various sources available. It was found that the common factor among all herbs is alkaloid. Another chemical compound found only in four of these poisoning herbs was the flavonoids. Regarding the physical properties, the investigation shows that there is no common factor. This result suggests that the impact of weather, ecosystem, and topography are the main factors in deciding the physical properties not the poisoning behavior of the herbs. The existence of alkaloid suggests to a certain degree of confident that poisoning effect is related to alkaloids.

Keywords: Poisoning herb, alkaloid, common factor, *Aconitum*, *Cannabis*.

1. Introduction

Herbs have long been used as a medicine to cure many illnesses and diseases. They are, to a certain extent, available all around the world naturally or by growing them for living. Most herbs nowadays are usually processed first before consumption, yet, they can also be consumed directly. Even though herbs have chemical components which are used to cure illnesses and diseases, some herbs also have poison or toxic effect which can be very lethal to living beings. Among thousands of herbs, there are some poisoning herbs. The six herbs chosen in this study were chosen based on classifications in the journals, books, and/or dictionaries and they were categorized under three categories. The morphology (genus's origin) and habitat (diversity) are not included in this study simply because there is no evidence to see either the morphology or habitat as factors in poisoning. However, we elect to mention briefly some of these characteristics in the text. The crucial purpose of this study is to determine any common factor, chemical or physical, that exists amongst the six chosen herbs, if any. It is away from the common tradition, the medicines are all considered poisoning in their nature within an accept percentage and, consequently medicines are poisons under control. The fear which could arise through this research is that the poisoning level could exceed the limit and become lethal.

Aconitum napellus, commonly known as Aconite, belongs to the family Ranunculaceae, which consists of about 100 species of the plant genus [1]. It is commonly found in alpine and subalpine regions [2]. It is usually perennial or biennial herbs, often with stout leafy stems, bulbs or creeping rhizomes. Its leaves are mostly cauline, lobed and rarely divided. Its flowers have simple or branched racemes. Aconitum is an essential component in formulations of Chinese and Japanese traditional medicine due to its various pharmacological properties such as analgesic, anti-inflammatory, cardio tonic effect, blood pressure elevation, and anesthetics effect [1]. Despite being a medicine to various illnesses, it is also used as a complete source of arrow poison in China due to one of its chemical components, diterpene alkaloid which is highly toxic [1].

Actaea spicata Linn, also known as Baneberry, belongs to the family Ranunculaceae [3]. According to a survey of ethnopharmacologic records, it reveals that the plant has been traditionally used in the treatment of inflammation, lumbago, chorea, rheumatism, scrofula, rheumatic fever, and nervous disorders [3]. It is also used as laxative, purgative, expectorant, emetic, and stomachic [3].

Cannabis sativa, also known as Marijuana, belongs to the Cannabaceae family and *Cannabis* genus [4]. The *Cannabis* plant have been grown and processed for many uses. Many of its plant parts are used as medicine for humans and livestock, the whole seeds and seed oil are consumed by humans, seeds and leaves of the plant are fed to animals, where else the seeds oil and stalks are burned for fuel [4]. It started being used in the Central and Northeast Asia region with its current use being spread all around the world as a recreational drug or as a medicine albeit unauthorized [5].

Datura stramonium L., also known as Jimson weed, belongs to the Solanaceae family and *Datura* L. genus [6]. The *Datura* plant is native to Asia, but it is also found in the United States, Canada, and the West Indies. It is usually widespread in

regions with high abundance in temperate, tropical and subtropical regions [6]. In Ayurvedic medicine, the *Datura* plant is described as a useful remedy for various human ailments such as inflammation, bruises and swellings, ulcers, wounds, toothache, asthma and bronchitis, rheumatism and gout, fever, and many more [6]. In addition, the ancient Hindu Physicians regarded it as sedative, tonic, antispasmodic, antiseptic, intoxicant, narcotic, and also useful in skin disorders and leucoderma [7].

Nicotiana tabacum L., which is commonly known as Tobacco, belongs to the Solanaceae family [8]. Tobacco is widely cultivated all over the world, especially in China. The tobacco is widely used in the tobacco industry. On the other hand, the tobacco seed gives linoleic acid, which can be used in formulation of plastics, protective coatings, as dispersants, biolubricant, surfactant, and cosmetics [8]. Another component found in tobacco seeds would be the glyceride oil, which is a raw material used in the coating industry, mainly for preparation of printing inks, dye etc. [9].

The *Lonicera xylosteum*, commonly known as Fly honeysuckle, belongs to the family Caprifoliaceae [10]. It can be found mainly in temperate region of the Northern Hemisphere, containing about 12 genera and 450 species [10]. Several species of the *Lonicera* genus was used for the treatment of respiratory infections, headache, and acute fever [10]. In addition, it was also used as antioxidant agent, hypotensive, sedative, and anti-pyretic medicines [10].

2. Methodology

This project focuses mainly in finding the common factor amongst the six poisoning herbs whether chemicals in their natural or physical in their appearance. The chemical composition of each herb is obtained through reviewed journal papers or other available sources. On the other hand, all details and descriptions of the physical properties of each poisoning herbs such as the appearances of the leaves, the shape of the stem, and the tree are also obtained through reviewed journal papers and herb dictionaries.

2.1 The Search for Common Factor in Chemical Composition

According to various reviewed journal papers, the poisoning herbs consist of many chemical components. Some of these six poisoning herbs has unique chemical components such that they were named after their genus, such as aconitine [1] in *Aconitum* plant and cannabinoids [5] in *Cannabis* plant. The chemical components found from reviewed papers are summarized in Table 1, Table 2, and Table 3 according to the toxicity levels of the herbs. They were tabulated in three different categories comprising high, medium, and low level toxicity.

Table 1. The Characteristics of High Level Poisoning Herbs

Herbs	Physical Properties	Habitat	Chemical Constituents	Reference
<i>Aconitum napellus</i> (Aconite)	• Tuberous roots • Spirally arranged palmate deeply • Palmately lobed leaves, dentate, rarely divided.	Alpine and subalpine regions, Northern hemisphere, Nepal.	Diterpenoid alkaloids, flavanol glycosides.	[1, 2, 11-13]
<i>Actaea spicata</i> (Baneberry)	• About 30–70 cm (12–28 in.) in height; shiny stem, angularly curved from nodes, base with 3–4 scales • White flowers, with weak fragrant • Alternate basal triangular blade shaped leaves, darkish green, usually with 3 leaflets	Native to Europe; grows in temperate Himalayas from Hazara to Bhutan.	Steroids, alkaloids, flavonoids, tannins, carbohydrates, proteins, pesticides, arsenic, heavy metals, aflatoxins, microbes.	[3, 14, 15]

Table 2. The Characteristics of Medium Level Poisoning Herbs

Herbs	Physical Properties	Habitat	Chemical Constituents	Reference
<i>Nicotiana tabacum</i> (Tobacco)	• An erect glandular-pubescent herb. • Leaves large, oblonglanceolate, acuminate, the lower semiamplexicaul and decurrent. • Flowers rosy or reddish, pedicelled, 4-5 cm long, in many-flowered, usually panicled racemes.	Native to tropical America; cultivated mainly in Andhra Pradesh, Maharashtra, Karnataka, Uttar Pradesh, West Bengal.	pyridine alkaloid, organic acids, glucosides, tahacinin, tahacilin, chlorogenic, caffeic, oxalic acids, terpenic, carcinogenic substances.	[14, 16]
<i>Datura stramonium</i> (Jimson weed)	• Large and coarse shrub of about 3 to 4 feet in height • Large, whitish roots • Green or purple, hairless, cylindrical, erect and leafy stem, branching repeatedly in a forked manner • Flowers are ebracteate, regular, pentamorous, and are hypogynous • Dry and spiny fruits; initially green, but becomes brown when matured • Seeds are dull, irregular, and dark-colored	The Himalaya from Kashmir to Sikkim up to 2,700 m, hilly districts of Central and South India.	tropane alkaloids, atropine, scopolamine, daturic acid, chlorogenic acid, ferulic acid.	[6, 14]

Table 3. The Characteristics of Low Level Poisoning Herbs

Herbs	Physical Properties	Habitat	Chemical Constituents	Reference
<i>Cannabis sativa</i> (Marijuana)	- Green or dark green leaves - Erect stems which vary from 0.2-2.0 m.	Cultivated all over the country. Commonly occurs in waste grounds, along road side, often becoming gregarious along the irrigation channels of gardens.	Cannabinoids, Cannabidiol, Tetrahydrocannabinol, amino acids, proteins, enzymes, hydrocarbons, simple aldehydes, simple ketones, steroids, alkaloids, flavanoids, flavonol glycosides.	[5, 17]
<i>Lonicera xylosteum</i> (European Fly honeysuckle)	- Has fairly small, irregular flower. 5 petals, united, corolla yellowish-white color - Tapering buds, brown, hairy. - Round seed, flattened, glandular hairy, deep red, glossy berry fruit.	Temperate region of Northern Hemisphere, Pakistan.	Iridoids, bisiridoids, alkaloids, glycosides, triterpenoids, saponins, coumarin glycosides, flavone glycosides.	[10, 18]

2.2 The Search for Common Factors in Physical Properties

Similarly, the physical properties of each poisoning herbs were obtained from various reviewed papers and herb dictionaries. Pictures relevant to each part of the herbs are also used to investigate if there is any common factor amongst these poisoning herbs chosen for study. The physical analysis relies on parts such as the leaves, the stem and the tree of each herb. All details are tabulated in Table 4, Table 5, and Table 6.

Table 4. Comparison of leaf characteristic between 6 poisoning herbs

	Leaf		Common Factor
High level poisoning	<i>Aconitum</i>	<i>Actaea</i>	• 3 leaves at the end of stem • has cavities
	• stem ends with leaves • leaves with 3 parts • sharp at the end • secretion is thick • blue in color	• 3 leaves at the end of stem • the angle between the midrib and the veins is about 30° • elliptical shape leaf • sharp ends around the leaf • green in color	
Medium level poisoning	<i>Nicotiana</i>	<i>Datura</i>	• no similarities
	• many leaves clusters at 1 branch • green in color • the angle between the midrib and the veins is about 80°	• the angle between the midrib and the veins is about 30° • elliptical shape leaf • irregular, messy cavities • 1 leaf at each stem	
Low level poisoning	<i>Cannabis</i>	<i>Lonicera</i>	• no similarities
	• the angle between the midrib and the veins is about 30° • 7 leaves at the end of stem • the point of branching for veins is the same • the border of leaves is like saw • symmetrical	• twin leaves • dark green in color • regular, no cavities • only 1 midrib with many veins • elliptical shape leaf • thick hair • curl at the end of leaf	

Table 5. Comparison of the stem between 6 poisoning herbs

	Stem		Common Factor
High level poisoning	<i>Aconitum</i> • 1.5m tall • divided at the end • big leaves • flowers are clustered • covers the plant like a helmet	<i>Actaea</i> • 2m tall • bad smell • big, triangular leaves • white, square shaped flowers • fruits are clustered	• big leaves
Medium level poisoning	<i>Nicotiana</i> • 1m tall • very big leaves • pink flowers, also has white flowers but very rare	<i>Datura</i> • 0.5m tall • bad smell • stem divided into 2 at the end • leaves very tall • cavities at the end • long and white flowers • leaves covered with spikes	• leaves are similarly big
Low level poisoning	<i>Cannabis</i> • 1.5m tall • leaves are very long • small and yellow flowers • rich of fibers	<i>Lonicera</i> • 2m tall • leaves facing each other • oval shape leaves • flowers appears as double at the end of stem	• no similarities

Table 6. Comparison of trees characteristic between 6 poisoning herbs

	Tree		Common Factor
High level poisoning	<i>Aconitum</i>	<i>Actaea</i>	flowering plant
	- cone-shape - tall - flowers at the end of stem - fruitless	- hemispherical shape - short - flowering plant - fruits at the end of the stem	
	<i>Nicotiana</i>	<i>Datura</i>	
	- flowering plant - leaves very dense - many flowers at each stem 1 main stem with many branches along the stem	- flowering plant - leaves very dense 1 flower at each stem - leaves branches out only at the end of the stem	
Medium level poisoning			- flowering plant - leaves densely packed
Low level poisoning	<i>Cannabis</i>	<i>Lonicera</i>	flowering plant
	1 tall shoot, leaves branching out along stem - flowering plant	- very dense - flowering plant	

3. Results and Discussion

Having all possible chemical constituents and physical properties, an extensive cross investigation was carried out to determine the common factors.

3.1 Common Factors in Chemical Composition

The six herbs as mentioned before were classified under three groups as high, medium, and low poisoning level. Regarding the chemical composition, it is found that the common chemical composition in all six herbs shown in Table 1, Table 2, and Table 3 is the *alkaloid* chemical compound. The *alkaloid* is an organic compound which usually contains at least one nitrogen atom in a heterocyclic ring. It is found that the *alkaloid* compound in each herb differs a little, yet all belong to same the same category of alkaloids. Based on the nature of this study, one can suggest that alkaloid is a common factor. Examining for another common factor, the findings shows that another chemical compound known as flavonoids is found in the high poisoning level (*Aconitum*, *Actaea*), in the medium level (*Datura*), and finally in the low level (*Cannabis*). Despite the fact that this flavonoids is not found in all six herbs it is possibly appear in very small undetectable amount or under different name.

Table 7 provides a summary of possible common chemical compound which exists in the six poisoning herbs under study.

Table 7. Possible common factor in 6 poisoning herbs

Herb	Alkaloid	Flavanoid
<i>Aconitum</i>	✓	✓
<i>Actaea</i>	✓	✓
<i>Datura</i>	✓	✓
<i>Nicotiana</i>	✓	
<i>Cannabis</i>	✓	✓
<i>Lonicera</i>	✓	

Some of the alkaloid compounds that exists in the six herbs under investigation are shown in Figure 1, Figure 2, Figure 3, and Figure 4. All these alkaloid compounds are believed to be responsible for the poisoning effect. The pharmaceutical companies are extracting these alkaloid compounds for their drug manufacturing which strongly suggests that these are poisons in their nature and the drug companies are trying to utilize these compounds for their products [1, 2, 6].

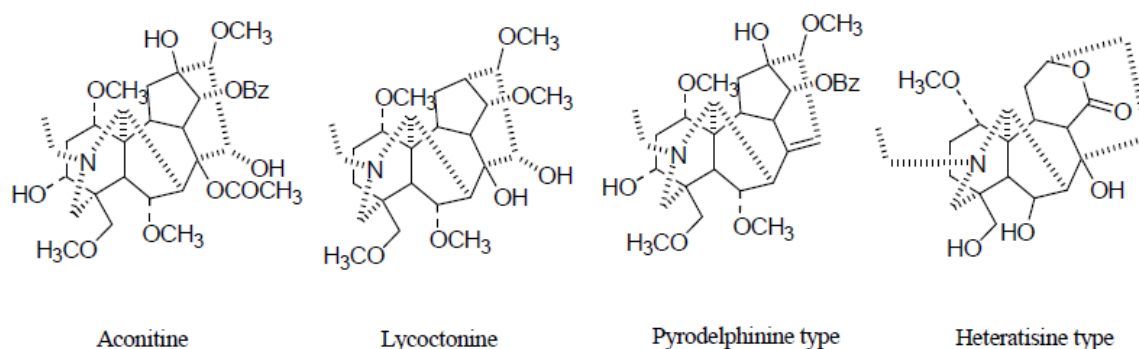


Figure 1 Various types of alkaloids found in *Aconitum* herb [2]

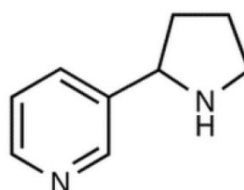


Figure 2 Alkaloid nornicotine found in *Nicotiana* herb [16]

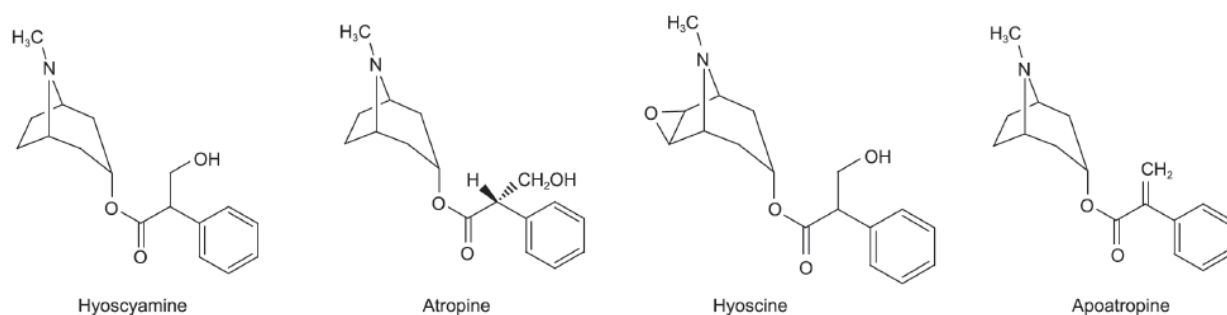


Figure 3 Various types of alkaloids found in *Datura* herb [6]

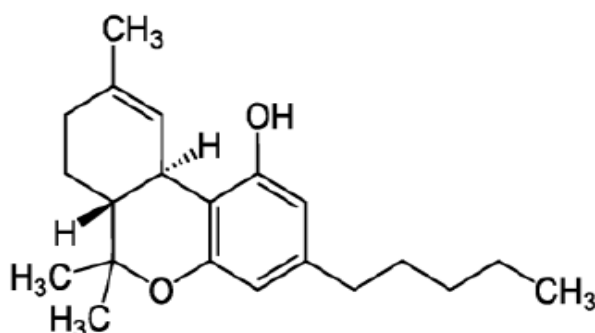


Figure 4 Tetrahydrocannabinol (THC) compound found in *Cannabis* herb [17]

3.2 Common Factor in Physical Properties

The physical appearance of the herbs was investigated and information was gathered in Table 4. The physical appearance under investigation are the structure of the leaves, how the leaves attached to the stem, the color of the leaves, the veins of the leaves, the structure of the border of the leaves, how dense the leaves are attached to the stem, the shape of the flower or the fruit of each herb. It is found that there are some similarities among each group but it is not conclusive amongst all chosen herbs. The color, seemingly, could be considered as a common factor since the color ranges from green to yellowish green. The structure of the leaves has shown that the leaves are mostly curled and not smoothly shaped. It is found that the leaves are attached to the stem in mainly cluster-like attachment –the case that could be considered as a common factor. The midrib and the veins show other similarity as they appear almost in a single structure. According to Table 5, for high and medium level category poisoning herbs, the leaves are similarly large. However, it is observed that not all six herbs share this property. The area of the leaves is not a common factor, however it is well-known that the environment and the climate (cold, dry, hot) has its influence on the area of the leaves.

The structure of the stem shown in Table 5 does show some similarities whether amongst all six herbs or between each group. Stems, for instance, are all having same color. The stems have all rooted in ground to almost similar depth. The stems are apparently not poisoning in their nature and no evidence was shown that the stems of these herbs are varied in their length which ranges between 20 cm to about 2 m. Regarding the physical appearance of the stems, Table 4 shows they share one property which is they are strong and erected almost in same fashion.

Lastly, the structure of the trees was shown in Table 6. It is shown that all six poisoning herbs listed in Table 6 have flowers. The importance of this observation comes with a conclusion that all poisoning herbs are a flowering plant. Keep in mind that not all flowering plants are poisoning in nature. The shape of these flowers vary amongst the six herbs, however, Table 6 shows some similarities among each group. The color of the flowers could be considered close enough to be listed as a common factor. Color, as it is biologically determined, is subjected to other factors such as the type of the soil, the amount of the sun that hits the stem and so on. The inspection of the stems could be very valuable if it is examined under microscope, for this, the study continues to show in more depth if any similarity could be concluded. The stems are not a part of the poisoning factor, but if it is found that they have been affected, even to a certain extent, this piece of knowledge will be very valuable.

4. Conclusion

Herbs are very important to our life since they are the source of nutritious ingredients and the pivot that the pharmaceutical studies are considering. Medicines are herbals in their chemical structures but, unfortunately, they were chemically synthesized. In this project, poisoning herbs are the only one considered for good reason which is to educate people how to deal with these herbs. People, lacking of knowledge, are smoking tobacco and marijuana without paying attention to the poisoning ingredients in them. The study shows evidence of some similarities among poisoning herbs despite how strong the poisoning ingredient is. It is found that a chemical compound such as alkaloids and flavonoids are common factors among poisoning herbs. Regarding physical properties, the study have shown some evidence of similarities such as the color of the leaves and existence of flowers in these herbs. It is similarity or dissimilarity, the study adds some basic knowledge in a comparative fashion to make sense when it comes to distinguishing herbs much easier that thought before.

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Desulphurization of Fuel Oil Using Ionic Liquid Analogue

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Abstract

Sulphur compounds are widely recognized as the most undesirable component to be existing in refinery processes nowadays. Since thiophene is one of the major sulphur component present in oil refinery and the presence of this particular impurity always causes difficulties to the refinery companies, the solubility of thiophene was studied and analysed in methyl triphenyl phosphonium bromide (MTPB) and choline chloride (ChCl) based deep eutectic solvents at temperatures of 25 °C, 35 °C and 45 °C under atmospheric pressure. The aim of this study is to research on the behaviour of specific type DESs towards thiophene, as a base for application of DESs in the field of desulfurization of fuel oil. Combinations of DESs which were chosen to be studied was prepared by mixing MTPB or ChCl as base and three different hydrogen bond donor (glycerol, ethylene glycol, triethylene glycol). After that, High performance liquid chromatography (HPLC) was used for quantitative analysis of solubility of thiophene in the each of the DESs synthesized. The experiment resulted that MTPB with ethylene glycol has the highest solubility of thiophene, with approximately 26.89% wt at temperature of 45°C. Whereas, DES with ChCl and glycerol combination had the lowest solubility of thiophene with approximately 3.9% wt at 25 °C.

Keywords: Deep Eutectic Solvents, Thiophene, Solubility, Sulphur, Refinery

1. Introduction

Fuel such as coal, oil and natural gas were formed from organic matter over millions of years [1, 2]. The fuels were formed by burying the organic matter under the earth, compressed by layers of sand, sediment and rocks. This process forms fuel in the underground which is known as fossil fuels after a long period of time. Until today, fossil fuels are still the primary fuel source for human. Fossil fuels branches into five main types, coal, natural gas, oil, petroleum and liquefied petroleum gas (LPG) [3]. Oil is the common name for crude oil and it exists in the form of liquid hydrocarbon fuels. The crude would be further processed into petroleum and LPG. Crude oil is a dense, dark fluid containing variety of complex hydrocarbon molecules, along with organic impurities such as, sulphur, nitrogen polycyclic aromatics and asphaltenes, heavy metals and metal salts [4].

The more impurities present in the oil, the lower the quality of the crude oil. It is important to remove the unwanted impurities because just by being present, specific impurities could affect the whole refinery process and causing a lot of problems in treatment process.

Sulphur is the third most abundant chemical element in petroleum, queuing behind carbon and hydrogen with concentrations may exceed 10% in some heavy crudes [4, 5]. This is because sulphur emissions from combustion of fuels have a great impact in human health and the overall environment. Emission of sulphur compound into environment is the root of production of SO_x , which will cause chain reaction into acid rain, ozone depletion, and respiratory insufficiency in human [6, 7].

Furthermore, the sulphur element that exists in fuels also reduces the performance of automotive catalytic converters. As a result, environmental regulations are now to decrease the level of sulphur in fuel [1, 4, 8, 9]. For example, the petroleum industry was bounded to produce ultra-low sulphur diesel (ULSD) which contains a maximum of 15ppm sulphur content by 2010 [7, 9, 10].

The aromatic sulphur compounds, thiophenes, benzothiophenes, and alkylated derivatives are more difficult to be removed from crude oil [6, 9-12]. The cause of difficulty of removal is due to the aromaticity and consequent low reactivity of the alkyl groups adding into the ring compound [10, 11]. The term dibenzothiophenes resulted from adding another ring to the benzothiophene family and this brings the compound the most difficult to desulphurized [4, 11].

In industry, the existing desulphurization methods are caustic washing method, dry gas desulphurization method, hydridesulphurization and biodesulphurization.

Table 1. The Existing Desulphurization Methods in Industry [6, 8, 9, 12, 13]

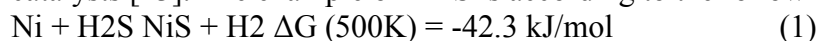
Desulphurization Technique	Working Mechanism	Advantages	Disadvantages
Caustic washing method	Using caustic solution to remove sulphides in crude oil	Simple process Low cost	Poor output quality Lower efficiency Cannot remove organic sulphides Produce too much sulphide containing wastewater
Dry gas desulphurization method	Two staged gas stripping process to remove sulphur content	Reduced corrosion in pipeline Better working condition Significantly reduce H ₂ S	Feed stock water content affects the efficiency Sulphate-reducing bacteria can convert organic sulphides into inorganic sulphides Low removal of other sulphur containing compound
Hydrodesulphurization	Catalytic desulphurization process which convert organic sulphur compound into H ₂ S and H ₂	Widely used in 1955 Efficient desulphurization	Complicated procedure High production cost High material consumption Shortened catalyst life
Biodesulphurization	Converting sulphur in oil into sulphur element by introducing C-S bond cleavage from enzyme catalyst	Non- harmful Quality of output will not be affected	Low efficiency Highly specific bacteria

Caustic washing method was the first desulfurization method and it is only mainly to remove the sulfides from the crude oil using a caustic solution. This process is very simple and it could be operated at a very low cost. But, this process could not remove many of the sulfur compounds, produces low quality crudes, has low desulfurization efficiency and produces a too much sulfide-containing wastewater [13].

Dry gas desulfurization method has advanced tremendously in after the 1990s, this process has high desulfurization efficiency with a minimum of 85% sulfur recovery and desulfurization efficiency of more than 95% [1]. In stage one, the sulfur compounds are removed from crude oil, then the sulfur compounds are removed via second stage after allowing the crude to settle and dehydrated [13]. However, some part of the process have been eliminated due to too high of investment cost [1]. But, this method has a major disadvantage which is the efficiency of the desulphurization will change with the water content of the feedstock [13, 14].

Commonly, the removal of sulfur content from oil is attained using conventional hydrodesulphurization process (HDS). HDS is a sulfur removal treatment which the sulfur components are hydrogenated into hydrogen sulfides and

hydrocarbons at high temperature and pressure with the presence of metal catalysts [6, 13]. However, this typical process requires high economic investments and operation costs [6, 8, 9, 12, 13] and HDS faces difficulties in removing stable and recalcitrant heterocyclic sulfur components such as dibenzothiophene (DBT) and its alkylated forms [8, 13]. Furthermore, the increasing ratio of heavy crude oil supply, the sulfur concentration in oil keeps increasing and this would lead to shortening the lifespan of catalysts [13]. The example of HDS is according to the following reaction:



As biodesulfurization (BDS) serves as an alternative method of desulfurization, microorganism that specialized in utilizing sulfur-containing compounds could be used to remove sulfur from fuel by breaking the carbon sulfur bond, thereby releasing sulfur in a water soluble form [4, 8, 13]. Although the capital cost and BDS is lower than HDS, this alternative has a very low conversion rate, various parameters needs to be controlled for enzyme's optimum working condition and the bacterium are highly specific [8, 13].

In 1990 when the concept of green chemistry introduced, Ionic Liquids (ILs) captured a lot of researcher's attention. ILs is a molten salts group that are generally consists of bulky an asymmetric organic cations and organic or inorganic anions [6, 15, 16]. ILs are environmentally friendly, non-volatile, easily designable, high solvating, non-flammable and have high thermal stability, and even have simple regeneration process [9]. Ionic liquids once aimed to replace the current inefficient and expensive desulphurization process and also have been considered a potential solvent to be used in extraction processes [6, 17]. Current literature hugely contrasts with the advantages if ILs. Most ILs has quite high hazardous toxicity and very poor biodegradable level [18-20]. In addition, the synthesis of ILs is a complicated, expensive and non-environmentally friendly process since it requires a large amount of salts and solvents to allow the anions to exchange completely [14, 17, 21].

To overcome the major disadvantages of ILs, a new generation of solvent, named Deep Eutectic Solvents has emerged. Deep eutectic solvents (DESSs) serve as a low cost alternative for ILs [14, 15, 17-19]. This is because DESSs has shown to have similar properties with ILs, especially the potential of the solvent to be tuned and customize according to the particular usage in chemistry [14, 17, 20]. Basically, DESSs can be obtained by simply mixing two safe components which are capable of forming a eutectic mixture through hydrogen bond interaction [15, 18]. For extraction of water, thiols and KOH, all of it are still under experimenting level. Through experiments, ILs such as 1-alkyl-3-methylimidazolium tetrafluoroborate, 1-alkyl-3-methylimidazolium hexafluorophosphate and trimethylamine hydrochloride showed high selectivity, particularly towards aromatic sulphur and nitrogen compounds [9]. Meanwhile, another research group have reported that a Lewis basic mixture of quaternary ammonium salt which glycerol was found to be successful as an extraction medium for glycerol from biodiesel based on rapeseed and soy beans and concluded the two classes of DESSs that has the most convincing potential in extraction process is ammonium salt and phosphonium salt based DESSs [14].

In this work, the aim is to synthesize DESSs with ammonium salt or phosphonium salt as a base that will be able to remove a specific type of aromatic sulphur component (thiophene) in fuel oil effectively by liquid-liquid solubility

experimental procedure under three different temperature and pressure. The solubility of thiophene in the synthesized DESs will be tested and the work also explores the behavior of DESs towards solvation of sulphur containing compound so that DESs could be used in the deep desulphurization field of liquid fuel in the future.

2. Methodology

For solubility testing, it is very important to ensure both of the solute and solvents has high purity because it may affect the measured solubility. Similarly, the samples taken from the saturated solution needs to be ensured to contain zero precipitated solute, which will overestimate the solubility values [22].

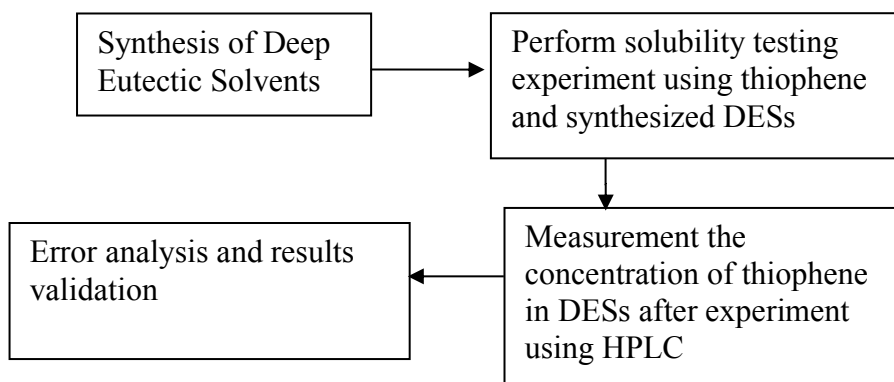


Figure 1. Overall Procedures for Research Methodology

According to Fig. 1, the overall procedure for research methodology were firstly, the DESs were synthesized according to the research work from Shahbaz et al. [23]. After the synthesizing, solubility testing experiment was carried out using thiophene as solute and DESs as solvent to measure the solubility limit of thiophene in DESs. After that, the content of thiophene in DESs was measured using HPLC and the results were analysed and validated.

When using the Karl Fisher Coulometer to determine the water content of DESs, it was impossible to avoid any air moisture to dissolve into the DESs. As DESs were immediately sealed with parafilm, it was impossible to completely remove the air moisture present inside the Schott bottles. This factor would slightly affect the accuracy of the water content measurement.

2.1 Materials

All of the materials that were used in this particular study were tabulated in Table 2.

Table 2. The list of all chemicals used

No	Chemical Name	Usage	Supplier	Purity (%)
1	Choline chloride	DES salt	Merck	>99
2	Methyl triphenyl phosphonium bromide	DES salt	Merck	>99
3	Glycerol	DES Hydrogen bond donor	Merck	>99
4	Ethylene glycol	DES Hydrogen bond donor	Merck	>99
5	Triethylene Glycol	DES Hydrogen bond donor	Merck	>99
6	Thiophene	Solubility testing	Merck	>99

2.2 Synthesis of DESs

The two different types of salts that are to be used to synthesis the DESs needed for the research are choline chloride and methyl triphenyl phosphonium bromide. As for the hydrogen bond donor (HBD), ethylene glycol, glycerol and triethylene glycol are to be used. And to increase the number of possible combinations, the DESs are prepared with different molar ratio of the salts to HBD. In Table 2, the composition and labeling of DESs that were to be synthesized are shown.

The steps of preparation of DESs used in this research work are referring to Shahbaz et al. [23]. According to the study done, different molar ratios of the salt- HBD combinations are poured controlled temperature into Schott bottles. After that, the bottles are placed on hot plate stirrer equipment with a temperature of approximately 80°C. Meanwhile, a cylindrical magnetic stirrer bar is to be inserted into the bottles and the equipment is to be functioning at approximately 800rpm agitation speed. The process of synthesizing only ends after a homogeneous transparent liquid is formed.

Table 3. The Compositions of DES to be synthesized

Salt	HBD	Molar Ratio (Salt : HBD)	Abbreviations
Choline chloride	Ethylene glycol	1:1.75	DES 1
Choline chloride	Ethylene glycol	1:2	DES 2
Choline chloride	Ethylene glycol	1:2.5	DES 3
Choline chloride	Triethylene glycol	1:3	DES 4
Choline chloride	Triethylene glycol	1:4	DES 5
Choline chloride	Triethylene glycol	1:5	DES 6
Choline chloride	Glycerol	1:1.5	DES 7
Choline chloride	Glycerol	1:2	DES 8
Choline chloride	Glycerol	1:3	DES 9
Methyl triphenyl phosphonium bromide	Ethylene glycol	1:3	DES 10
Methyl triphenyl phosphonium bromide	Ethylene glycol	1:4	DES 11
Methyl triphenyl phosphonium bromide	Ethylene glycol	1:4	DES 12
Methyl triphenyl phosphonium bromide	Triethylene glycol	1:3	DES 13
Methyl triphenyl phosphonium bromide	Triethylene glycol	1:4	DES 14
Methyl triphenyl phosphonium bromide	Triethylene glycol	1:5	DES 15
Methyl triphenyl phosphonium bromide	Glycerol	1:2	DES 16
Methyl triphenyl phosphonium bromide	Glycerol	1:3	DES 17
Methyl triphenyl phosphonium bromide	Glycerol	1:4	DES 18

According to Table 3, by changing the molar ratio and conducting the mixing at 25°C - 45°C, it could save a lot of budget during scaling up of the reaction. A lot of energy cost could be saved for mixing of DESs and fuel at room temperature. And by changing the molar ratio, different types of DESs could be synthesized and enlarged the area of testing of this work.

2.3 Solubility of Thiophene in DESs

The conventional shake flask method of determining the equilibrium solubility of any solute in solvents at any given temperature, which is the most accurate method for solubility determination, was adopted for this work. In this work, 5 mL of thiophene was added to 5mL of each DESs. The samples were then mixed at 298.15K with an orbital shaker operating at 200rpm for 1 hour. The above procedure was repeated for different temperatures (308.15 K and 318.15 K) to determine the highest value of thiophene solubility in DES. After allowing overnight settling, 100mg of

DES layer was diluted with 10mL acetonitrile which was the mobile phase for High Performance Liquid Chromatogram (HPLC). The solutions were then analysed using HPLC to determine the content of thiophene in DESs.[22].

The HPLC model, specifications and analysis conditions are as below, in Table 4.

Table 4. The HPLC specifications and analysis conditions

Item(s)	Specifications
Column oven:	CTO-10AS
Auto injector:	SIL-10 AD
System controller:	SCL-10A
Detector:	SPD-10A
Liquid chromatography:	LC-10AD
Degasser:	DGU-10AL
Solvent proportioning valve:	FCV-10AL
Column:	Eclipse plus C18 3.5 μ m 4.6 $\times$ 100mm
Mobile phase:	Acetonitrile
Flow rate:	1 mL/min
Column temperature:	298.18 K
Detector temperature:	308.15 K
Injection volume:	10 μ L

3.0 Results and Discussion

The HPLC was calibrated by injecting five different concentrations of thiophene in acetonitrile solutions, which created a calibration curve for thiophene. Each sample was analyzed three times to get the accurate results from HPLC analysis.

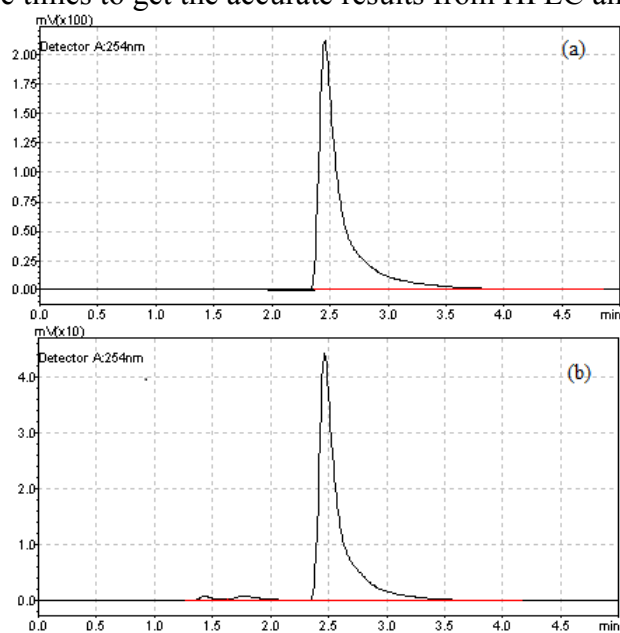


Figure 2. Standard chromatographs and chromatograms obtained from samples shows typical thiophene standard chromatographs and (b) represents the typical chromatograms obtained from samples.

In Fig. 2, the calibration of HPLC was performed before actually analyse the content of DESs. The standard chromatographs peak was noted to be tally with the typical chromatograms obtained from samples. This shows that the content measured was 99% accurate. The linear correlation coefficient (R^2) for curve was found to be 0.99 which represented excellent linearity.

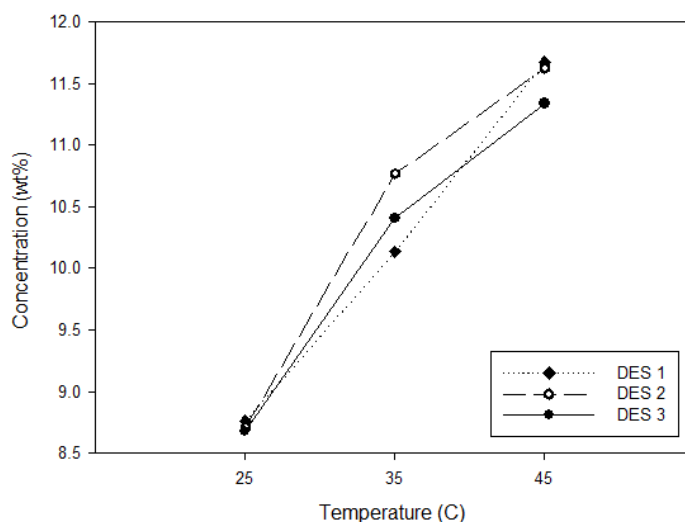


Figure 3. The graph of thiophene solubility against temperature for DES 1, 2 and 3

According to Fig. 3 above, DES 1 has the highest value of thiophene solubility (8.76%) at 25°C followed by DES 2 (8.71%) and DES 3 (8.67%). All three DESs solubility increases when temperature increases. This happens due to the increase in kinetic energy between the particles in the solution that enhances the percentage of the thiophene molecules to dissolve into the DESs particles. But at 45°C, the solubility of DES 1 had started to exceed DES 2 which was the leading solubility at 35°C and 45°C.

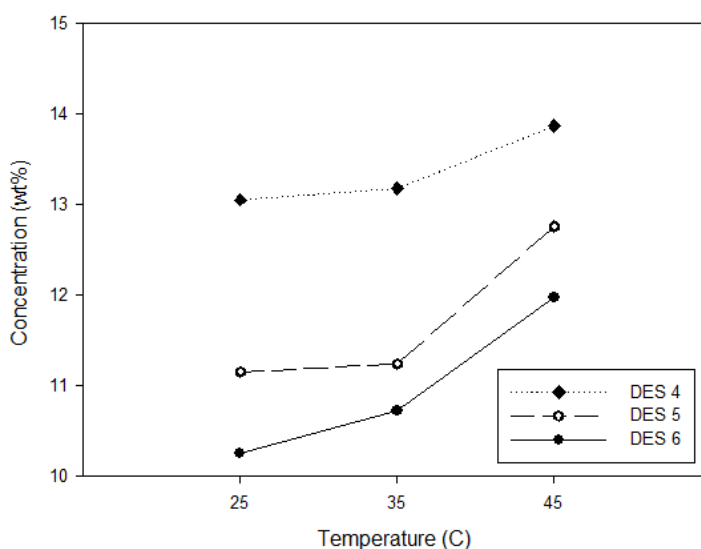


Figure 4. The graph of thiophene solubility against temperature for DES 4, 5 and 6

According to Fig. 4 above, DES 4 has the highest value of thiophene solubility (13.05%) at 25°C followed by DES 5 (11.15%) and DES 6 (10.25%). All three DESs solubility increases when temperature increases. This happens due to the increase in kinetic energy between the particles in the solution that enhances the percentage of the thiophene molecules to dissolve into the DESs particles. At 45°C, the solubility of DES 4 continued to lead after 5 and 6.

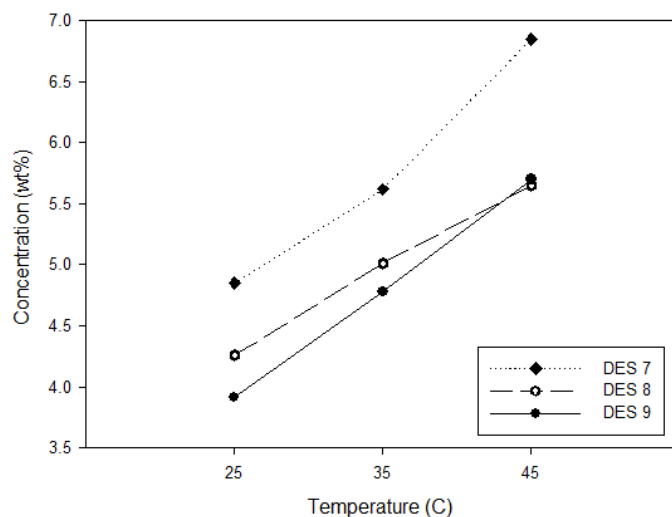


Figure 5. The graph of thiophene solubility against temperature for DES 7, 8 and 9

DES 9 had the lowest thiophene solubility among all 18 DESs under 3 different temperature. Whereas according to Fig. 5, at 25°C DES 7 has the highest value of thiophene solubility (4.85%) followed by DES 8 (4.26%) and DES 9 (3.91%). All three DESs solubility increases when temperature increases. This happens due to the increase in kinetic energy between the particles in the solution that enhances the percentage of the thiophene molecules to dissolve into the DESs particles.

Among all of the ChCl based DESs, the DES combination that was able to dissolve the highest number of thiophene was DES 4 (13.05%), ChCl – Ethylene Glycol with molar ratio 1:1.75 at 45°C. The theoretical reason behind this value was the 45°C provides the highest kinetic energy to the molecules of DESs in compared to 25°C and 35°C. The increasing movement of molecules of DES, it provides more space for solute (thiophene) to dissolve. For ChCl – glycerol combination, it provides the lowest solubility was because glycerol consists of three hydroxyl group, compared to two hydroxyl group from ethylene glycol and triethylene glycol. The increase in number of hydroxyl group increases the strength of intermolecular forces. Therefore, decreases the solubility of thiophene. This showed that DES 1 to 6 would have stronger solute – solvent attraction than DES 7, 8 and 9.

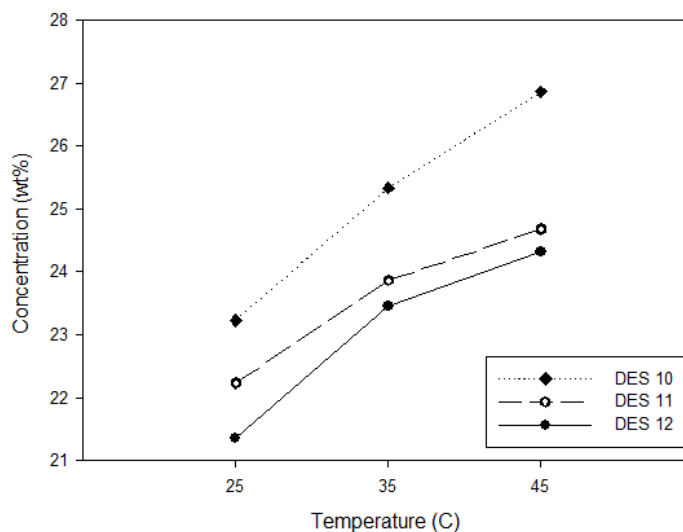


Figure 6. The graph of thiophene solubility against temperature for DES 10, 11 and 12

DES 10 had the highest thiophene solubility among all 18 DESs under 3 different temperature. Whereas according to Fig. 6, at 25°C DES 10 had the highest value of thiophene solubility (23.23%) followed by DES 11 (22.24%) and DES 12 (21.34%). All three DESs solubility increases when temperature increases. This happens due to the increase in kinetic energy between the particles in the solution that enhances the percentage of the thiophene molecules to dissolve into the DESs particles.

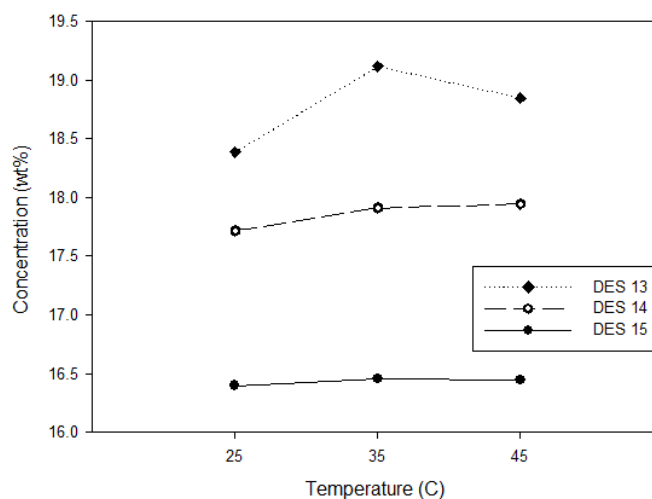


Figure 7. The graph of thiophene solubility against temperature for DES 13, 14 and 15

According to Fig. 7 above, DES 13 has the highest value of thiophene solubility (18.39%) at 25°C followed by DES 14 (17.72%) and DES 15 (16.40%). Furthermore, a possible theoretical explanation for decrease of solubility in DES 13 and 15 was the result of the dominating chemical bond between the thiophene and the hydrogen bond donor present in the DESs (triethylene glycol) over that between the sulfuric compounds and the salt (MTPB). These interactions are perceived to go in opposite directions to each other due to the presence of Br which serves as the

hydrogen bond donor in the formation of the DES. As the temperature increased, the interaction from the side of hydrogen bond donor in the DESs became weakened and overtaken by the interaction from the side of the salt, which consequently gave rise to the sudden drop in the measured solubility values [22].

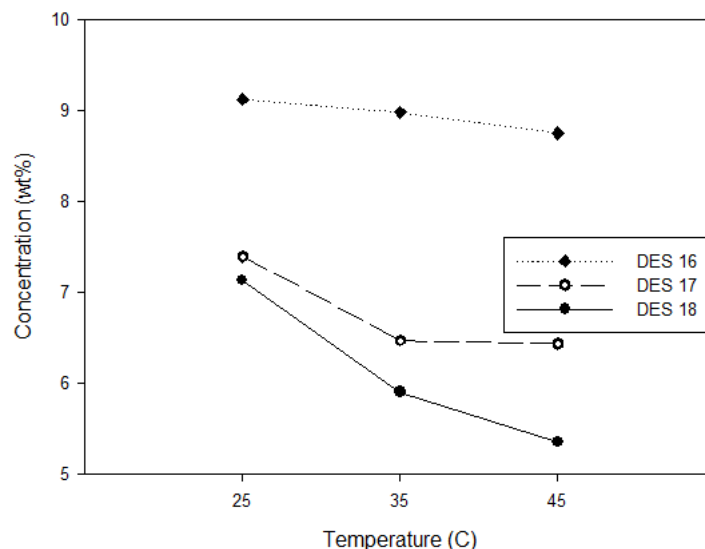


Figure 8. The graph of thiophene solubility against temperature for DES 16, 17 and 18

According to Fig. 8 above, DES 16 has the highest value of thiophene solubility (9.13%) at 25°C followed by DES 17 (7.40%) and DES 18 (7.14%). Furthermore, a possible theoretical explanation for decrease of solubility in all three of these DESs is as the same as DES 13, 14 and 15.

Among all of the MTPB based DESs, the DES with combination that was able to dissolve the highest number of thiophene was DES 10 (23.23%), MTPB – triethylene glycol with molar ratio 1:3 at 45°C. The theoretical reason behind this value was the 45°C provides the highest kinetic energy to the molecules of DESs in compared to 25°C and 35°C. The increasing movement of molecules of DES, it provides more space for solute (thiophene) to dissolve. For MTPB – glycerol combination, it provides the lowest solubility was because glycerol consists of three hydroxyl group, compared to two hydroxyl group from ethylene glycol and triethylene glycol. The increase in number of hydroxyl group increases the strength of intermolecular forces. Therefore, decreases the solubility of thiophene. This showed that DES 10 to 15 would have stronger solute – solvent attraction than DES 16, 17 and 18.

Overall, MTPB based DESs had higher solubility than ChCl based DESs. This may due to the sulphide group in thiophene having higher solute – solvent attraction force with MTPB molecule than ChCl molecules. Meanwhile, ChCl based DESs did not faced decreasing solubility with increasing temperature, only MTPB based had. This strongly proved that theoretical chemical bonding regarding presence of Br atoms as mentioned above was true.

Basically, the range of the experimental testing was small (25°C - 45°C) because this may be helpful during scaling up. In industrial refinery, operating at

atmospheric temperature is widely encouraged as this would save millions of money in industrial refinery zones.

4.0 Conclusion

The solubility of thiophene in MTPB and ChCl based DES with a combination of different salt to HBD was studied at different temperatures under atmospheric pressure. It was found that MTPB – ethylene glycol (1:3) had the highest thiophene solubility with 26.87% wt at 45°C. Whereas ChCl – glycerol (1:3) had the lowest solubility results with 3.91% wt at 25°C. The results clearly reflected the structure of DESs heavily affect the sulphuric compound dissolving rate. Actually, the usage potential of DESs in desulfurization of crude oil is still a fresh topic. The idea of manipulating the affinity properties in DESs and sulphur content in crude oil is very doable and logical as DESs has already been used in some extraction process.

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Investigation on Used Tea Leaves-Derived CO₂ Adsorbent

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Abstract

In this study, used tea leaves are used as raw material to produce activated carbon (AC). Characterization of used tea leaves-derived AC is studied as low-cost adsorbents to capture carbon dioxide (CO₂) which has been a major contributing factor in relation to global warming recently. Effects of parameters such as production method, activating chemical agent and ratio of chemical to tea leaves during chemical activation to the characterization of AC and its potential to adsorb CO₂ are investigated. The production methods selected for investigation are chemical activation and pre-treated chemical activation. Where else, for the activating chemicals, potassium hydroxide (KOH) and phosphoric acid (H₃PO₄) were chosen. The mass ratio of activating chemical to used tea leaves of 2:1 and 1:1 are studied. The characterization of the used tea leaves-derived AC was analysed by using Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric analysis (TGA) and Brunauer-Emmett-Teller (BET). In order for CO₂ adsorption, it is desired that properties such as large surface area, considerable amount of micropores and good surface reactivity are developed during AC production. From the results obtained, the specific surface area and total pore volume of the ACs produced varied from 336m²/g to 1044 m²/g and 0.17cm³/g to 0.59cm³/g respectively. The AC with the highest potential for CO₂ adsorption is the AC produced by chemical activation with H₃PO₄ at ratio of 2:1.

Keywords: Activated carbon, Used Tea Leaves, Adsorption, Carbon dioxide, Biomass.

1. Introduction

In recent decades, air pollution has become a major concern amongst the community. The increase in volume of human activities such as industrialization and urbanization has been the major contributing factor to air pollution. One of the primary air pollutants is carbon dioxide (CO₂). CO₂ is primarily produced from the combustion of fossil fuels such as coal and petroleum distillates which are widely used as a source of energy in transportation and electricity generation. In accordance to the International Agency report (2007) on world energy statistics, coal contributed at about 29 billion metric tons of CO₂ which made up to 42% of the world CO₂ emissions in 2007 alone [1]. Unfortunately, the utilization of fossil fuels in these areas is unlikely to reduce in the near future as there is no practical alternative yet. Thus, preventing CO₂ emissions from these activities is very unlikely at this stage. Therefore, there is an urgent need to capture and control the emission of CO₂.

There are many available technologies for CO₂ removal. The technology that is recently receiving much attention is adsorption due to its simple process and low cost of operations[1]. Adsorption uses adsorbents as a capturing material, and one of the most widely used adsorbent is activated carbon (AC). AC's large active surface area, favorable pore size distribution, surface chemistry and the degree of polarity makes it very suitable for many environmental applications [2-5]. Charcoal is the most suitable raw material for AC production due to its rich carbon content. Unfortunately, the source of charcoal is limited and expensive. Therefore, alternative carbonaceous sources which are sustainable, easily available and cheap are being investigated. Numerous studies have been done to investigate the potential of biomass materials as an alternative raw material for AC production and many have been proven effective. Coconut husk, palm oil materials, grass cuttings, horse manure, wood, orange peel, treated sewage, wall nut shell are a few example of effective biomass derived AC [5-9].

For this research, the potential of used tea leaves as AC on CO₂ adsorption will be investigated? Tea leaves are chosen because it is largely produced in Malaysia. Tea leaves are widely used all over the world to produce the world's second most consumed beverage, tea. The waste tea leaves are mostly discarded as waste. Only a small amount of the used tea leaves are used as fertilizers. Therefore, tea leaves produce a lot of waste. This makes tea leaves a fairly cheap and environmental friendly carbonaceous source for AC production. Studies have been done previously to investigate the potential of tea leaves as AC. E.Akar et al. (2013) investigated the potential of tea leaves as AC for removal of malachite green from aqueous solution and the results showed that the AC produced can be used as an efficient adsorbent for the removal of malachite green [3]. Besides that, A. Gundogdu et al. performed an investigation to study the physicochemical characteristics of activated carbon produce from tea industry waste. The ACs produced from this study showed good characteristic of AC [4]. Therefore, it is evident that tea leaves are good raw material for AC preparation. However, no investigation have been made on used tea leaves derived AC for CO₂ removal applications. Thus, this study will investigate the potential of used tea leaves-derived CO₂ adsorbent.

There are many parameters that influence the quality of the produced AC. The effect of preparation method, activating agent and ratio of activating agent to tea

leaves will be determine in this investigation? Two different approach of AC preparation which are chemical activation and pre-treated chemical activation are investigated. For chemical activation, tea leaves are initially impregnated in two separate activating agents which are phosphoric acid and potassium hydroxide at ratio of activating agent to tea leaves of 1:1 and 2:1 (g/g) [2]. On the other hand, for pre-treated chemical activation, the raw tea leaves are firstly carbonized prior to impregnation with phosphoric acid and potassium hydroxide at the same ratio of 1:1 and 2:1 (g/g) [10,11].

The two main objectives to be achieved from this investigation is to produce an effective AC derived from used tea leaves to capture carbon dioxide and to study the effect of activation method, impregnation chemical and its ratio on CO₂ adsorption based on the characterization of the produced used tea leaves-derived AC.

2. Research Methodology

The purpose of this research is to produce AC that is capable of adsorbing carbon dioxide (CO₂) from used tea leaves. This investigation involves two major sections which are AC preparation and AC characterization. While conducting this investigation, parameters that will impact the performance of the AC such preparation methods, type of impregnation chemicals and ratio of impregnation chemical to tea leaves will be studied. The steps to be taken for this investigation are represented in the flow chart shown in Fig 1.

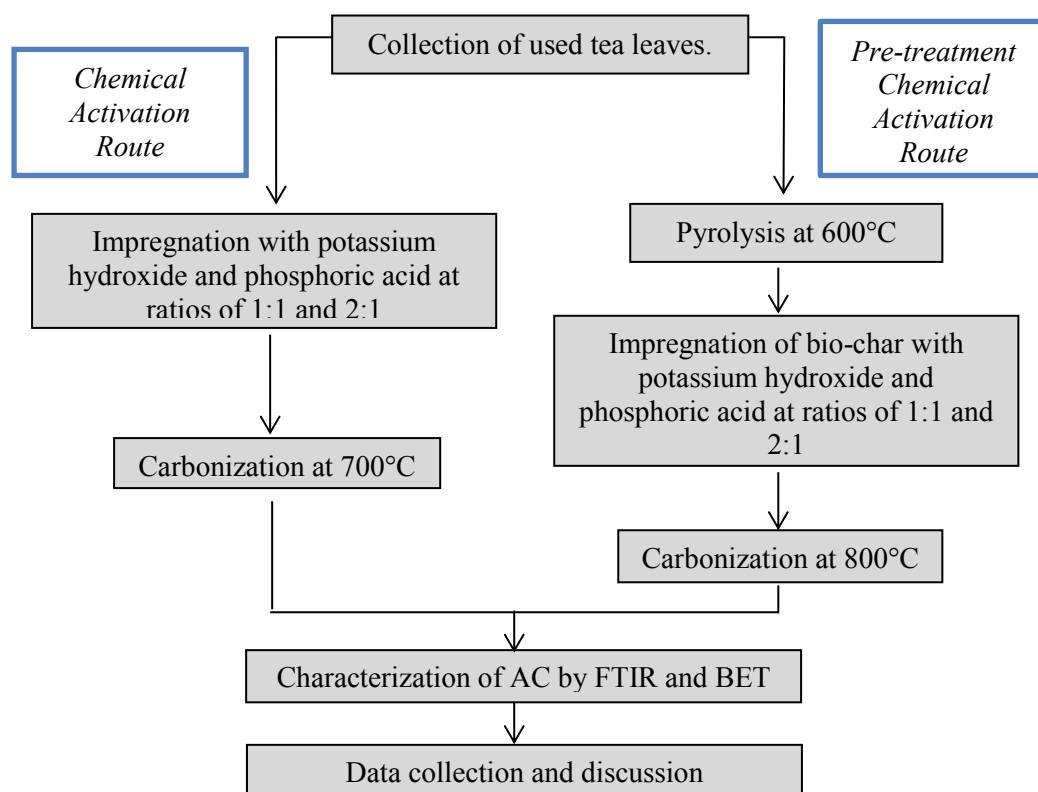


Figure 1. Methodology flow chart

2.1 Materials

Used tea leaves are collected from Selvi's Corner Curry House situated in Bandar Puteri, Selangor, Malaysia. Potassium hydroxide and phosphoric acid are purchased from Sigma-Aldrich that has purity greater than 85% and assay of 85% respectively.

2.2 Collection and storage of used tea leaves.

The leaves are collected batch by batch for an interval of 2-3 days to ensure that fungus or any microorganism do not grow on the tea leaves while it is being stored for collection. The tea leaves are first subjected to series of washing with distilled water to remove impurities such as milk and sugar that may be present in it. The washed tea leaves are then pre-dried under the sun for about 4-5 hours. The process is followed by placing the pre-dried tea leaves into an oven at 110°C for about 15 hours to ensure the tea leaves are completely dry. Finally, the tea leaves are filled in a sealable container and stored in a dry cool place.

2.3 Preparation of AC

Two different methods of AC production will be studied: chemical activation and pre-treated chemical activation. For chemical activation, the dried tea leaves are first impregnated in 20%wt phosphoric acid with impregnation chemical to tea leaves ratios of 1:1 and 2:1 (g/g). The tea leaves are allowed to stand for 24 hours at room temperature. After that, the mixture is filtered and the impregnated product is dried for about 15 hours in an oven at 110°C. The product is then carbonized at temperature of 700°C for 2 hours in a furnace. After being cooled down to room temperature, the product is neutralized with an alkaline solution until neutral pH of 7 is achieved. Finally, the product is washed with distilled water to remove any impurities. The same steps are repeated by replacing phosphoric acid with 50%wt potassium hydroxide as the impregnation chemical.

For pre-treated chemical activation, the dried tea leaves are first pyrolysed (carbonized) in a furnace under nitrogen gas flow. The furnace is run at a rate of 10°C/min to the optimal temperature of 600°C. The carbonized substance is then impregnated with 20wt% phosphoric acid with activating agent to tea leaves ratios of 1:1 and 2:1(g/g). The mixture is allowed to stand for 24 hours at room temperature. After 24 hours, the excess solution is removed by filter and the impregnated tea leaves are dried at 110°C for about 15 hours in an oven. The obtained sample is then heated at 800°C for 2 hours in a furnace. After being cooled down to room temperature, the product is neutralized by an alkaline solution until pH value of 7 is obtained. Finally, the product is washed with distilled water and dried at 110°C in an oven for about 15 hours. The same steps are repeated by using 50%wt potassium hydroxide as the impregnation chemical. Acid solution will be used as a neutralizing chemical.

2.4 Characterization of samples

2.4.1 Proximate analysis

TGA analyzer is used to perform proximate analysis to obtain information on moisture, ash, fixed carbon and volatile matter content in used tea leaves.

To run TGA, firstly, 0.1g of tea leaves sample is heated to 110°C under nitrogen gas for 20 minutes to eliminate the moisture content in the sample. Then the temperature is increased to 950°C and held for 30 minutes under nitrogen flow to remove volatile matters from the sample. After 30 minutes of heating at 950°C, the nitrogen gas supply is cut off and switched to air for 20 minutes to allow combustion of carbon to take place, leaving only ash behind. The heating is done at a rate of 10°C/min.

2.4.2 Ultimate analysis

Elemental analyzer (Euro EA3000 series) is used to perform ultimate analysis in which carbon, hydrogen, nitrogen and sulfur contents of used tea leaves and pre-treated used tea leaves can be determined.

Firstly, 0.5 g of sample is combusted in sample of tin and vanadium pentoxide catalyst, purified by a reactor packed with electrolytic copper and copper oxide. Gasses such as N₂, CO₂, H₂O and SO₂ enter the chromatographic column for separation to take place. Eluted gasses are sent to the thermal conductivity (TCD) where electrical signals processes by the Eager 300 sotfware provide values of nitrogen, carbon, hydrogen and sulfur content in percentage that is in the sample.

2.4.3 Fourier Transform Infrared Spectroscopy (FTIR) analysis

Fourier Transform Infrared Spectrometer is used to perform FTIR. FTIR is analysis provides information about functional groups and covalent bonds present in the sample.

To prepare the sample for FTIR analysis, a small amount of sample and KBr powder are first added into a mortar at ratio of 1:99 respectively. The mixture is grinded until homogeneous with a pestel. After that, die is assembled with lower die, polished face up. A small amount of the mixture is inserted into the cylinder bore (just enough to cover the surface) and even out with a plunger. Then the second die is gently inserted, polished face down into the bore, followed by the plunger. The assembled die with the plunger is then placed into the hydraulic press. The knob of the hydraulic press is tighten to ensure that the cylinder bore is held in place firmly. Force is increased to roughly 10 tons under vacuum by pulling the hydraulic pump handle downwards. The die is left under pressure for 20 seconds. After 20 seconds, the vacuum is released and die is removed from the press. Dies are dismantled and formed pellet disk is placed onto disk holder. Finally, the disk holder is mounted in the spectrometer for analysis.

2.4.4 Brunauer-Emmett-Teller (BET) analysis

Brunauer-Emmett-Teller (BET) analyzer is used to perform this analysis. BET is run to determine the surface characteristic of the samples such as total surface area and pore size.

To carry out BET analysis, 0.5 grams of sample is first degassed at 90°C for 60 minutes followed by 300°C for the subsequent 480 minutes. N₂ are used as adsorption gas and the adsorption is studied at 0°C under circulating water bath.

3. Results and Discussion

3.1 Proximate and Ultimate analysis

The results from the proximate and ultimate analysis show that used tea leaves have good potential for AC production. High percentage of carbon content which is necessary to produce good quality AC is available in used tea leaves. Besides that, the volatile matter in used tea leaves which helps the pore structure formation is relatively high. Moisture content made up a small percentage of the used tea leaves which is desired for AC production because the moisture present may combine with char carbon during pyrolysis to produce gaseous by-products which may result in low yield of porous carbon [12]. Overall, used tea leaves showed good properties of precursor to be used for AC production.

Table 1. Proximate analysis of used tea leaves and pre-treated used tea leaves.

No	Sample	Moisture [%]	Volatile Matter [%]	Fixed Carbon [%]	Ash [%]
1	Used tea leaves	7	70	22	1
2	Pre-treated used tea leaves	6	17	67	10

Table 2. Ultimate analysis of used tea leaves and pre-treated used tea leaves.

No	Sample	N[%]	C[%]	H[%]	S[%]
1	Used tea leaves	3.83	46.4	6.809	1.019
2	Pre-treated use tea leaves	4.07	71.91	2.415	2.303

3.2 BET analysis

In Table 3, it is shown that CAP2 developed the largest surface area at 1044m²/g and PCAP1 developed the lowest total surface area with only 336m²/g. Besides that, Table 3 also shows that all H₃PO₄ activated AC samples prepared in this experiment are microporous because more than 70% of the total pore volume of these samples was contributed by micropore volume. The only sample with low percentage of micropore volume is CAK1 which is the only KOH activated sample.

Table 3. Textural parameters of the prepared activated carbon.

No	Sample	Method	Activating Agent	Impregnation ratio	BET surface area (m ² /g)	Micropore Surface area (m ² /g)	Total pore Volume (cm ³ /g)	Micropore Volume (cm ³ /g)
1	CAP2	Chemical Activation	H ₃ PO ₄	2:1	1044	930	0.59	0.451
2	CAK1	Chemical Activation	KOH	1:1	478	357	0.412	0.17
3	CAP1	Chemical Activation	H ₃ PO ₄	1:1	761	713	0.377	0.27
4	PCAP1	Pre-treated Chemical Activation	H ₃ PO ₄	1:1	336	312	0.166	0.13

3.3 Effect of Parameters

The type of preparation method, activating agent and impregnation ratio seems to have a significant effect on the properties of the used tea leaves-derived AC as can be seen in Table 3. The AC produced by chemical activation with H₃PO₄ at ratio of 1:1 (CAP1) had larger BET surface area, micropore surface area, total volume and micropore volume compared to the chemical activation with KOH at ratio of 1:1 sample (CAK1). This suggests that H₃PO₄ is more suitable to be used as an activating agent to prepare used tea leaves-derived AC compared to KOH. For preparation method, chemical activation method produced used tea leaves-derived AC with significantly higher quality compared to pre-treated chemical activation method. This can be noticed when properties of CAP1 is compared with PCAP1. CAP1 which is prepared by chemical activation was able to developed 760m²/g of surface area while PCAP1 which was prepared by pre-treated chemical activation only developed 336m²/g of surface area. This can be justified by to loss of most volatile matter during pre-treatment process at 600°C. As stated in literature, raw material with high volatile matter is desired for AC production because volatile matter plays an important role in the formation of pores in AC [12]. The pre-treatment process has eliminated most of the volatile matter from used tea leaves (decreased from 70%-17%) that has affected the pore formation for pre-treated method. Lastly, the effect of impregnation ratio of the activating agent to used tea leaves can be studied by comparison of CAP2 and CAP1. CAP2 which was prepared by H₃PO₄ at ratio 2:1 produced larger surface area compared to CAP1 which was prepared by H₃PO₄ at ratio 1:1. This is due to the fact that activating agent reduces the formation of tars and any other liquids that may cause blocking of the pores and restrict the formation of porous structure in the AC [6]. Thus, larger ratio of activating agent produces AC with better adsorption properties.

3.4 CO₂ adsorption

The CO₂ adsorption potential of the used tea leaves-derived AC is determined based on the characterization of the ACs produced. The main properties that is required for effective adsorption of CO₂ are high total surface area, high micropore surface area and high pore volume[4]. All the used tea leaves-derived AC produced in this study

developed high percentage of micropore surface area which made up more than 70% of the total surface area for each samples. The micropore volumes for almost all the ACs produced (except CAK1) are relatively high as well, comprising more than 70% of the total volume. However, not all AC produced exhibit large total surface area. CAK1 and PCAP1 developed total surface area that is too low to be used for CO₂ adsorption as it will not be efficient. Nevertheless, CAP2 and CAP1 samples developed considerable amount of total surface area to be used in CO₂ adsorption application. A study done by W.Hao et al (2013) showed that AC produced by horse manure with total surface area of 841m²/g of which 742m²/g is made up of micropore surface area and has a micropore volume of 0.379cm³/g, had a CO₂ adsorption capacity of 1.45mmol/g [2]. This horse manure-derived AC had the highest CO₂ capacity compared to the other AC produced in this same study. Besides that, A.S Ello et al. produced AC with total surface area of 1130m²/g and micropore volume of 0.48cm³/g [13]. This particular AC had a CO₂ adsorption capacity of 3.9mmol/g [13]. Therefore, by comparing the results from these two studies with the results from this experiment, it is safe to state that used tea leaves do have potential to produce effective AC to be used in CO₂ adsorption and the best combination of parameters for AC preparation with used tea leaves are chemical activation with H₃PO₄ at ratio of 2:1.

4. Conclusion

Used tea leaves-derived activated carbons (ACs) were prepared by chemical activation and pre-treated chemical activation with H₃PO₄ and KOH as activating agent at ratio of activating agent to used tea leaves of 1:1 and 2:1. From the results obtained and comparison with other studies, used tea leaves AC displayed desirable properties to be used as adsorbent in CO₂ removal applications. For parameters investigated in this experiment, it was found that the preparation method, activating agent and ratio of activating agent did influence the characteristic/properties of the used tea leaves prepared AC. Chemical activation method produced AC with better properties compared to pre-treated activation method. H₃PO₄ is a better activating agent compared to KOH for used tea leaves prepared AC. Lastly, larger ratio of activating agent to used tea leaves produced AC with larger surface area and better micropore distribution. The best combination of parameters investigated in this study for used tea leaves-derived AC are chemical activation with H₃PO₄ at ratio of 2:1. These combination of parameter produced AC with the highest total surface area of 1044m²/g in which 930m²/g is made up of micropore surface area.

5. Reference

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Optimising Yield and Production Cost of Bioactive Compounds using Process Synthesis and Design Approach

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Abstract

Herbs are well known for medicinal purposes throughout human history. The benefits of herbs are wide which include healing of different diseases, maintaining and restoring body balances. Bioactive compounds of herbs are found in herbs which recognize as the compounds that help in defending human body by deterring formation of free radical chain reaction to attack human body's cells. However, postharvest processing of herbs using drying and extraction methods influenced the quality and quantity of the bioactive compounds. This paper presents a systematic conceptual synthesis and design approach for optimization of bioactive compounds extraction from herbs. In this work, Pro II 9.1 is used for process simulation and analysis on the bioactive compound production. To demonstrate the proposed approach of process optimization, a case study on *Strobilanthes Crispus* production is presented. Selection of technologies and parameters in design processes can optimise the productivity and minimize the operation cost for bioactive compounds production. The optimized process configurations found in this study is Convective air drying- supercritical fluid extraction and ultrafiltration. It is able to retain most of the phenolic acids without overshooting the operating cost. The operating cost of this process is \$US29304.94 kg/annual which is 1.26 times lower than combined microwave vacuum drying- supercritical fluid extraction- ultrafiltration and product yield of 56494.06 kg/annual which is 5.23 times higher than Convective air drying- conventional solvent extraction - ultrafiltration .

Keywords: Bioactive compounds, Process synthesis, *Strobilanthes Crispus*, Extraction, Drying

1. Introduction

For centuries, natural herbs are being studied for their medicinal purposes throughout human history. Natural antioxidants are considered more favourable compared to synthetic drugs which contain possibility of side effect when consumed long term. Moreover, modern medicines are more expensive compared to herbal medicine that can be grown and gathered easily with little or no cost (Conde *et al.*, 2010). Therefore, in recent years, there is an increase of extracting the bioactive compounds of herbs to produce medicine. World Health Organization (WHO) estimated that 80% of the world populations are depended on herbal medicine for their primary health care (Ranilla *et al.*, 2010). Malaysia's herbs have the potential to produce medicine which possess high antioxidant activity, anti-AIDS, and anticancer properties (Liza *et al.*, 2010).

Bioactive compounds are generally produced as secondary metabolites in plants other than the primary biosynthetic compounds such as amino acids, proteins, carbohydrates and lipids (Azmir *et al.*, 2013). Various types of bioactive components can be found in herbs, for example, glycosides (saponins and anthraquinone glycosides), resins and antioxidant compounds (flavonoids, phenolic acids and quinones). The natural components that are of interest is the antioxidants specifically phenolic compounds. Natural antioxidant compounds are much effective than the synthetic compounds which contain toxicity and carcinogenicity (Ernst 1998). These compounds help to defend human bodies by deterring formation of free radicals chain reaction. Hence, formation of hydroperoxides and attacks of free radicals to human body's cells are prevented (Karakaya and Kavas, 1999). Moreover, they are responsible for preventing degenerative diseases such as aging, cancer, cardiovascular disease, Alzheimer's disease and muscular degeneration (Wootton-Beard and Ryan 2011).

The family species of *Strobilanthes crispus* is *Acanthaceae* which its common name is 'pecah kaca' in Malaysia and 'daun picah beling' in Jakarta. It is used widely for traditional medicine of antidiabetic, antilytic, diuretic and laxative. It is also proved scientifically to have antioxidant effects antihyperglycemic, and hypolipidemic effects (Ismail *et al.*, 2000), anti-AIDS, anticancer activity (Liza *et al.*, 2010) and exhibit antioxidant activity (Afrizal, 2008). Therefore, *Strobilanthes Crispus* is chosen for analysis in this work. The objective of this work is to maximize the production yield and reducing production cost via different technologies and process configurations.

The post-harvesting process of medicinal herbs is crucial in the industry as it affects the quantity and quality of the bioactive components production (Khorshidi *et al.*, 2009). According to the previous works, the processes that are commonly used to produce bioactive compound such as antioxidant are drying, extraction and concentration (Ceron *et al.*, 2014). Note that in order to optimize the bioactive compound production, systematic process synthesis and design is needed. In this work, a systematic approach for synthesizing and optimizing the processes in pharmaceutical industry is presented.

This work is in line with process intensification (PI) as presented in Ponce-Ortega *et al.*, (Ponce-Ortega *et al.*, 2012). PI is defined as an approach to develop novel methods in comparing the traditional processes to improve the existing processes

which leads to a substantial production. Some strategies to achieve PI are reducing equipment size, minimizing waste generation, energy consumption, increasing production efficiency, etc. (Lutze *et al.*, 2011). In this work, a systematic approach is presented for production of bioactive compounds. A case study on extraction of bioactive compound from *Strobilanthes Crispus* is presented. Following the proposed approach, reviewing and selection of technologies and process configurations based on techno-economic criteria is first performed. Next, the selected technologies and process is analyzed by process synthesis and simulation. In this work, PRO II 9.1 (Invensys Software, USA) is used as the simulator to analyze the process performance and interactions of processes and to adapt a fuzzy optimization to identify the synthesized process configurations where operating cost is minimized and product yield is maximized.

2. Production of Bioactive Compounds in Pharmaceutical Industry

2.1. Pretreatment Technologies

Drying is the process of reducing water content by means of heat and mass transfer which helps to preserve the product from decomposition of microbial growth, reduce weight for transportation and save storage space (Karimi *et al.*, 2012). The application of drying for pre-treatment of extraction is reported to give a better productivity of antioxidant reported by Ceron *et al.*, 2014 (Ceron *et al.*, 2014). In the study, drying process is important as the tissue of raw materials will be more brittle which allows a rapid cell wall breakdown for grinding and homogenization steps in extraction process. With proper pretreatment process, more bioactive components are released into the solvents and minimized enzymatic degradation and loss of antioxidants compounds.

As most of the bioactive compounds are not stable at high temperature and long drying time, freeze drying (FD) which operate at low temperature and pressure can be used. However, FD is a time-consuming process and high operation cost as it consume high amount of energy. On the other hand, air drying (AD) has the lowest operating cost, but it is unable to preserve much bioactive compounds during the pretreatment process. Due to the limitations of the conventional drying processes, advanced technologies such as ultrasonic, microwave, heat pump, vacuum and hybrid system have also been developed (Chong *et al.*, 2014).

Microwave assisted drying technologies has been reported to have shorter drying time compare to convective hot air drying. The application of combined vacuum microwave drying (C/MVD) reduces the drying time as there is rapid removal of internal moisture due to large vapour pressure difference between the outer and inner of the targeted substances (Chong *et al.*, 2014). The molecules with permanent dipolar moment rotate rapidly in the change of electric field that give rise to friction force and collision of free ions due to the electric field will generate heat. As water molecules are polar component, it is suitable to use microwave energy for dehydration process. Compare to the conventional hot air drying it is an improvement of drying technology. This is because hot air drying has lower drying rate that takes longer time. The product surface has to be dried first and subsequently mass transfer occurs from inner of the substance being dried to external surface. However, the dried outer layer is a poor conductor of heat throughout the drying process. Whereas microwave drying can penetrate the dry outer layer and heat the substances throughout all high moisture area.

C/MVD is a technology that combines microwave heating with vacuum drying. This hybrid system is able to dry thermo sensitive products as the vacuum conditions lower the liquid vapor and is performed in the absence of oxygen. C/MVD also promotes efficient water which reduces structural changes by preventing shrinkage and induces porous tissues (Schulze *et al.*, 2014).

2.2.Extraction Technologies

The extraction process of bioactive components is intricate due to delicate properties of low boiling point of the components that easily disintegrate when expose to high temperature. Studies have been conducted throughout the year to preserve and ways to glean high amount of bioactive constituents from herbs. There are two types of extraction processes are being applied in industry, which are solvent extraction and supercritical fluid extraction (SFE). It is noted that extraction of bioactive compound from medicinal herbs is mainly SFE for higher yield. The common used fluid is carbon dioxide (CO₂). Supercritical CO₂ has high diffusivity than other fluids which enhance mass transfer for higher extraction rate (Chen *et al.*, 2011). The significant disadvantage of SFE is high capital and operation cost. Therefore, process optimization is a critical step to improve the process performance. Studies show that the addition of solvent to SFE process is economically viable. This is because bioactive compounds such as flavonoids and tannins are polar compound. Hence, co-solvent (ethanol) is added to increase the polarity of CO₂ which eventually increase the extraction yield. Liza *et al.* investigated on the extraction performance of flavonoid bioactive compounds from *Strobilanthes Crispus* with the use of supercritical CO₂ and ethanol mixture (Liza *et al.*, 2010). The solvation power of supercritical fluid can be manipulated by changing pressure and temperature to achieve high selectivity. According to Liza *et al.*, the pressure of SFE is an important factor that affects the yield of bioactive compound followed by extraction time and temperature.

On the other hand, solvent extraction is a traditional and state of the art method in obtaining bioactive compound from herbs. It deals with transporting solute (bioactive compounds) from one phase (raw materials) into another one (solvent) until it reaches the final equilibrium distribution. A recent discovery is natural product components such as sugars, organic acids, amino acid, choline or urea are excellent solvent in extraction of bioactive compounds which is known as natural deep eutectic solvents (NaDES). Yuntao Dai (2014) investigated NaDES as a new extraction solvent for phenolic metabolites form *Carthamus tinctorius* (Dai *et al.*, 2013). Based on the result, the characteristic of this solvent is beneficial for extraction compared to deep eutectic solvent (DES) and ionic liquid (IL) as it have adjustable viscosity, more sustainable and exist as liquid state even below 0°C. However, this solvent inherits high viscosity properties which will hinder the extraction efficiency. Few methods were suggested to increase the yield by mixing water with NaDES, increase the operating temperature or increase the transport rate by mechanical agitation. The report stated that the yield of phenolic compounds by using NaDES as solvent is up to 14% higher than water and ethanol. Therefore, NaDES is chosen to be used in the extraction method as solvent in this case study rather than the conventional ethanol solvent.

3. Proposed Systematic Approach

By reviewing all the available technologies in the literature, two most reliable and efficient processes were selected for further analysis. Fig. 1 shows the processing steps of production of bioactive compound from herbs. As shown, different processing pathways compiled and showed in a superstructure. Note that the processing steps are divided into three stages which are pretreatment, extraction and concentration. In the first stage, the potential technologies, which taken into consideration, are convective air drying (CAD) and combined vacuum microwave drying (C/MVD) system. After the pretreatment process, the bioactive compound is expected to be extracted via conventional extraction (CE) by using novel solvent NaDES (sucrose-choline chloride) or supercritical fluid. Once the compounds are extracted, concentration process is needed to increase the value of the products. The final stage is concentration by vacuum distillation (VD) or ultrafiltration (UF)

Once the process configuration is fixed, the process can be further analyzed via process simulation to estimate the performance and interactions of the system. In addition, the operatin cost can also be estimated. Note that this proposed systematic approach able to assist design engineers and decision makers to compare and design various process alternatives to reach the same objective. For the conventional extraction, the concentration is done by back extraction (BE) which will be classified as VD.

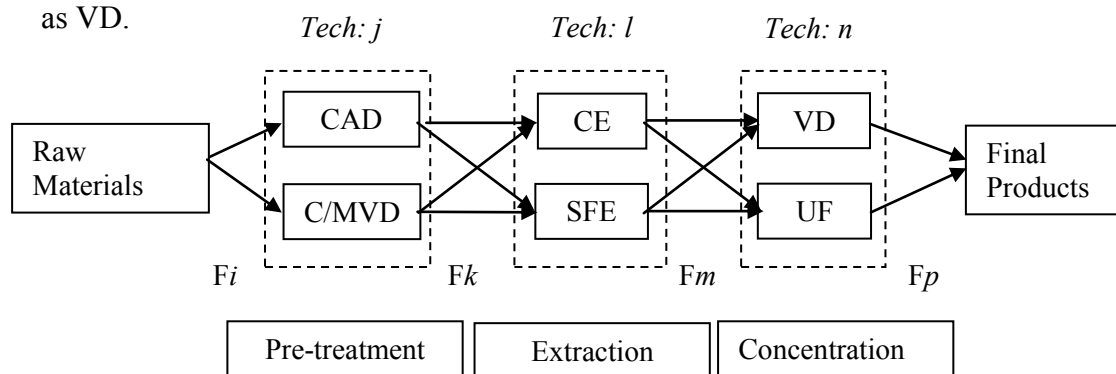


Figure. 1. Superstructure for process synthesis design

4. Case Study

To demonstrate the proposed approach, a case study on production of pheolic compound from *Strobilanthes Crispus* herb is solved. In this case study, it is expected to design a process with capacity of 1000 kg/hr of *Strobilanthes Crispus* herb and working hours of 8330 per year. The operating conditions for each technology are shown in Table 1. These data was reviewed and acquired from secondary source from journals that have investigated comprehensively the optimum conditions of each technology. To analyze the process performance, production of bioactive compound was simulated via PRO II 9.1 (Invensys Software, USA). The detail simulation procedure is discussed in the following section.

Table 1: Operating conditions for each technology

Technologies	Parameter	Value	Ref.
PRETREATMENT:			
• Combined	Pressure, kPa	4-6	(Wojdyło <i>et al.</i> , 2009)
microwave vacuum drying	Microwave power, W	480	
• Convective air drying	Air Velocity, m/s	0.8	(Jałoszyński <i>et al.</i> , 2008)
	Temperature, °C	50	
EXTRACTION:	Ethanol Concentration, %	60	
• Supercritical Fluid extraction	Temperature, °C	45	(Lenucci <i>et al.</i> , 2010)
• Conventional Solvent Extraction	Pressure, MPa	30	
	NaDES Concentration, %	75	(Dai <i>et al.</i> , 2013)
	Temperature	40	
CONCENTRATION:			
• Ultrafiltration	Transmembrane pressure, kPa	240	(Vladisavljević <i>et al.</i> , 2003)
Membrane	Temperature, °C	25	
• Vacuum Distillation	Temperature, °C	45	(Cerón <i>et al.</i> , 2014)

First of all, the input components and desired products need to be defined in the simulation for conventional and non-conventional components. The input stream of the solid feedstock is only taken into account of main components of the herbs such as lignin, cellulose, sugars (glucose), protein (lysine) and the biological molecules are caffeic acid, ferulic acid, gentisic acid, vanillic acid, syringic acid, p-coumaric acid and p-hydroxy acid which are found in the tropical herb (Afrizal 2008). Next, the suitable physicochemical properties for calculations in the simulation are selected. In this work, NRTL is used to model the thermodynamic properties because NRTL can use to model phase behavior of vapour-liquid extraction and liquid-liquid extraction. While Peng-Robinson is applied for the supercritical fluid extraction for calculation of the solubility of CO₂ (Kondo *et al.*, 2002). Next, the unit operations are chosen and connected with operating condition set accordingly in the simulation environment. The outputs of the simulator including mass and energy balance can be obtained for further evaluation of the feasibility of the process.

Fuzzy optimization is used to balance out techno-economic analysis (e.g. production yield and economic). The results from previous process flow designs are not easily satisfied as the two objectives contrast with each other whereby high efficiency of equipment will increase the operating cost. Hence, optimisation comes in place to find a balance between these parameters. In the optimisation model, the λ represented the multiple objective functions. The range of λ is between 1 and 0. Hence, λ will be near to 1 when final product flow rate, F_p comes close to the upper limit and OC reaches the lower limit. On the other hand, the operating cost (OC) which is the constraint has the inverse response compare to F_p which is the goal of the study. Therefore, upper and lower limit has to be predetermined to reach a satisfaction degree for the fuzzy goals to be maximized (Cerón *et al.*, 2014; Ng *et al.*, 2012; Sánchez and Cardona 2012). The fuzzy optimisation equations are as follow:

$$\frac{oc^U - oc}{oc^U - oc^L} \geq \lambda \quad (1)$$

$$\frac{F_p - F_p^L}{F_p^U - F_p^L} \geq \lambda, (0 \leq \lambda \leq 1) \quad (2)$$

Where OCU and OCL are the upper and lower limit of operating cost (OC), F_p^U and F_p^L is the upper and lower limit of each process flow rate respectively. λ is the interdependence variable. This generic model is able to be applied into different case studies (Tay (Tay *et al.*, 2011) *et al.*, 2011). For this study, the optimization models are used to maximize product flow rate, F_p and minimize operating cost, OC. Mixed linear integer programming (MILP) is applied for this optimization problem. The model is solved by using LINGO version 15.0.

$$F_j \leq I_j F_i^{max}; \sum_{j=1}^z I_j = 1 \quad (3)$$

$$F_l \leq I_l F_k^{max}; \sum_{l=1}^z I_l = 1 \quad (4)$$

$$F_m \leq I_n F_m^{max}; \sum_{n=1}^z I_n = 1 \quad (5)$$

Where I_j , I_l and I_n is the binary integer which represent the presence (=1) or absence (=0) of the technology $j/l/n$. The maximum number of technology will be restricted by this eq. 14-16. The maximum flow rate of F_i^{max} is depended on the raw material input while F_k^{max} and F_m^{max} is depended on the type of technology chosen and yield.

5. Results and Discussion

Table 2 shows the result of final product flow rates generated by process simulator SCISIM Pro/II v.9.1. Phenolic compounds are able to be obtained from all process configurations. The solvent is also recovered and recycled back to the extraction column and so it shows low trace of ethanol or SUCH in the final product. For example, CAD-SFE-UF contained 15.71 wt% of ethanol which is 13.4 kg/hr and the input flow rate is 160 kg/hr. 12 times of the solvent is recycles back to minimize the cost for raw material. For CAD-CSE-BE, only 2.05 wt% of SUCH in the final product. Besides that, the product flow rate are differ for SFE and CSE. This can be explained as the back extraction after CE will have input of sodium hydroxide solution that increase the total amount of product flow rate. Sodium hydroxide is partially retained in the product but it will not cause harm as the concentration is low. The input concentration of NaOH is 0.02 M.

Table 3 clearly presents the percentage yield and operating cost for each process configurations. The descending order of %yield of total phenolic acid from the *Strobilanthes Crispus* is C/MVD SFE UF, CAD SFE UF, C/MVD SFE VD, CAD SFE VD, C/MVD CE VD and the least is CAD CE VD. The yield from C/MVD SFE UF is the highest which is 10.28% and 10.23% different from C/MVD CSE BE and CAD CSE BE configurations respectively. When comparing the pretreatment technologies, C/MVD will have higher yield than CAD. This may due to the oxidation of phenolic acid whereby air is introduced in the drying process (Ceron Salazar 2013). CAD is less effective in retaining the phenolic acid because the drying rate is slower than C/MVD which in turn needed long drying time. The exposure to the high heat environment will contribute to the degradation of the compounds. Microwave drying is effective in removing water which has polar attributes. Water molecules rotates when microwave is introduced that increase the kinetic energy for internal heating (Chong *et al.*, 2014). Therefore, the result clearly depicts that C/MVD is effective in removing water and preserving the oxygen and heat sensitive phenolic compounds.

Table 2 : Mass flow rate of product breakdown in each process configuration

	Solvent SFE	Solvent CE	Product (kg/hr)					
			CAD-SFE-UF	C/MVD -SFE-UF	CAD-SFE-VD	C/MVD-SFE-VD	CAD-CSE-BE	C/MVD-CSE-BE
Mass Flow Rate (kg/hr)	160	100	85.3	98.78	85	200	845.4	835.26
Mass Fraction, %								
Ethanol	0.95		15.7101	15.8877	42.1314	49.9969		
CO ₂			31.0592	31.6656		15.8938		
Water	0.5	0.25	0.4606	0.5282	0.5794	0.6066	52.7921	53.1864
Lysine			38.4717	38.4659	40.6418	21.7244	20.1147	20.3029
Caffeic Acid			1.0800	0.9346	1.0854	0.4631		
Ferulic Acid			2.3599	2.0420	2.3712	1.0114		
Gentisic Acid			1.4716	1.2797	1.4828	0.6380	0.0006	0.0006
Vanillic Acid			1.5001	1.3301	1.5235	0.6760	0.0310	0.0320
Syringic Acid			1.8425	1.6022	1.8560	0.7983	0.0001	0.0002
P-coumaric Acid			1.6627	1.4832	1.6929	0.7585	0.0968	0.0995
P-hydroxy Acid			1.1905	1.1311	1.2381	0.6115	0.5319	0.5386
SUCH		0.75					2.0493	2.0749
NAOH							3.2292	3.2684
Cellulose							0.0000	0.0000

Table 3 :Yield and operating cost of each process configuration

Configurations	Yield, %	OC, \$US/hr	OC, \$US/yr
CAD SFE VD	23.58	4.436	36953.35
C/MVD SFE VD	23.92	4.444	37017.18
CAD SFE UF	23.89	4.368	36383.24
C/MVD SFE UF	24.41	4.375	36447.07
CAD CSE BE	14.08	1.296	10795.69
C/MVD CSE BE	14.13	1.304	10859.53

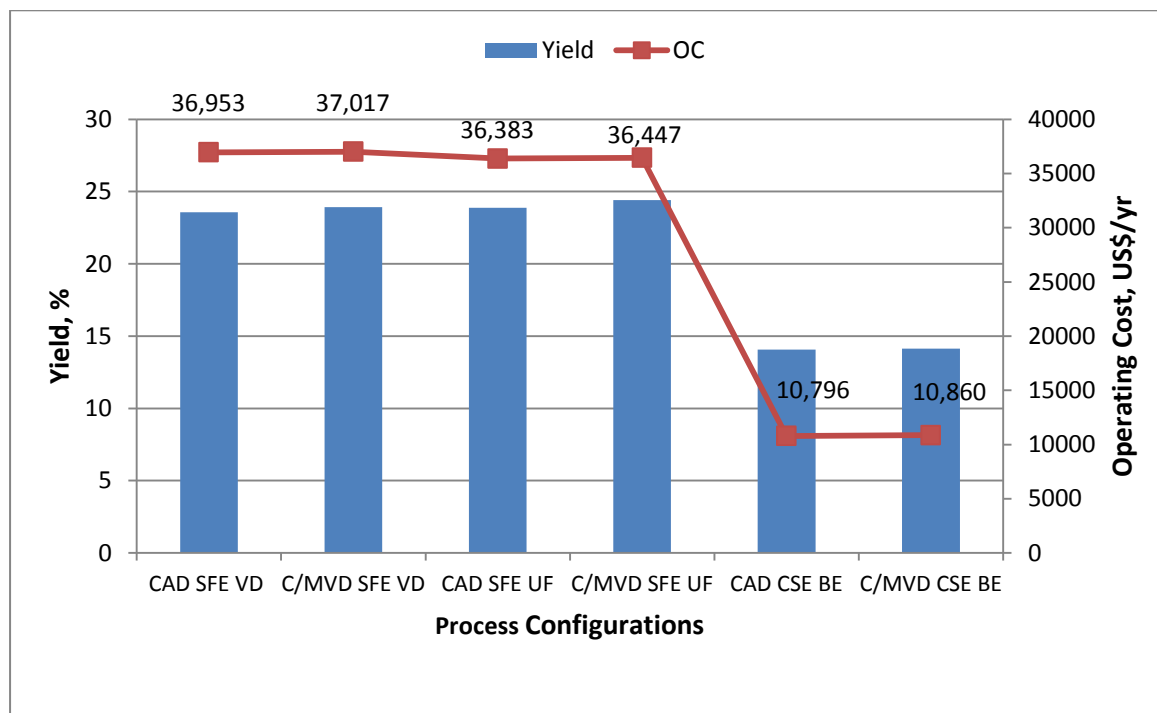


Figure 2: Yield and operating cost of each process configuration

From Figure 2, the highest operating cost for phenolic acids production is C/MVD SFE VD with a total of \$US 37017 per annual follow by CAD SFE VD, C/MVD SFE UF and then CAD SFE UF. The operating cost for conventional solvent extraction is lower with \$US 10860 and \$US 10795 for C/MVD CSE BE and CAD CSE BE respectively. The results from Figure 2 elucidated that technology with supercritical fluid extractor will have a higher production cost. However, this high end technologies will retain the most desire product. The cost of SFE is significantly high compare to CE due to high pressure vessel which needs high electricity and maintenance cost. On the flip side, this equipment is able to reduce process time which has economical benefits. For CSE will requires 6 hours of processing while SFE process only requires 2 hours (Catchpole *et al.*, 2012). In economic point of view, C/MVD result in higher operating cost compare to CAD due to higher amount of electricity is needed to convert electrical energy to microwave energy. However, the yield from C/MVD is higher by 2% compare to CAD. Hence, optimisation has to be done in order to determine the most adequate process configuration.

6. Fuzzy Optimization

The process configurations are undergo optimization to obtain phenolic compounds that maximize production yield and minimize operating cost. The operating hour is set at 8330 hours per year. The fuzzy targets are shown in table 4 with energy cost of respective technologies.

Table 4 : Fuzzy target for respective configurations

Fuzzy Target	C/MVD SFE UF	CAD CSE BE	CAD SFE UF
λ	-	-	0.294
F_p (kg/hr)	9.683	5.603	6.782
F_p (kg/annual)	196428	10795.7	56494.06
OC (US\$/hr)	4.444	1.296	3.518
OC (US\$/annual)	37017	10859.53	29304.94
Energy cost _j (US\$/annual)	421.29	357.46	214.6
Energy cost _l (US\$/annual)	17800	115.59	7535.32
Energy cost _n (US\$/annual)	79.74	649.85	528.08

j : pretreatment technology, l : extraction technology and n : concentration technology

Configuration 1:

The production yield and the total operating cost for configuration 1 are 9.683 kg/hr (196428 kg/annual) and \$US4.444 kg/hr (\$US37017 per annual) from 83.3 ton per yr of *Strobilanthes Crispus*. This process configuration has the highest production yield with the high-end technologies of convective vacuum microwave dryer (C/MVD), supercritical fluid extractor (SFE) and ultrafiltration (UF) for the pretreatment, extraction and concentration technology respectively. The operating cost is mostly influence by SFE of 48.8% follow by C/MVD with 1.15% of the total operating cost. This is due to the high pressure vessel and microwave generation that requires lots of energy for pumps and electricity.

Configuration 2:

The lower limit of the 6 process configurations is CAD CSE BE which has lower cost and purity. This process minimize OC as it operates at atmospheric pressure so the use of pump is lesser. The estimated operating cost is \$US 1.296 kg/hr (\$US10859.53 kg/annual) and production yield of 1.296 kg/hr (10795.7 kg/annual). The OC is lower due to the absent of high-end technology of SFE that contribute the most to the energy cost. It is clearly shows that the total operating cost is mostly affected by the technology pathway chosen.

Configuration 3:

As shown above, both configurations show a huge contrast for phenolic compounds yield and operating cost. Configuration 1 will has high yield and OC while configuration 2 has low values for both parameters. Therefore, optimization is done to satisfy the objective function of maximizing F_p and minimizing OC. From Eq. 1 and 2, the fuzzy model is constructed as follow:

$$\frac{4.444 - OC}{4.444 - 1.296} \geq \lambda \quad (6)$$

$$\frac{F_p - 5.583}{9.683 - 5.583} \geq \lambda, (0 \leq \lambda \leq 1) \text{ in kg/hr} \quad (7)$$

Table 4 shows the results for λ which is the degree of satisfaction for minimizing operating cost and maximizing production yield where λ is 0.29. The optimized process configuration is CAD SFE UF with operating cost of \$US3.518 kg/hr (\$US29304.94 kg/annual) and product yield of 3.518 kg/hr (56494.06 kg/annual). As compare to previous configuration, this process generates 3.5 times lesser and 5.23 times higher than configurations 1 and 2 respectively. The operating cost is 1.26 times lesser and 2.7 times higher than configurations 1 and 2 respectively. This shows that the high-end technology has a better economic viability. The chosen technologies able to generate high production yield with less degradation without overshooting the operating cost.

7. Conclusions

Process simulation is a great tool to obtain mass and energy balance for techno-economic analysis. Production yield and energy flow rate is acquired for different process configuration. Fuzzy optimization helps to determine the balance of techno-economic as both production yield and operating cost are contradicting to each other. The optimized process configurations have various combinations of conventional and high-end technologies which is CAD SFE UF. It is able to retain most of the phenolic acids without overshooting the operating cost. The operating cost of this process is \$US29304.94 kg/annual which is 1.26 times lower than C/MVD SFE UF and product yield of 56494.06 kg/annual which is 5.23 times higher than CAD SFE UF.

Nomenclature

CAD	Convective Air Drying	F_p^U	Upper Limit of Each Process Flow Rate
C/MVD	Microwave Vacuum Drying	F	Flow Rate
CSE	Conventional Solvent Extraction	OC	Operating Cost
SFE	Supercritical Fluid Extraction	OCU	Upper Limit of Operating Cost
BE	Back Extraction	OCL	Lower Limit of Operating Cost
UF	Ultrafiltration	Y	Yield
MW	Microwave	λ	Multiple Objective Functions
DES	Deep Eutectic Solvent	j	Pre-treatment
IL	Ionic Liquid	k	Output from technology j
NaDES	Natural Deep Eutectic Solvent	l	Extraction
F_p	Final Product Flow Rate	n	Concentration
F_p^L	Lower Limit of Each Process Flow Rate		

Acknowledgements

The authors acknowledge financial support by Polish Ministry of Science and Higher Education through research project N312 031 32/2036 and N N310 146835.

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Antioxidant potential of Malaysian Medicinal Plant

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Abstract

The objective of this research is to study the phytochemical content of Malaysian medicinal plants (*Andrographis paniculata*, *Morinda Citrifolia* and *Ficus Deltoidea*). This study involves the investigation on total phenolic content, total flavonoid content and DPPH scavenging activity using different method of extraction - hot water extraction and ultrasonic assisted extraction and different solvents – water, 80% ethanol and 80% methanol. In addition to that, synergistic effect of these plants was also studied. Effect of freeze drying on plant extracts was studied. From the experiment, *Ficus deltoidea* leaves has the highest amount of phenolic content, flavonoid content and better scavenging activity compared to *Andrographis paniculata* and *Morinda citrifolia* when extracted with ultrasonic method using 80% methanol. As for synergistic effect, plant combination shows lower phytochemical content and scavenging activity compared to *Ficus deltoidea*. From this research, it is found that freeze drying increases the scavenging activity of plant extracts.

Keywords: *Morinda citrifolia*, *Ficus deltoidea*, *Andrographis paniculata*, antioxidant, free radicals

1. Introduction

It is expected that more than 366 million of the world population will be affected by diabetes mellitus by the year 2030[1]. Diabetes mellitus is a disease caused by hyperglycemia and disruption in fat and protein which results from the defects in insulin secretion and insulin action [2]. Type 1 diabetes is caused by the destruction β -cells of the pancreas and abnormalities in carbohydrate, fat and protein metabolism which shows resistance to insulin [3]. People with type 1 diabetes require insulin for survival. Type 2 diabetes is the common type of diabetes with 90% of the total cases caused by the failure of the insulin to act against the glucose level [3]. Without insulin action in human body, the amount of glucose rises and poses more health threats like retinopathy, nephropathy and neuropathy [1].

Recent study has shown that oxidative stress has been linked with the development of diabetes mellitus [4]. Oxidative stress does play an important role in diabetes mellitus. Oxidative stress creates complications at microvascular and macrovascular level [3]. Oxidative stress contributes to the malfunction of two major mechanisms involved in maintaining glucose level – insulin resistance and insulin secretion [3]. Oxidative stress is basically the imbalance between the oxidants and the antioxidants [2]. When the ability of the oxidants is limited to defend the system from the oxidants, oxidative stress is exerted on the cells [3]. The damage created by oxidative stress is permanent [5]. Free radicals are electrically charged molecules where they have an unpaired electron [6]. Hence, these free radicals seek another electron to neutralize themselves [6]. After capturing the electron, another free radical is created in the process triggering a chain reaction producing thousands of free radicals within seconds [7]. These free radicals need to be deactivated using antioxidants [5]. If the antioxidants are unable to control the free radicals, these free radicals would cause damages to proteins, lipids and DNA [8]. This would lead to cell death or physiological dysfunctions such as diabetes and cancer [3].

Hence, there must be a balance between oxidants and antioxidants [2]. When antioxidants ability to deactivate the oxidants is limited, the damages to the cells are extensive [5]. Two mechanisms of antioxidants were identified – chain-breaking mechanisms and removal of Reactive Oxygen Species initiators [9]. Plant phenolic compounds have been proven to protect the cells from oxidants [10]. Plant phenolic compound could actually protect against degenerative disease due to oxidative stress [11]. Plant phenolic compounds have been proven to protect the cells from oxidants [10]. It has been proven that this phytochemical exists in all the three plants used in this research [13, 14, 15].

Phenolic compounds are divided into two major groups - flavonoids and non-flavonoids [16]. Flavonoids are used for anti-allergenic, anti-inflammatory, anti-bacterial and also anti-hepatotoxic purposes [17]. The flavonoid level in each plant differs as they are affected by various factors such as species, light and etc. [18]. In plants, it has been proven that to resist infection or radiation, plants produce more of flavone or flavonol which are the constituents of flavonoids [17]. This proves that the level of flavonoids in plants is vital for the resistance of external threats. This increase in flavonoid level is vital as it is capable of free radical scavenging [17]. This is the basis of DPPH free radical scavenging. DPPH is used to replicate the free radicals.

Hence any impact on DPPH can be interrelated to oxidative damage caused by free radicals.

Medicinal plants have been used for years to limit the effects of diabetes mellitus. In recent years, many studies have been carried out to find a safer cure for diabetes mellitus. More than 200 bioactive components from plants have been identified as glucose reducing components [19]. Some of the bioactive components identified are phenolic, flavonoids, triterpenoids and alkaloids [20, 21, 22]. These bioactive components play a crucial role as antioxidants. Flavonoids are the largest group of phenolic compound [16]. These two phytochemicals are often related to cure of diabetes mellitus [23]. Flavonoid is a major component involved in antidiabetic activity. This proved by a research carried out on type 2 diabetic rats strongly suggest that flavonoids is indeed an active component involved in antidiabetic [10]. This is also further validated by another study done – both in- vitro and in vivo studies shows that phenolics has positive effects on glucose homeostasis.

The medicinal plants chosen to carry out the experiments are Mengkudu (*Morinda citrifolia*), Mas Cotek (*Ficus deltoidea*) and Hempedu Bumi (*Andrographis paniculata*). These plants are chosen based on the following criteria. Firstly, these plants are listed as plants with potential anti-diabetic activity. [24]. Secondly, these medicinal plants are part of the priority species for the development programme in Malaysia [25]. Finally, the availability of the plants in Malaysia is also taken into account.

Flavonoids are the main chemical component in *Andrographis paniculata* which are responsible for the plants' biological activities [24]. Hence the plant exhibits antioxidant properties. *Ficus deltoidea* exhibits medicinal properties as they possess phenolic compounds in them [25]. Flavonoids are also a major component of *Morinda citrifolia* [26]. Total phenolic content and total flavonoid content for the leaves are low compared to the fruits [27].

For extraction of the plants – water, methanol and ethanol are often used. It was found that methanol extraction is better compared to aqueous extraction and ethanol extraction as the total phenolic content and the total flavonoid content were the highest compared to other method of extraction. But DPPH scavenging activity was higher in aqueous extraction followed by ethanol extraction and methanol extraction [24]. Total phenolic content and total flavonoid content were higher in samples extracted by methanol [25]. DPPH scavenging activity was also higher in methanol extraction compared to aqueous extraction. Binary solvent system is used in this study as it has been proven to maximize the active compounds in the plants [28].

It has to be understood that even though flavonoids are vital for health, flavonoids would not be as effective as a component on its own [13]. Flavonoids rely on different phytochemicals which gives flavonoids the ability to defend the cells from oxidants [13]. Rutin along with vitamin C and vitamin E when combined produced better free radical scavenging [14]. Combination of fruits actually yielded better antioxidant activity compared to just one fruit [29]. One single purified phytochemical can never replace the health benefits of the combination of natural phytochemicals which exists in plants [30].

Plant phenolic is heat sensitive hence using freeze drying would be a better choice compared to oven drying [31]. Freeze drying prevents the growth of microorganisms [31]. In addition to that, freeze drying slows down lipid oxidation significantly [31]. Freeze drying is the best method to preserve antioxidant activity and nutrient content of plants as it actually increases the level of phenolic compounds [32]. But it has been argued that freeze drying might cause reduction in antioxidant activity due to degradation of certain compounds (phenolics and flavonoids) [31].

The study is carried out to measure the antioxidant activity of *Andrographis paniculata*, *Ficus deltoidea* and *Morinda citrifolia* individually and synergistically using the leaves of these plants for total phenolic content and total flavonoid content measurement and DPPH Free Radical Scavenging. Different solvents (water, 80% methanol and 80% ethanol) are used to extract the plants in two methods of extraction – hot water extraction and ultrasonic assisted extraction. The study is also carried out to study the effect of freeze drying on plant extracts with the highest antioxidant activity. The bioactive component - rutin is identified through HPLC analysis.

2. Research methodology

2.1 Material and Method

2.1.1 Plant material

Hempedu Bumi (*Andrographis paniculata*), Noni (*Morinda citrifolia*) and Mas Cotek (*Ficus deltoidea*) were purchased from a plant supplier in Sungai Buloh, Selangor, Malaysia. The leaves are cleaned and sun-dried for 24 hours before cutting into small pieces using a clean scissors.

2.1.2 Chemicals

Distilled water, Methanol, Ethanol (96%), Sodium hydroxide, +(-)catechin, Sodium carbonate, Sodium nitrite, Folic-Ciocalteu reagent, Gallic acid, Aluminium chloride, 2,2-diphenyl-1-picrylhydrazyl (DPPH)

2.1.3 Apparatus

Water bath, Ultrasonic cleaner, 100 ml and 500ml measuring cylinder, Whatman No.1 filter paper, Beaker, Aluminium foil, Laboratory bottles.

2.2 Extraction

The conditions were standardised for both the extraction methods. This is done to study the efficiency of each method with different solvents. Solid to solvent ratio used is 1:15, the temperature used is 45°C and the duration for extraction is 40 minutes. Three different solvents are used - distilled water, 80% methanol and 80% ethanol to extract the plants.

2.2.1 Hot water extraction

The leaves are cut into pieces and placed into conical flasks. The conical flask is then filled with 15 ml of solvent. The conical flask is then placed in a water bath (CloudLab Scientific Sdn. Bhd., Model MT-1034, Malaysia) at 45°C for 45 minutes. The extracts are then filtered using filter paper (Whatman International Ltd., England) into beakers. The extraction is done in triplicates for each solvent.

2.2.2 Ultrasonic assisted extraction

The leaves are cut into pieces and placed into laboratory bottles. The conical flask is then filled with 15 ml of solvent. The laboratory bottles are then placed into the ultrasonic cleaner (Soluzioni Tecnologiche Inc., Model Sonica 5300EP S3, Italy) at 45°C for 45 minutes. The extracts are then filtered into beakers. The extraction is done in triplicates for each solvent.



Figure 1: Ultrasonic cleaner (Soluzioni Tecnologiche Inc., Model Sonica 5300EP S3, Italy) [33]

2.2.3 Preparation of combination of extracts (synergistic energy)

2.5 ml of each plant extract are mixed thoroughly. The plant is extracted using the solvent which shows the highest phenolic content. The solvent is then centrifuged at 2500 rpm for 10 minutes.

2.3 Phytochemical content

2.3.1 Total phenolic content

It is measured using Folin-Ciocalteu colorimetric [34]. A total of 0.1 ml of plant extract is added 0.2 ml of Folin-Ciocalteu reagent. The mixture is then added with 2 ml of distilled water. The mixture is then left to rest at room temperature for 3 minutes. Then, 1 ml of 20% sodium carbonate is added to the mixture. The mixture is left to be incubated at room temperature for an hour. The absorbance of the mixture was measured at 765 nm using an UV-Spectrophotometer (Dynamica, Model RB-10). Blank sample was prepared as explained above except by replacing the plant extract with distilled water. Determinations of total phenolic content were carried out with

the respect to gallic acid standard curve. Measurements were carried out in triplicates. The results were expressed in term of milligrams of gallic acid per 100 g dried weight (mg GAE/100 g DW). The total phenolic content (mg GAE/ 100 g DW) was gauged using the following the equation:

$$\text{Total phenolic content (mg GAE/100 g DW)} = \text{GAE} \times \frac{V}{M} \times 100 \quad (1)$$

GAE: Gallic acid equivalence (mg/ml) attained from the standard curve

V: Total volume of solvent used during the assay (ml)

M: Mass of plants used during the assay (g)

2.3.2 Preparation of Standard Curve for Total Phenolic Content

Gallic acid with different concentrations (0.2, 0.4, 0.6, 0.8 and 1.0 mg/ml) were prepared. 0.1 ml of the gallic acid solution is added with 0.2 ml of Folin-Ciocalteu reagent. The mixture is the added with 2 ml of distilled water. Then, 1 ml of 20% sodium carbonate is added to the mixture. The mixture is left to be incubated at room temperature for an hour. The absorbance of the mixture was measured at 765 nm using an UV-Spectrophotometer. Blank sample was preparing the mixture as explained above except by replacing the plant extract with distilled water. A standard curve is plotted - y-axis represents the absorbance while x-axis represents the concentration of the gallic acid. The calibrated equation obtained from the standard curve is $y=2.5899x+0.5302$ ($R^2=0.8704$).

2.3.3 Total flavonoid content [35]

Plant extracts (0.25 ml) were mixed with 1.25ml of distilled water and 0.075 ml of 5% (w/v) sodium nitrite solution. The mixture was incubated at room temperature for 6 minutes and 0.15 ml of 10% (w/v) aluminium chloride was added to the mixture. 1 M of sodium hydroxide (0.5 ml) was added to the mixture and then 0.275 ml of distilled water was added. The absorbance of the mixture was measured at 510 nm using an UV-Spectrophotometer. Blank sample was prepared as explained above except by replacing the plant extract with distilled water. Determinations of total flavonoid content were carried out with the respect to (+)-catechin standard curve. Measurements were carried out in triplicates. The results were expressed in term of milligrams of (+)-catechin per 100 g dried weight (mg CE/100 g DW). The total phenolic content (mg CE/ 100 g DW) was gauged using the following the equation:

$$\text{Total flavonoid content (mg CE/100 g DW)} = \text{CE} \times \frac{V}{M} \times 100$$

CE: (+)-catechin equivalence (mg/ml) attained from the standard curve

V: Total volume of solvent used during the assay (ml)

M: Mass of plants used during the assay (g)

2.3.4 Preparation of Standard Curve for Total Flavonoid Content

(+)-catechin with different concentrations (0.1, 0.3, 0.5 and 0.7 mg/ml) were prepared. Plant extracts (0.25 ml) were mixed with 1.25ml of distilled water and 0.075 ml of 5% (w/v) sodium nitrite solution. The mixture was incubated at room temperature for 6 minutes and 0.15 ml of 10% (w/v) aluminium chloride was added to the mixture. 1 M of sodium hydroxide (0.5 ml) was added to the mixture and then 0.275 ml of distilled water was added. The absorbance of the mixture was measured at 510 nm using an UV-Spectrophotometer Blank sample was prepared as explained above except by replacing the plant extract with distilled water. A standard curve is plotted - y-axis represents the absorbance while x-axis represents the concentration of the (+)-catechin. The calibrated equation obtained from the standard curve is $y = 3.3216x + 7E-05$ ($R^2=0.9821$) [36].

2.3.5 DPPH scavenging activity [37]

Plant extracts (0.1 ml) is added with 3.9 ml of ethanolic DPPH (60×10^{-5} M). The mixture is then kept in the dark for 30 minutes at room temperature. This is done to block UV light as UV light would trigger free radicals [37]. This will disrupt the results of the experiment. The solution is then measured for absorbance using spectrophotometer at 517 nm. Due to the reaction, the colour of the solution will change from deep violet to light yellow. Radical scavenging activity is calculated using the following formula:

$$\% \text{Inhibition} = \frac{A_B - A_A}{A_B} \quad (3)$$

A_A = Absorption of extract

A_B = Absorption of blank sample

This is carried out for all the plant extracts including the combination of the extracts. Determinations are carried out in triplicates.

2.3.6 HPLC analysis

10 mg of plant extract is dissolved in 10 ml of diluents. Since water, methanol and ethanol were used – water extracts are dissolved in water, extracts using methanol are dissolved in methanol and ethanol extract are dissolved in ethanol. The wavelength used is 280 nm. The mobile phase A will be 1% acetic acid and mobile phase B will be acetonitrile. Flow rate will be 1ml per minute. This would be carried out at room temperature [37]. HPLC analysis is carried out to identify the components in the plants and also to quantify them. This will be done for all the plant extracts including the combinations of the extracts.

2.3.7 Freeze drying

The plant extract with the highest antioxidant activity will be freeze dried. After freeze drying, all the phytochemical analysis and the antioxidant activity will be carried out on the extract. This is carried out to determine the effectiveness of freeze drying on antioxidants. Freeze drying is carried out over a span of 3 days. The equipment used is a vacuum freeze dryer. The sample is placed in a sealed container.

The container is then placed in the freeze dryer. The standard temperature used is -80°C and the pressure of vacuum is varies between 0.6 mB.

3. Results and Discussion

3.1 Phytochemical Content and Antioxidant Scavenging Activity Analysis

Based on figure 2 and 3, it can be observed that the recovery of phenolics is the higher in ultrasonic extraction compared to hot water extraction. 80% methanol gives the highest recovery of phenolics followed by 80% ethanol and water for each plant species. From this experiment, it was found that *Ficus deltoidea* has the highest phenolic content as compared to *Andrographis paniculata* and *Morinda citrifolia*.

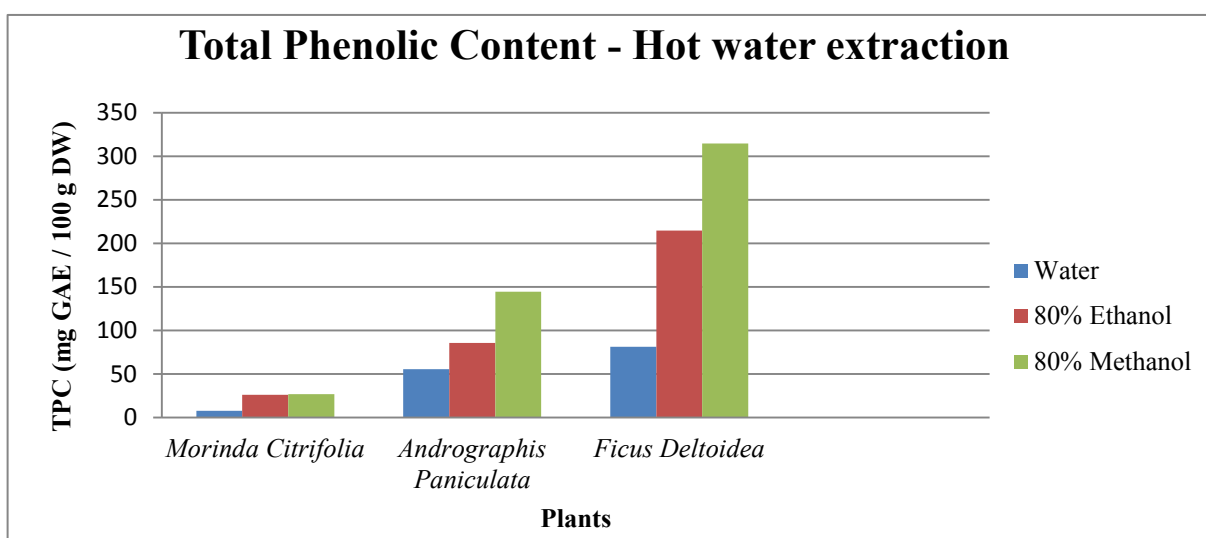


Figure 2: Total phenolic content for hot water extraction

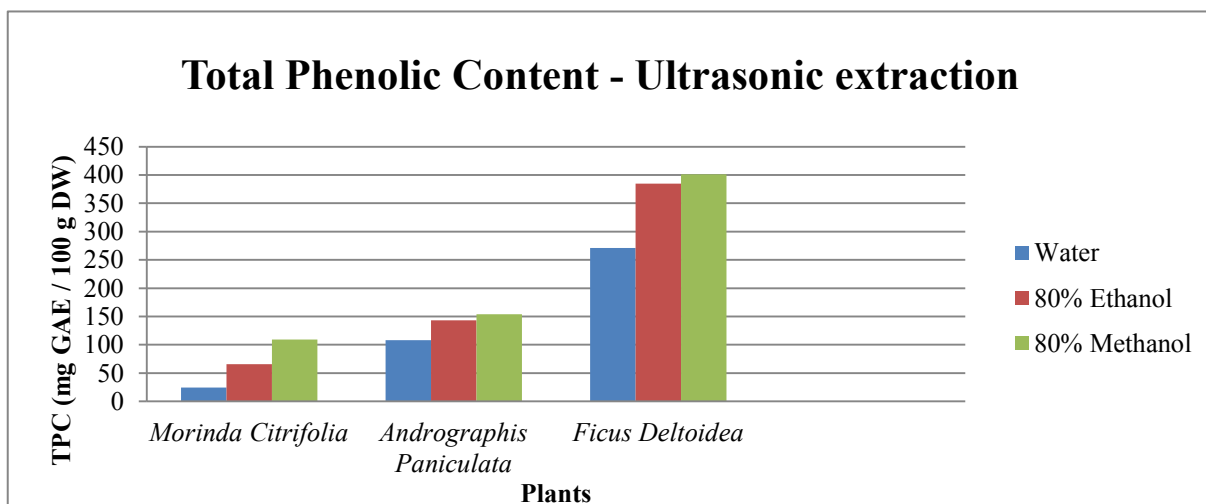


Figure 3: Total phenolic content for ultrasonic extraction

Based on figure 4 and 5, it can be seen that the recovery of flavonoids are highest in ultrasonic extraction compared to hot water extraction. 80% methanol gives the highest recovery of phenolics followed by 80% ethanol and water for each plant species. For the recovery of flavonoids, it can be established that it is better to extract the plants using ultrasonic and using methanol as the solvent.

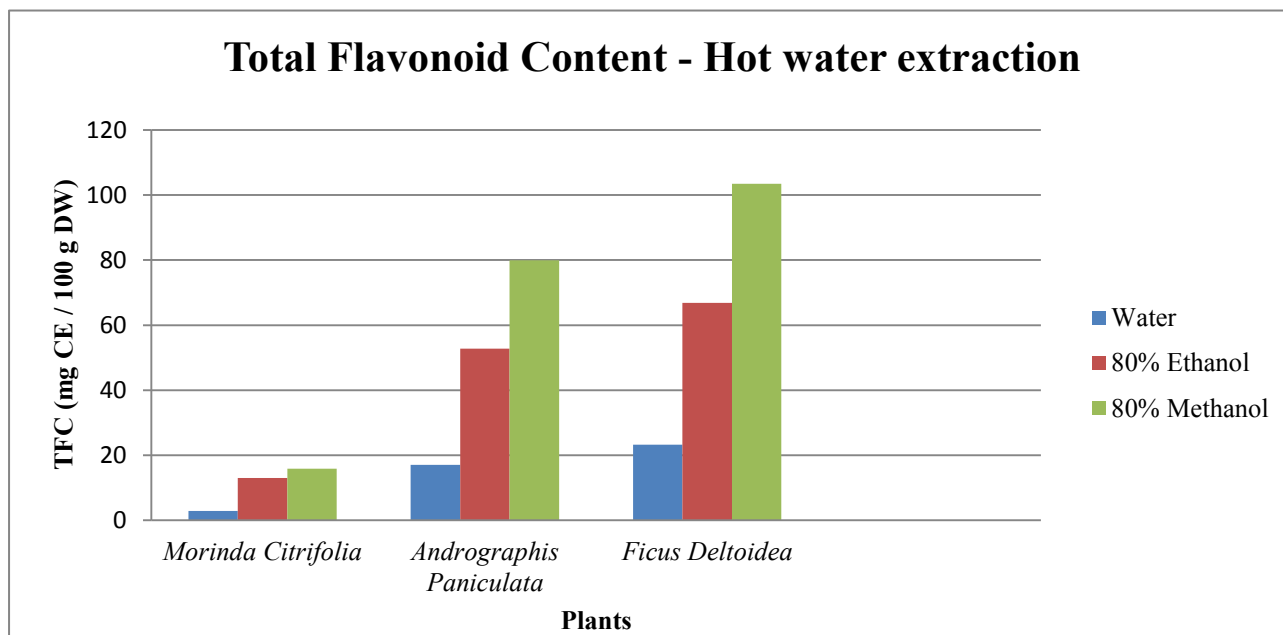


Figure 4: Total flavonoid Content for hot water extraction

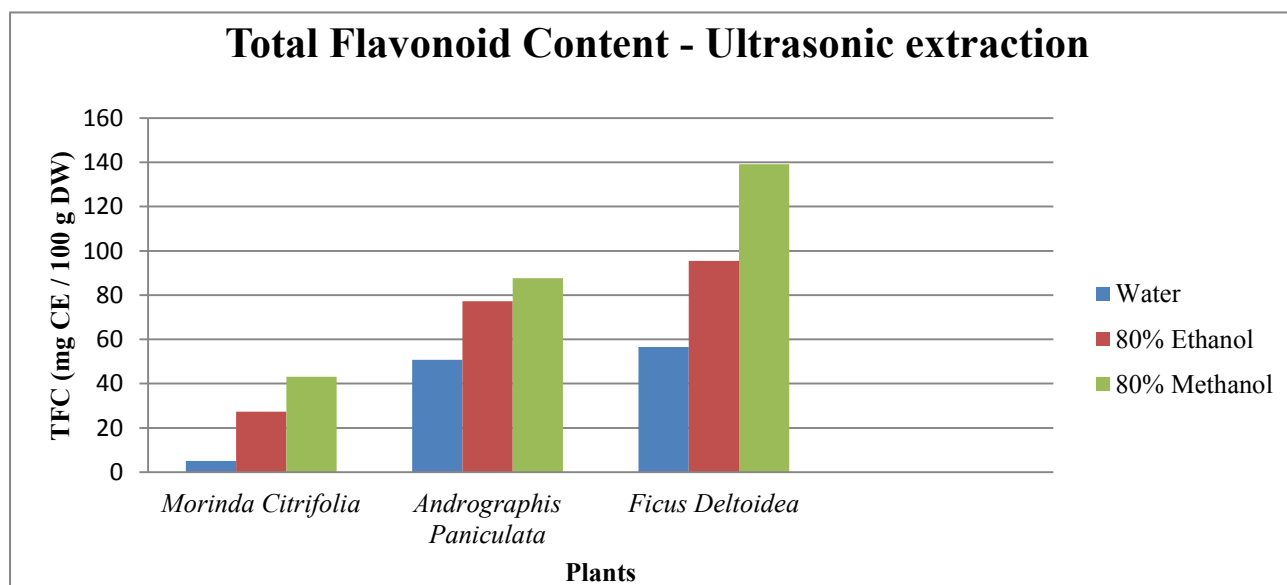


Figure 5: Total flavonoid Content for ultrasonic extraction

As for DPPH scavenging activity – based on figure 6 and 7, it is observed that DPPH scavenging activity is the highest for ultrasonic extracted plants as compared to hot water extraction. Plants extracted using 80% methanol has the highest scavenging activity followed by 80% ethanol and water. Plant species are significant for the high scavenging activity and the solvents used for extraction are also significant for the high scavenging activity. In addition to that, the method of extraction does not affect the scavenging activity. But to ensure higher scavenging activity, plant species,

solvents and method of extraction used to extract the plants are essential to achieve high scavenging activity.

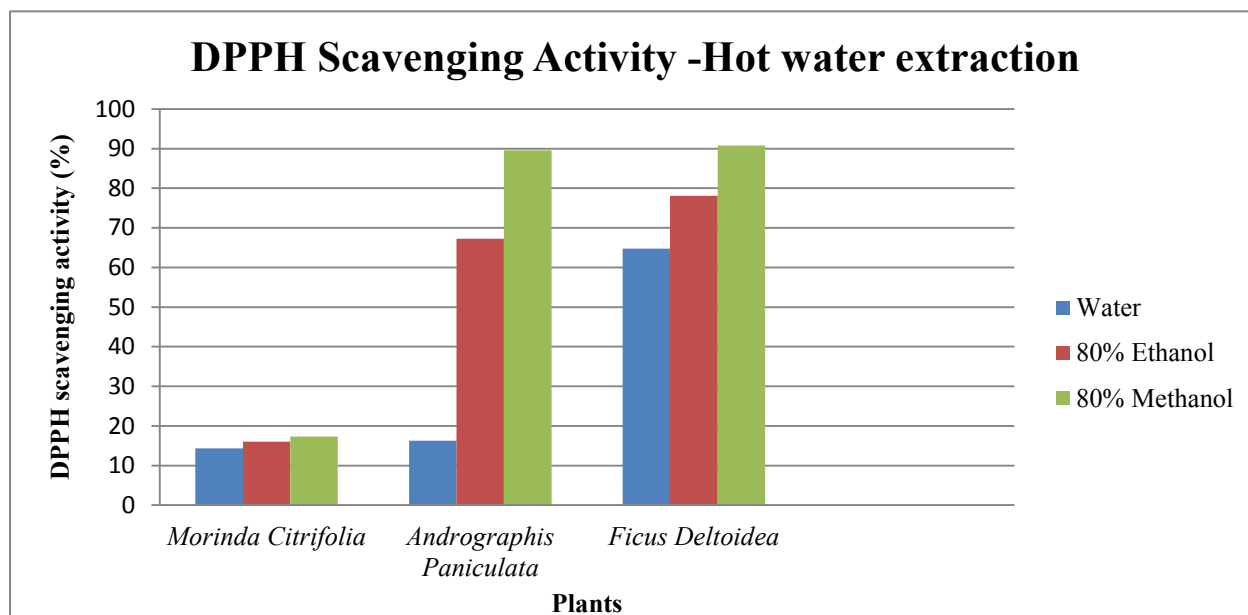


Figure 6: DPPH scavenging for hot water extraction

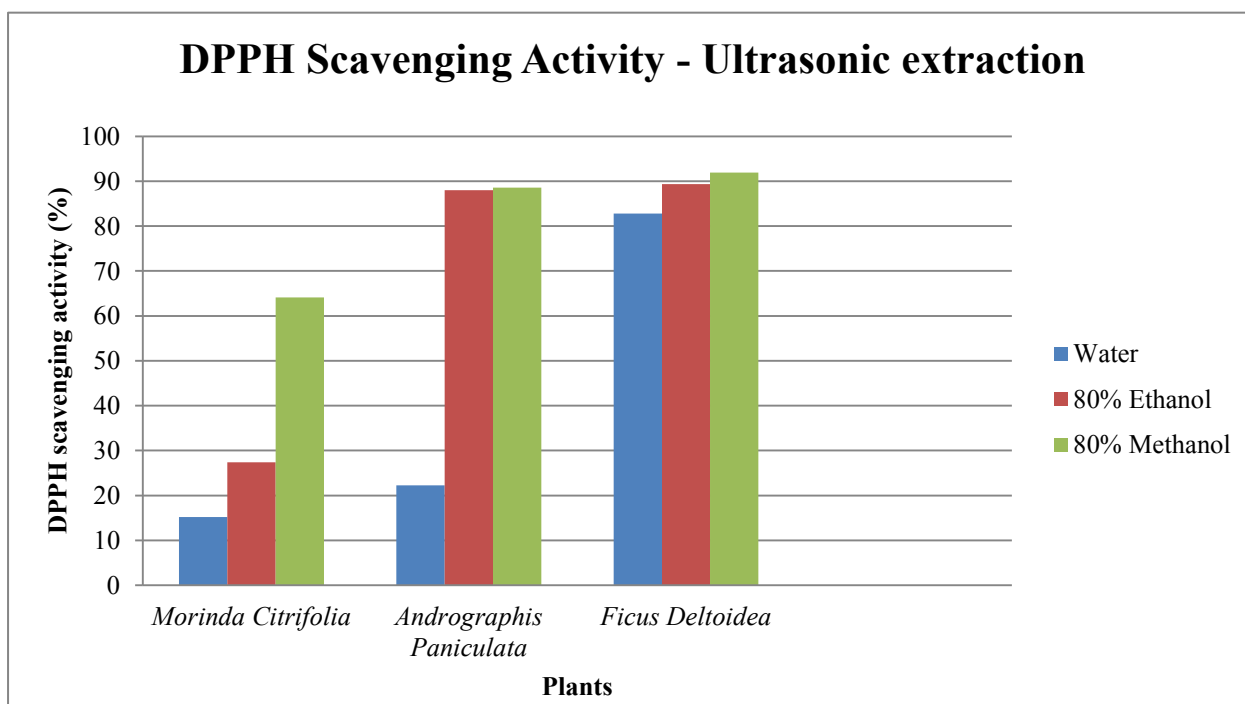


Figure 7: DPPH scavenging for ultrasonic extraction

From all the data measured, it is established that *Ficus deltoidea* is the best among the three plant species to be used as a cure or a prevention supplement for diabetes mellitus. It has the highest phenolic content - 401.15 mg GAE/100 g DW, flavonoid content - 139.16 mg CE/100 g DW and DPPH scavenging activity - 91.91% compared to *Andrographis paniculata* and *Morinda citrifolia*. *Andrographis paniculata* has phenolic content of 154.03 mg GAE/100 g DW, flavonoid content of

87.6 mg CE/100 g DW and scavenging activity of 88.602% while *Morinda citrifolia* has the lowest phenolic content - 109.47 mg GAE/100 g DW), flavonoid content - 43.09 mg CE/100 g DW and scavenging activity - 64.08%. It is established that *Ficus deltoidea* extracted with ultrasonic using 80% methanol has the highest recovery of phenolics, flavonoids and the highest scavenging activity. Hence, in this experiment, it is established that ultrasonic extraction and methanol are the most effective way to extract phytochemicals from plants. It also can be established that flavonoid and antioxidant activity increases with the increase in phenolic content. The increase in phytochemical content and scavenging activity of the plants extracted with ultrasonic extraction and methanol as solvent are similar to other plant species such as *Vernonia cinerea*, *Senna alata*, *Zingiber cassumunar* and *Tinospora crispaalbam*. [38]

3.2 Synergistic effect

Using the data obtained from the previous section, *Ficus deltoidea* extracted with ultrasonic using 80% methanol is used as a benchmark for synergistic effect experiment. It can be observed combination of plants has lower phenolic content compared to *Ficus deltoidea* in figure 8. From figure 9, it can be seen that *Ficus deltoidea* provides flavonoids even more effectively as compared to plant combination. From figure 10, *Ficus deltoidea* provides higher scavenging activity compared plant combination. It can be established that plant combination provides antagonistic effect in terms of phytochemical content and scavenging activity.

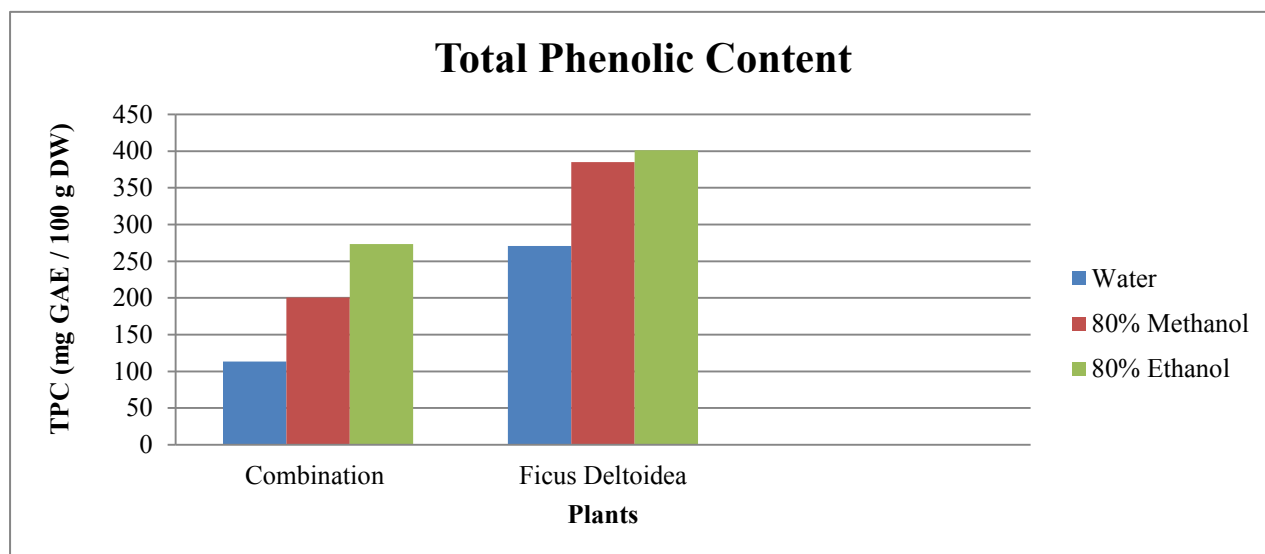


Figure 8: Total phenolic content for plant combination and *Ficus deltoidea*

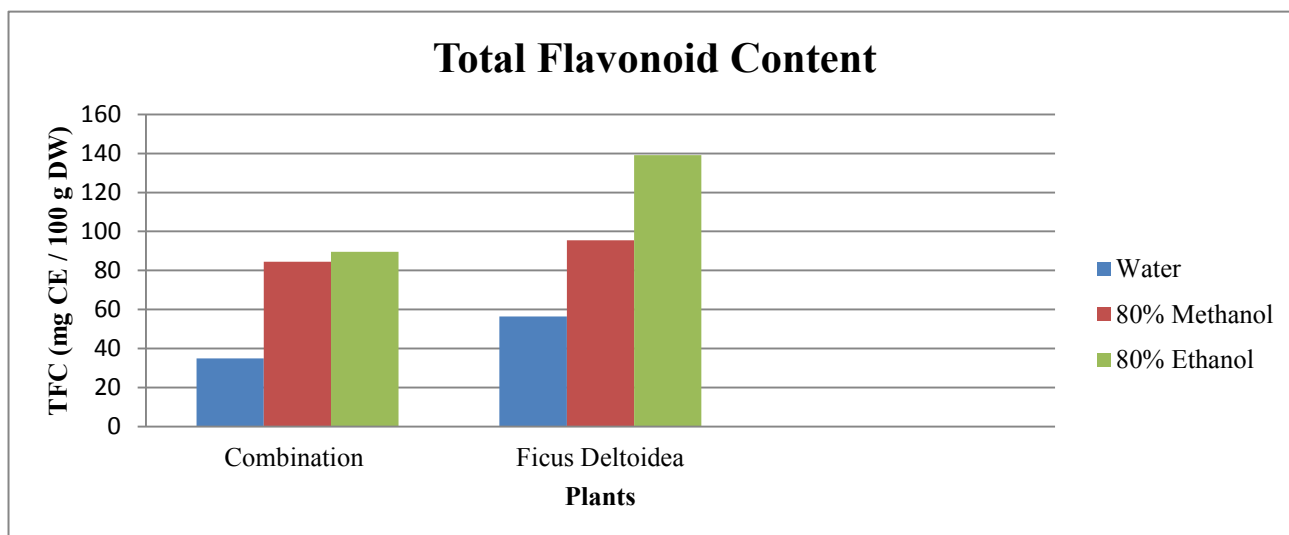


Figure 9: Total flavonoid content for plant combination and *Ficus deltoidea*

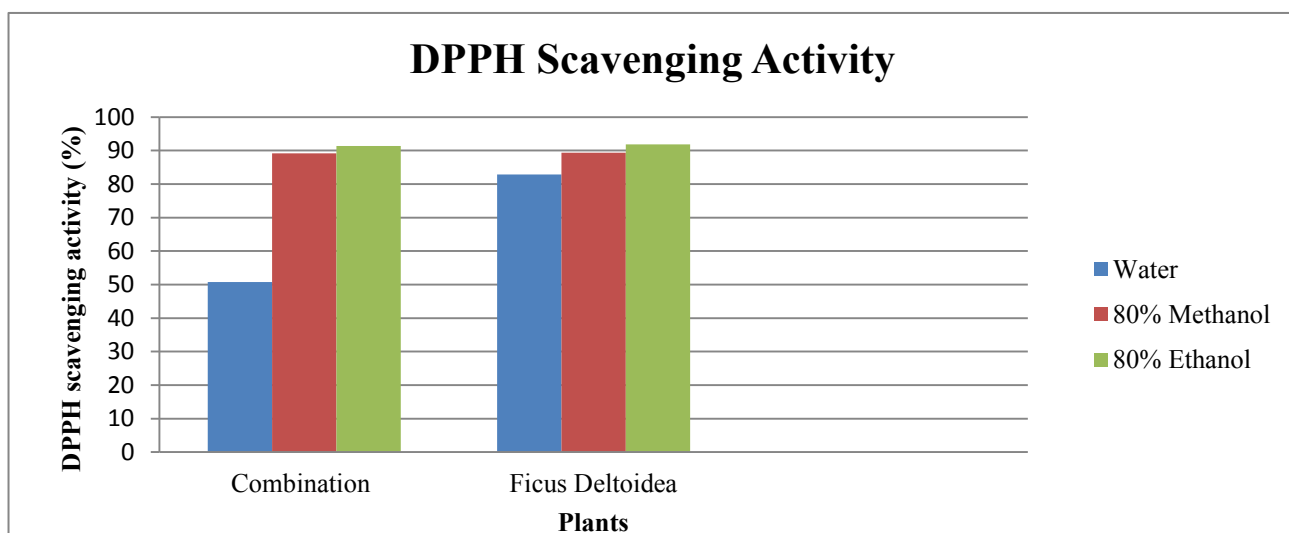


Figure 10: DPPH scavenging for plant combination and *Ficus deltoidea*

For the solvents used for extraction, 80% methanol has the highest recovery of phytochemicals and highest scavenging activity. Methanol has a polarity index of 5.1. Methanol is an amphiphilic compound which consists of single atom of tetraedic carbon which is connected to 3 hydrogen atoms and –OH group. –Oh group is the polar group while the hydrogen atoms are the water insoluble hydrocarbon chain. Due to its structure consisting of polar and non-polar groups, polar and non-polar molecules can be dissolved in the methanol [40]. This makes methanol a better solvent in extracting phytochemicals compared to ethanol and water. [41].

As for extraction method, it has to be understood that plant cells are enclosed in cell wall. This primary cell wall is made up of tough material called cellulose [42]. Cellulose decomposes at 500°C [43]. This cellulose can withstand high pressure [42]. While the secondary cell wall is made up of highly cross-linked phenolic molecules [44]. High amount of force is needed to overcome the structure of the cell. Ultrasonic waves create cavitations which grow in volume until it collapses [45]. This creates a

strong force which is strong enough to rupture the cell wall of the plant cell. This allows solvent diffusion into the cell thus increasing the contact surface area between the cell contents and the solvent used for extraction [46].

For the study synergistic effect - combining *Andrographis paniculata*, *Ficus deltoidea* and *Morinda citrifolia* provides negative synergistic effect. Plant combination creates interaction between phenolics which is called co-pigmentation reactions [47]. This creates more complex molecules [48]. With complex molecules created, it allows polymerization to occur [47]. Significant changes to molecular structures of the phenolics will affect the antioxidant capacity of the phenolic compounds [49]. It was suggested that hydrogen bonding occurs between the phenolic compounds. This affects the ability of the hydroxyl group. This directly results in the reduction of antioxidant activity of the phenolic compounds [50, 51].

3.3 Freeze drying

As *Ficus deltoidea* extracted using ultrasonic method with 80% methanol has the highest scavenging activity overall, it is subjected to freeze drying. Based on figure 8, it can be seen that scavenging activity has increased from 91.91% to 93.62% after freeze drying. It has been established that freeze drying has a significant effect on the scavenging activity. It proves that freeze drying can be a suitable preservation method for plant extracts – preserving the phenolics and flavonoids of the plants.

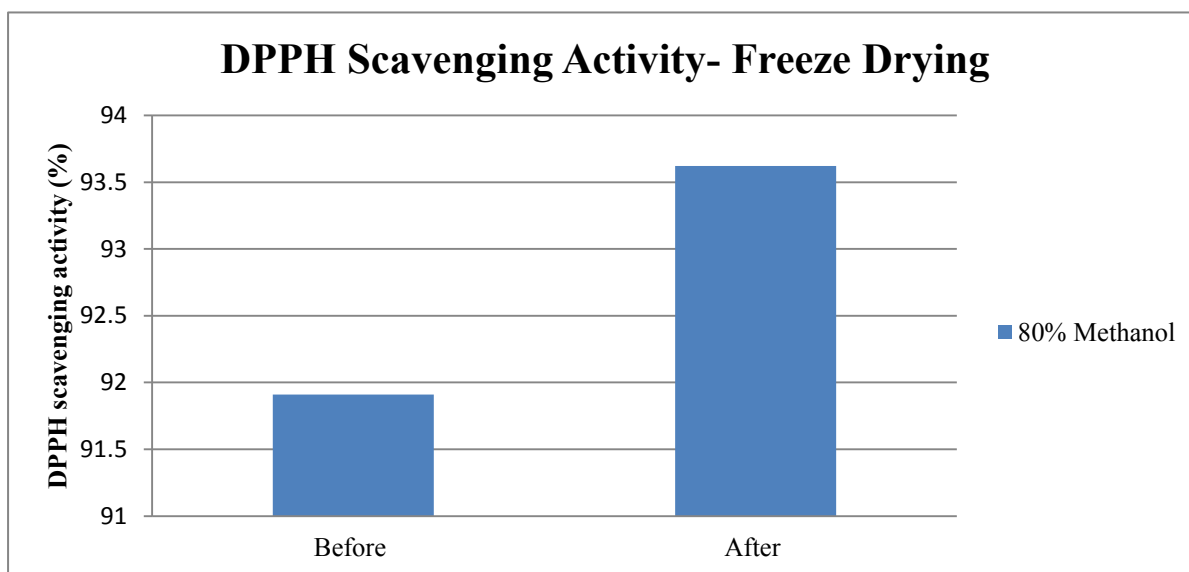


Figure 11: Scavenging activity before and after freeze drying

3.4 HPLC Analysis

For HPLC analysis, flavonoid focused in this research is rutin. From HPLC profile of *Morinda citrifolia* (retention time of 5.135 minutes), peak height of rutin of 54 is low compared to other flavonoids present in the plant extract. This applies to the other two plant species – *Andrographis paniculata* and *Ficus deltoidea*. HPLC profile of *Andrographis paniculata* shows no presence of rutin. This could be due to the degradation of the plant extract. While for *Ficus deltoidea*, the HPLC profile shows low traces of rutin in the extract (retention time of 4.921 minutes) with peak height of

60 compared to other flavonoids present in the plant extract. Although the amount of rutin is low, it has a significant positive effect on the glucose homeostasis [59, 60]. Presence of rutin in supplements for diabetes would definitely help stabilise the glucose level in human body along with other flavonoids. *Ficus deltoidea* has the highest amount of rutin compared to the other two plant species.

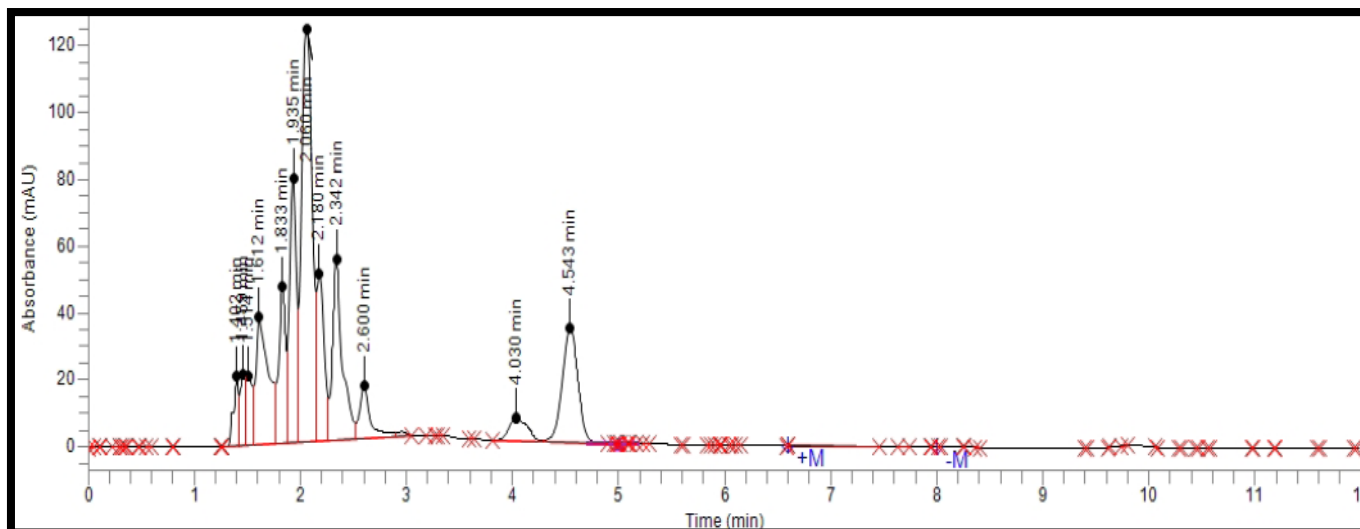


Figure 10: HPLC profile of *Morinda citrifolia*

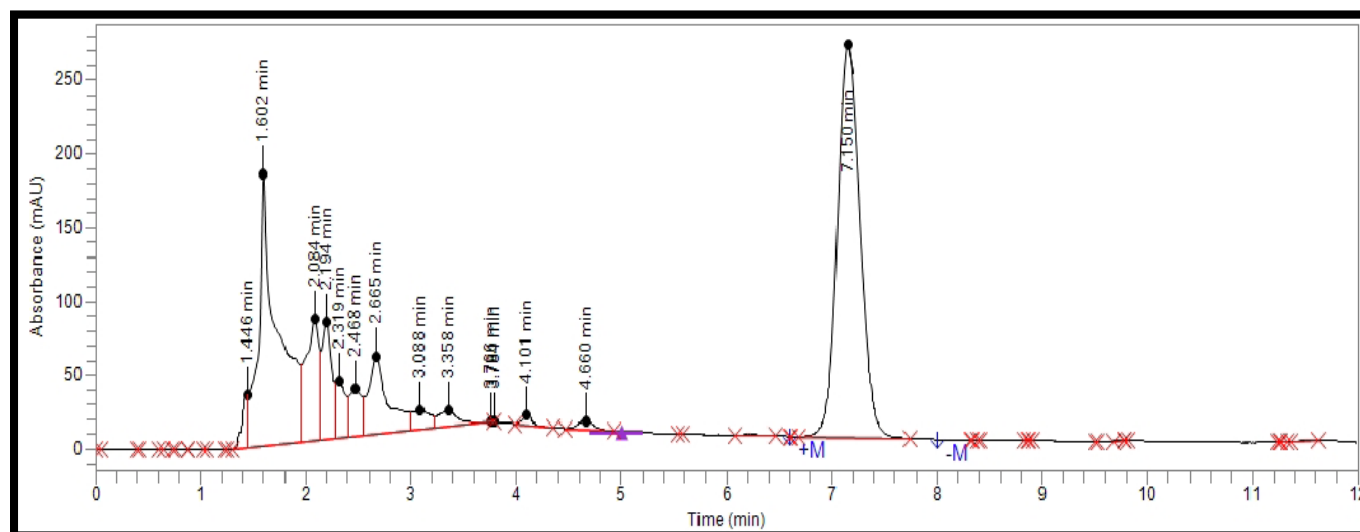


Figure 11: HPLC profile of *Andrographis paniculata*

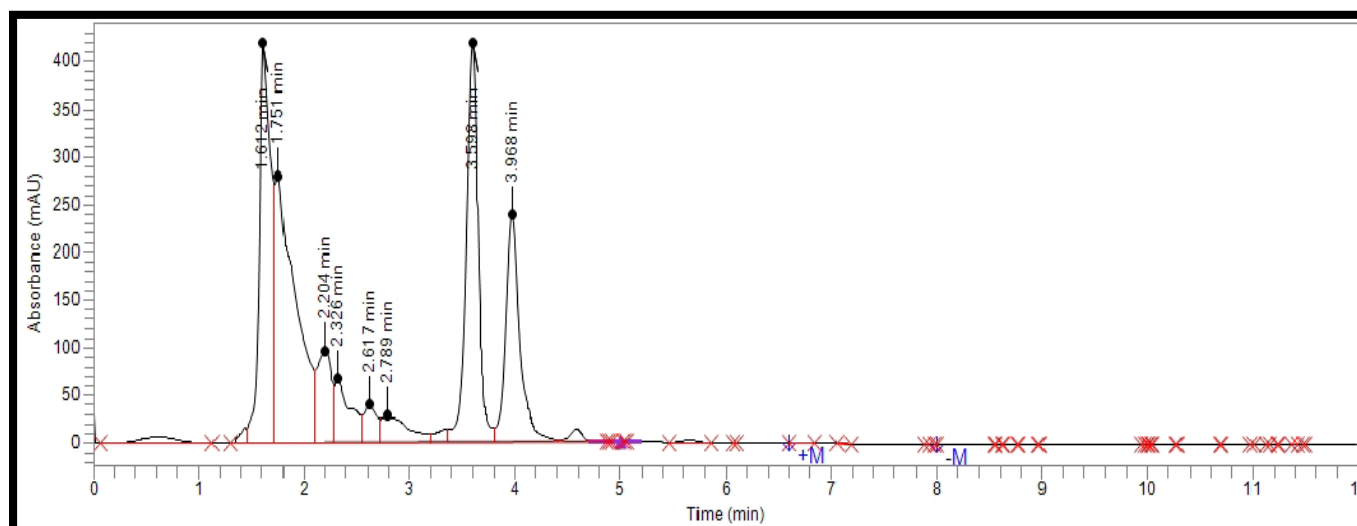


Figure 12: HPLC profile of *Ficus deltoidea*

3.5 Error analysis

Errors are inevitable in an experiment. In order to reduce random errors in the study, replication is carried out. Extraction of each plant is carried out in triplicates in order to increase accuracy. The phytochemical content and DPPH scavenging activity also carried out in triplicates. Average of the value is then measured.

Systematic errors are present throughout the study. Weighing balance used in the study is extremely sensitive. It has to be calibrated each time before using it. The weighing balance responds to any vibrations around it making the values fluctuate. Hence, the weighing balance is used carefully by keeping any source of vibration. In addition to that, the UV spectrophotometer was used extensively in this study. The UV spectrophotometer is calibrated using a blank sample. It was calibrated after each measurement to ensure that the value is accurate. The auto zero option is used for each measurement to reduce the systematic error. The linearity of standard curves is affected by systematic error in this study. The equations obtained from standard curves are not accurate as the value of R^2 is not 1.

4. Conclusion

As a conclusion, the objectives of this study are to measure phenolic content, flavonoid content and DPPH scavenging activity of *Andrographis paniculata*, *Ficus deltoidea* and *Morinda citrifolia*. The extraction methods – hot water extraction method and ultrasonic assisted extraction used are different to observe the efficiency of each method in extracting the phytochemicals from the leaves. Different solvents are used in this study to extract the leaves – 80% ethanol, 80% methanol and water. From the study, it is found that the ultrasonic assisted extraction is a better method to extract compared to hot water extraction. In addition to that, the best solvent to extract the leaves would be 80% methanol. The best plant to use as a remedy for diabetes among these three plants would *Ficus deltoidea*.

The finding from this study would be useful as the comparison is done for three different plants and two different methods of extractions. The solvents used for

extraction are also different. The factors involved in this study are many. The plants used are known to the locals. The plants can be used to their advantage in terms of health care. Using natural remedies for health care is better than using synthetic medicines to cure.

The results from the study can be used by pharmaceutical industry to combat diabetes mellitus. By using the proper method of extraction and proper binary solvent system, the industry can maximize the extraction of the leaves thus increasing the phenolic content and flavonoid content and subsequently increasing the scavenging ability of each plant. The process of extraction should be economical in order save energy which includes proper usage of chemicals and method of extraction.

There are a few recommendations for the future work of this study. The study should be further improved by adding more chemical analysis. Sulforhodamine B (SRB) Cytotoxicity Assay should be carried for the plant extracts to observe the efficiency of the extracts on human cells. This would properly show the level of effectiveness of phenolics and flavonoids. Superoxide scavenging activity should also be carried out to further study the effect of phenolics on superoxide anion. In mitochondria, 3% of oxygen content is completely changed into superoxide anion which is a major source for free radicals. Hence testing of phenolics and flavonoids on superoxide anion should be carried out.

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Treatment of Palm Oil Refinery Effluent using Advanced Oxidation Process

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Abstract

Palm oil refinery effluent (PORE) is a type of wastewater that produces from palm oil industries. High demand and constant production of refined palm oil in worldwide cause the volume of PORE to be continuously increases. PORE has high level of chemical oxygen demand (COD) and biochemical oxygen demand (BOD) due to the presence of organic matters. These organic matters are harmful to environment such as aquatic lives. Hence, it is essential to treat PORE before discharging it back to environment. In this research, Advanced Oxidation Process is used to treat PORE to reduce COD and BOD level as well as composition of organic matters. The treatment method that is chosen is Fenton Process from Advanced Oxidation Process. For the Fenton process, it uses two chemicals to produce hydroxyl radicals. Then, the hydroxyl radicals produced that have high oxidizing power will break down the organic matters presence in PORE. Thus, COD and BOD level of PORE is reduced and safe to discharge back to environment thus reduce harmfulness to aquatic lives as well. Besides Fenton process, physical treatment conducted for this research in order to study the characteristic of organic matters in PORE. Physical treatment has been conducted by only changing pH and temperature of raw PORE samples without adding chemicals or Fenton reagent. The experiment samples also tested the COD and BOD testing. As a result, 0.5M of Fenton reagent obtained highest reduction of percentage of COD and BOD level which are 63.6% and 61.3% respectively. Furthermore, COD and BOD level of PORE for pH treatment obtained highest reduction at pH 7 which COD and BOD level is 37.5% and 34.9% respectively. Apart from that, temperature treatment of obtained highest reduction at temperature of 80°C which COD and BOD level of PORE is 25.6% and 23.1% respectively.

Keywords: Palm Oil Refinery Effluent (PORE), Wastewater Treatment, Advanced Oxidation Process (AOP), Fenton Process, Hydroxyl Radicals.

1. Introduction

Malaysia is one of the largest palm oil producers in the world and palm oil refinery effluent is the significant pollutants from the palm oil mill [1]. There were approximately 60 million tonnes of palm oil refinery effluent (PORE) produced in year 2010 [2]. High demand of palm oil from worldwide causes the increment of PORE produced after the process. PORE is produced during the process of refinery of palm oil. As a result, refined palm oil will be produced and PORE will be treated as wastewater from the refinery process. PORE contains 95-96% of water, 4-5% of total solids and 0.6-0.7% of oil [3]. PORE that produced from the refinery process contains of oil and grease and suspended solids. There are traces of organic matters presence in PORE. This is due to the chemicals that used during the refinery process. The COD and BOD level of the suspension is high because of the presence of organic matters. BOD stands for Biochemical Oxygen Demand and it measures the amount of oxygen that needed by aerobic organisms in the water to degrade the organic matters whereas for COD stands for Chemical Oxygen Demand and it measures amount of organic compounds in the water [4]. BOD is used to measure the amount of oxygen that required by microorganisms while stabilizing the organic matters that present in PORE while COD measures oxygen equivalent of organic matters in PORE [4]. High level of COD and BOD level could harm the aquatic lives. The high BOD and COD level of PORE could cause death of the aquatic lives and hence ecosystem would be imbalance. Thus, PORE has to be treated to achieve the standard of DOE before discharging it to the environment.

There are several ways to treat the PORE such as biological treatment and physical treatment as well as physical-chemical treatment. These types of treatments aim to reduce COD and BOD level of PORE before discharging back to environment. Wastewater treatment is important for the palm oil refinery process as the process is ongoing for everyday. Hence, many types of treatment are proposed to treat PORE. Currently, PORE is treated by using conventional method which is biological method. The conventional treatment method needed microorganism to breakdown the organic matters that contains in PORE. Since microorganisms are used, an optimum environment must be created for the microorganism to grow. For instance, temperature of the wastewater could not be higher than 30°C. Hence, wastewater has to be cooled down to optimum temperature for microorganisms to grow before starting the treatment. In addition, pH level of wastewater has to be maintained and adjusted to the optimum level. It is to provide optimum and suitable environment for the microorganisms to grow to decompose organic matters that presence in wastewater. Besides, there will be time delayed on treatment when the microorganisms are dead.

In this research, a chemical treatment has been chosen to treat PORE which is Advanced Oxidation Process. There are many types of advanced oxidation process such as Fenton process, Ozonation process, Hydrogen Peroxide Oxidation process, Photocatalytic Oxidation process [5]. For this research, Fenton process from Advanced Oxidation Process has been chosen to treat PORE. Fenton process was discovered by H.J.H Fenton in year 1894 in and he stated hydrogen peroxide could decompose by using iron salt to the form of hydroxyl radicals (*OH) to degrade organic matters [6]. Currently, Fenton reagent is often used in wastewater that are from several industries such as olive oil production industries and dye industries, paper production industries, pharmaceutical industries [6,7]. Fenton reagent that used

in this research consists of iron (II) sulphate and hydrogen peroxide. Fenton reagent generates OH radicals from hydrogen peroxide that have high oxidative power and it obtains general organic pollutant abatement [6].

Then, iron (II) sulphate acts as the catalyst of the Fenton process which catalyses and enhances the production of hydroxyl radicals. The rate of production of OH radicals directly reflects to the duration of decomposition of organic matters in wastewater. When the rate of production of hydroxyl radical is high, the duration needed to decompose organic matters in wastewater would be shorter. Fenton process that chosen in this research could be used at ambient temperature and pressure, hence it is easy to conduct the experiments using Fenton reagent. However, PORE must be maintained at pH 3 because the precipitation of ferric hydroxide will produced when the Fenton reagent is operating at higher pH whereas iron complex ions will be produced when it is operating at pH lower than pH 3 [6]. Overall, it is an effective treatment in decomposing organic matters that are presence in the wastewater.

By applying Fenton Process to treat PORE, organic matters content in PORE could be reduced before it discharges to the environment. Then, as the composition of organic matters is reduced, COD and BOD levels of PORE will be reduced as well. Thus, pollution of the water by PORE is expected to be minimised after treating PORE with Fenton Reagent. In this research, experiments with different parameters of Fenton Reagent were conducted in order to obtain optimum concentration of Fenton Reagent for PORE treatment. Besides, physical treatments such as pH treatment and temperature treatment also were conducted in order to compare with the results of Fenton process. Furthermore, COD and BOD testing of samples are conducted to determine the effectiveness of Fenton Reagent as well as the physical treatments of PORE.

3. Research Methodology

3.1 Overall Research Design

This research is based on quantitative research. The main objective of this research is to decompose organic matters in wastewater (PORE). Hence, initial and final value of BOD and COD level in PORE will be determined. For physical treatment, pH and temperature of raw PORE are changed in order to observe the effect of pH and temperature change on raw PORE without adding Fenton reagent. Whereas for the experiments of chemical treatment were conducting at ambient temperature and pressure as well as maintained the pH of PORE at pH 3. By changing the concentration of the Fenton Reagent, an optimum and suitable concentration of reagent would be obtained to decompose the organic matters in PORE effectively.

3.2 Treatment Methods

3.2.1 Chemical Treatment

Chemical treatment is used to treat PORE in this research. The main chemicals that use would be iron (II) sulphate and hydrogen peroxide. The preparation of Fenton reagent was based on the selected ratio. In this project, the selected ratio for both chemicals was 1:2 which indicates ratio of iron (II) sulphate: hydrogen peroxide respectively. The calculation of required concentration of Fenton reagent is shown in Equation (1):

$$\text{No. of moles} = \frac{\text{Mass of chemical}}{\text{Molecular weight of chemical}} \quad (1)$$

From the Equation 1, number of moles for the Fenton reagent was selected before calculating the required mass for Fenton reagent. Then, mass of chemical indicates the total mass of iron (II) sulphate and hydrogen peroxide and it was prepared based on the selected ratio. Lastly, the molecular weight of chemical indicates total molecular weight of Fenton reagent which is summation of molecular weight of iron (II) sulphate and hydrogen peroxide.

After calculating the required mass of iron (II) sulphate and hydrogen peroxide, Fenton process was then conducted. First, iron (II) sulphate was dissolve in 500ml of PORE sample. Then, pH of sample was adjusted to pH 3 with 0.1M of sulphuric acid. After that, hydrogen peroxide was added into sample. The mixture was then left for 30 minutes for the reaction between PORE and Fenton Reagent to be completed. The experiments were conducted with 0.1M increment from 0.1-0.5M of Fenton reagent. Then, each parameter was repeated until concurrence results were obtained.

3.2.2 Physical Treatment

Physical treatment that use in this project was conducted by adjusting the pH and temperature of PORE. This treatment was conducted with the absence of Fenton reagent. In this treatment, pH range that use for experiments is from pH 2 to pH 10. The difference of pH between each sample was 2. In this treatment, 0.01M of sulphuric acid/sodium hydroxide was added into the raw sample in order to change the pH of PORE. After final pH of raw PORE, COD and BOD testing were conducted.

Then, another batch of experiments will be conducted by changing temperature of raw PORE. The range of temperature will be 20-100°C with 20°C difference for each sample. The sample of PORE will be heated to reach desired temperature. After the heating process, samples will be used to conduct COD and BOD tests as well.

3.3 Sample Testing

3.3.1 COD Testing

In this experiment, COD test was conducted to observe effectiveness of Fenton Reagent and also physical treatment in decomposing organic matters in PORE. The procedure of COD testing was referred to section 5220 C. Closed Reflux, Titrimetric Method for COD from the Standard Methods for the Examination of Water and Wastewater [8]. There were several reagents needed for this testing which are standard potassium dichromate digestion solution, sulphuric acid reagent, ferrion indicator solution, standard ferrous ammonium sulphate titrant (FAS). Thermoreactor Type ECO 8 instrument was used for COD testing. This COD testing required a blank sample for reference purposed. Blank sample needed distilled water as the sample of testing. First step of the test was to wash the culture tube with 20% H₂SO₄, the aim was to prevent any contamination of the culture tube [8]. Then, placed 2.5ml of sample in culture tube and potassium dichromate digestion solution was added. After that, 3.5ml of sulphuric acid reagent was added. Lastly, the testing tube was closed and gentle mixing by inverting the tube for several times. For this testing, sample

heated to 150°C and left to reflux for two hours. Then, Ferroin indicator and FAS were added to the sample for titration after it cools to room temperature. The end point of titration was the colour changed of sample from blue-green to reddish brown [8].

There are some precautions needed to take in account during the testing. Face shield and glove was worn when handling the samples. The reason was there will be some gases releases during the heating process of the samples. Besides, the samples were heated to 150°C which required glove to protect hand when handling.

3.3.2 BOD Testing

For BOD test, it was referred to section 5210 B. 5-Day BOD Test from Standard Methods for the Examination of Water and Wastewater [8]. The duration of testing for BOD was five days for each sample. The model of instrument that use for testing was Eutech Instrument (TN-100). Before conducting the test, the pH of sample of PORE was determined. Then, it was adjusted to the optimum range of pH 7.0-7.2 and sulphuric acid or sodium hydroxide can be used to adjust the pH of the sample.

Besides, optimum temperature which samples needed adjust to the temperature of 20 ± 3 °C [8]. After preparing the samples, BOD test was conducted. The samples were diluted for experimental testing. First, 1ml of diluted sample added into the bottle and dilution water will be added until the neck of bottle for further dilution. Next, aluminium foil was used to wrap the solution bottle for incubation purposed after gentle mixing. In this testing, blank solution which contains deionized water was used as reference of BOD test. The procedure to prepare blank solutions was identical as procedure to prepare BOD samples for PORE. Then, value of Dissolved Oxygen (DO) of sample was measured from day-0 to day-5.

3.4 Data Analysis

For the data analysis, results of experiments as well as sample testing were collected for further analysis. Each parameter was repeated until concurrence value of results obtained. One of the main objectives of this project is to determine the effectiveness of Fenton Reagent in decomposing organic matters. Hence, the data for initial and final reading of the treated sample such as COD and BOD were recorded. Then, all the results were tabulated in table forms in order to calculate the efficiency of Fenton Reagent in decomposing organic matters. Besides, data of experiments for physical treatment were recorded and tabulated in a graph as well.

4.0 Results and Discussion

4.1 Chemical Treatment

4.1.2 Fenton Process

Fenton Process is a type of Advanced Oxidation Process that utilizes iron (II) sulphate and hydrogen peroxide to produce free radicals. The free radicals that produce have high oxidizing power and it is an effective way to decompose organic compounds due to the unselectively of the free radicals [5]. In this project, Fenton process with different concentrations was chosen to treat PORE and the effectiveness of Fenton reagent was determined as well. The effectiveness of Fenton reagent was determined by the COD and BOD testing.

4.1.2 pH of Fenton

There is a condition when conducting Fenton process for PORE which it has to be adjusted at pH 3. The organic compounds removal efficiency decreases when the pH level of Fenton process is higher than pH 4.0 and also when pH level is lower than pH 3 [9]. Then, the outcome of this project research shows that percentage of removal of organic compounds increases as the concentration of Fenton reagent increases. This is because at different pH, production of hydroxyl radicals would be affected as well. The hydroxyl radicals have oxidation potential of 1.8V and 2.7V when it is at neutral pH and acidic solution respectively [10, 11]. However, when pH of Fenton reagent is lower than pH 3, hydroxyl radicals will be scavenging by the hydrogen ions. Hence, it causes the reduction in generation of hydroxyl radicals [12]. In addition, hydrogen peroxide will self-decompose when the pH of solution is higher than pH 3 [13].

4.1.3 Concentration of Fenton Reagent

In this research, range of concentration of Fenton reagent was set at 0.1M to 0.5M with the difference of 0.1M for each testing. Table 1 shows the results for Fenton process that conducted to treat PORE and the COD as well as BOD results are expressed as mean value of the results.

Table 1. Results of PORE after treated with Fenton Reagent

Parameters	Raw PORE	Concentration of Fenton Reagent (M)				
		0.1	0.2	0.3	0.4	0.5
pH	5.76	3.00	3.00	3.00	3.00	3.00
COD (mg/L)	1408	960	832	704	640	512
BOD (mg/L)	1359	913	794	680	577	494

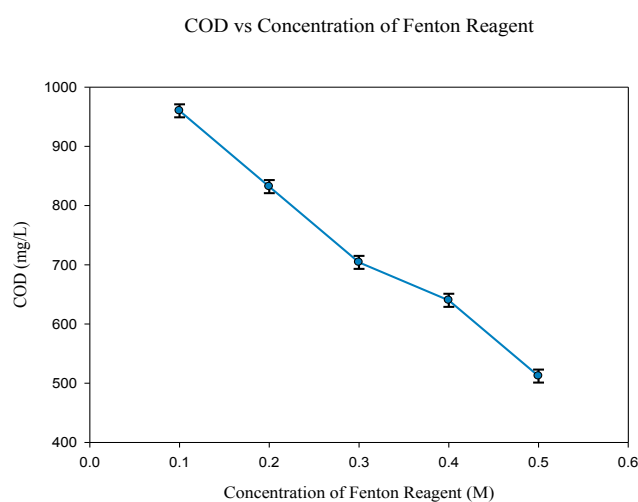


Figure 1: Results of COD level of PORE after Fenton Process Treatment with standard deviation value

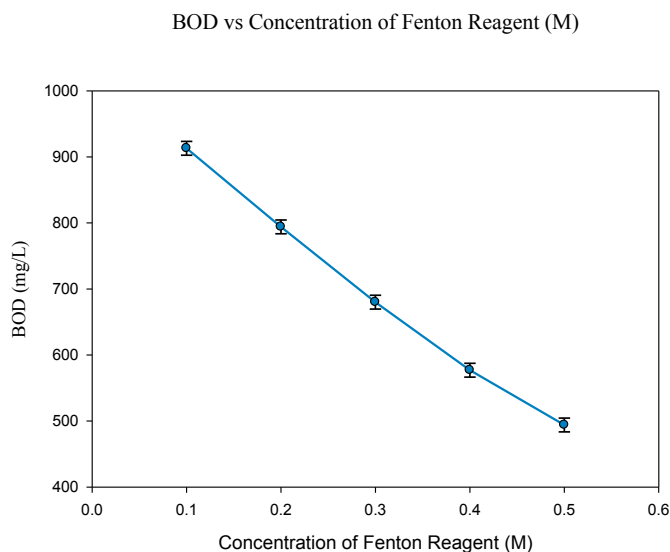


Figure 2. Results of BOD level of PORE after Fenton Process Treatment with standard deviation value

As refer to Table 1, it shows that the COD value and BOD for each sample are reduced after the Fenton treatment. Form Table 1, 0.5M of Fenton reagent removed highest amount of organic compounds in PORE. It reduced total of 896 mg/L of COD and 865 mg/L of BOD level. The reason is because the hydroxyl radicals that produced in 0.5M Fenton reagent is highest among the samples. Moreover, sample that used 0.1M of Fenton reagent reduced the least amount of COD and BOD level. From the data, it shows that sample react with 0.1M of Fenton reagent has only removed 448 mg/L of COD level and 446 mg/L of BOD level.

Furthermore, Fig. 1 and Fig. 2 show the trend of COD and BOD reduction in each sample after the treatment. The values of COD and BOD level were included the respective standard deviation for Fig. 1 and Fig. 2. The standard deviation for COD and BOD level is 11 mg/L and 10.5 mg/L respectively. The concentration of Fenton reagent affects the outcome of treatment due to the hydroxyl radicals that produced during the treatment process. At higher concentration of Fenton reagent, larger amount of hydroxyl radicals could be produced for decompose the organic compounds unselectively in PORE [6, 14]. Fenton reagent is effective in decomposing organic compounds in PORE in which the effectiveness is measured by obtaining reduction in COD and BOD level. Table 2 shows the percentage of reduction of COD and BOD level in Fenton process with different concentration.

Table 2. Percentage of Reduction of COD and BOD level by Fenton Process

Percentage of Reduction (%)	Concentration of Fenton Reagent (M)				
	0.1	0.2	0.3	0.4	0.5
COD (mg/L)	31.8	40.9	50	54.5	63.6
BOD (mg/L)	32.8	33.2	49.9	57.5	61.3

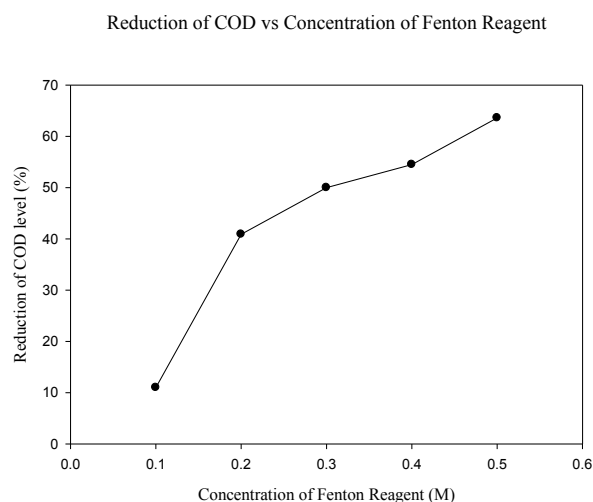


Figure 3. Percentage of Reduction of COD level in PORE

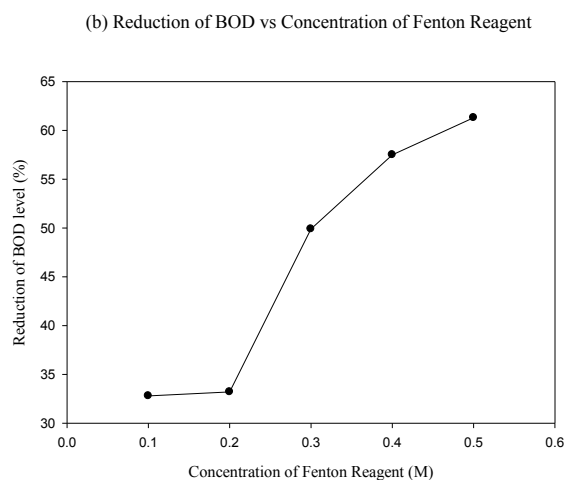


Figure 4. Percentage of Reduction of BOD level in PORE

As refer to Table 2, Fenton reagent that reduced highest amount of COD and BOD level is 0.5M while 0.1M reduced the least amount of COD and BOD level. From the data, 0.5M of Fenton reagent reduced 63.6% of COD level and 61.3% of BOD level whereas 0.1M of Fenton reagent reduced 31.8% of COD level and 32.8% of BOD level. Hence, the results of Fenton process have only approximately 60% of COD and 35% of BOD reduction obtained respectively.

During the Fenton process, the reagent that reacted with organic compounds in PORE would break down the organic compounds into carbon dioxide gas and water. When the concentration of Fenton reagent is high, more carbon dioxide would be

produced during the experiment. There were bubbles formed and gas released during the process due to the decomposition of organic compounds. The organic compounds will be released carbon dioxide gas, water and salts will be formed after the treatment [5, 6]. Furthermore, there was a layer of precipitate deposited at the bottom of the beaker. The layer is iron salt which is a result from the decomposition of organic compounds. The gas releases and salt formed indicates that COD and BOD level of PORE reduced. The Fenton process is more effective when concentration is higher as there were more available hydroxyl radicals that can attack the organic compounds readily [9]. Hence, COD and BOD level of PORE would be reduced.

4.1.4 Effects of Concentration of Iron (II) Sulphate and Hydrogen Peroxide

There was some deposition of salts after the Fenton process that caused by the high concentration of Fe^{2+} to produce Fe^{3+} (ferrous ions) which are less reactive towards hydroxyl peroxide. Hence, the effectiveness of Fenton reagent would be reduced. In addition, when the iron salts formed, it causes additional cost has to spend in order to get rid of the iron sludge [15]. Thus, concentration of iron is important to obtain effective Fenton Process. Besides, concentration of hydrogen peroxides is also a crucial factor for the Fenton process. For instance, hydroxyl radicals that excess will formed other structure with the organic compounds instead for decompose it [9]. As a result, more research should be done to obtain better and more effective Fenton process to decompose organic compounds in PORE.

4.2 Physical Treatment

Besides Fenton process, physical treatment also conducted in order to study the characteristic of organic compounds in PORE. First, the organic compounds that contains in PORE are mostly free fatty acids that obtained after the degumming process from the refinery process of palm oil [16]. There are some saturated and unsaturated fatty acids contain in PORE. The fatty acid sensitive towards pH and temperature changes in which the bonds in fatty acid will be broken down and form a new product.

In this research, pH and temperature treatment were conducted on PORE with different range. After the treatment, COD and BOD level tests were conducted for the results of physical treatment. Table 12 and Table 13 show the results of the physical treatment.

Table 3. COD and BOD Results of pH Treatment

pH	COD (mg/L)	Percentage Reduction (%)	of BOD (mg/L)	Percentage Reduction (%)
3.0	576	25	532	23
5.0	672	12.5	641	7.2
5.76 (RAW)	768	-	691	-
7.0	480	37.5	450	34.9
9.0	512	33.3	483	30.1

For the pH treatment, 0.1M of sulphuric acid and sodium hydroxide were used to adjust the pH of the PORE. In this experiment, there was no Fenton reagent added

inside the PORE. From Table 3, it shows that pH does affect the composition of organic compounds. This is because the organic compounds will change structure when it at different pH. Besides, changes of pH would cause organic compounds to change its structure into another stable type of organic compound as well [17]. Hence, the COD and BOD level of pH treatment has slight reduction which is less than 40% for overall pH treatment. Next, temperature treatment was conducted by heating up PORE with Bunsen burner. Table 4 shows the results of temperature treatment for this research.

Table 4. COD and BOD results of Temperature Treatment

Temperature (°C)	COD (mg/L)	Percentage Reduction (%)	of BOD (mg/L)	Percentage Reduction (%)	of
22 (RAW)	1248	-	1217	-	
40	998	20	994	18.3	
60	1064	14.7	986	19	
80	928	25.6	936	23.1	
100	1023	18	964	20.8	

From Table 4, it shows that percentage of reduction of organic compound in temperature treatment is less than 30%. This situation occurs due to the organic compounds that contains in PORE will decompose into another stable compound when the temperature is high [18]. In contrast, saturated organic compounds in the solution were increased. Consequently, composition of saturated acids was increased when composition of unsaturated acids reduced. As a result, COD and BOD level of PORE is not reducing drastically because there is minimal reduction of organic compounds in PORE.

4.4 Error Analysis

There were errors occurred during the experiments that conduct for chemical and physical treatment. For example, there will be errors occurred during the preparation of reagent for the experiments. The error could occur when distilled water was measured by using measuring cylinder during the process of preparation of reagent for chemical treatment. The 50ml measuring cylinder has uncertainty of $\pm 0.75\text{ml}$. So for every 50ml that measured using measuring cylinder will have almost 1ml of uncertainty. It would affect the dilution preparation of reagents for the treatment because volume of distilled water measured to dilute chemicals might not be the same as desired.

Secondly, there would be transferral error occurred as well when conducting the experiments. This is due to the experiments of this research required to transfer chemicals or distilled water to the other apparatus for further testing. For example, COD testing samples were required to transfer from a small tube into the conical flask. This step of transferring is to allow the titration with FAS to be much easier. Hence, there would be some leftover COD samples inside the small tube during the transferring process. As a result, the titration result would be affected as well.

There is a way to minimise the errors that occurred during the experiments. The way is to repeat the experiments until the concurrence values are obtained. Then, all the apparatus and equipment used must be in good conditions such as no crack and all the label or indications on the apparatus are cleared. Lastly, all the reagents that used in treatments must be handled with care. It is to avoid contaminations happens to the reagents that have been prepared for the experiments. The contamination of reagents affects the final results of testing and hence reliability of final results of treatments will be reduced. Overall, precautions have to be taken in to account in order to minimize the errors that occur during the treatment process.

5.0 Conclusions

In a conclusion, the objectives of this research which are to treat PORE with 5 parameters of Fenton reagent to obtain at least 50% of reduction of COD and BOD level as well as study the characteristics of organic compounds in the PORE were achieved. The objectives of this research could be achieved due to deep study of experiments and literature studies as well as methods of analysis have been completed. It has been concluded that 0.5M of Fenton reagent has the highest efficiency of reducing COD and BOD level of PORE as it reduced 63.6% and 61.3% of COD and BOD level respectively. The percentage of reduction of COD and BOD level for 0.5M of Fenton reagent is the highest compared to the other parameters while the 0.1M of Fenton reagent has lowest of percentage of reduction of COD and BOD level. For 0.1M of Fenton reagent, COD and BOD level that reduced was 31.8% and 32.8% respectively. Besides, physical treatment that conducted experiments obtained reduction of COD and BOD level as well. For pH treatment, the highest reduction of COD and BOD level obtained at pH 7. And the result for percentage of reduction of COD and BOD level is 37.5% and 34.9% respectively. While for temperature treatment, the highest reduction of COD and BOD level obtained at temperature of 80°C. Then, the results of reduction of COD and BOD level for the parameter are 25.6% and 23.1% respectively. The physical treatment reduced lower percentage of COD and BOD due to the organic compounds in PORE was not decomposed fully. Instead, some of the organic compounds changed structure to a more stable form in which from unsaturated fatty acids to saturated acids. Overall, chemical treatment has higher reduction of COD and BOD level because organic compounds in PORE were decomposed fully during the Fenton process whereas organic compounds did not decompose fully during physical treatment process which results in lower reduction in COD and BOD level.

There is always room for improvement hence some recommendations are recommended for the future work of this project. First recommendation is the concentration of Fenton reagent could be fixed at wider range such as from 0.1 to 1.0M. The study about effectiveness of Fenton reagent could be done more intensively with the help of wide range of Fenton reagent for chemical treatment. Besides, the limitation of Fenton reagent could be studied as well by using wider range of concentration. Furthermore, more testing could be done such as HPLC testing in order to determine the content of PORE before and after the treatment and effectiveness of Fenton reagent can be further study as well. Apart from that, more research must be done to study to improve the mechanism of Fenton process on the PORE in order to scale up the Fenton process for PORE treatment process in

industries scale. For instance, research on widen the range of pH required for Fenton process as well as method for reduction of formation of iron sludge during the Fenton process should be studied in order to optimized the Fenton process.

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Characterization and Theoretical Modelling of DES Based Nano-Fluid

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Abstract- In this research, the stability of functionalized Graphene (Graphene Oxide) nano-particles dispersed in, different deep eutectic solvents (by molar ratios) base liquid composed of ethylene glycol as a hydrogen bond donor and methyl tri-phenyl phosphonium bromide as a salt, at weight fractions of 0.01%, 0.02% and 0.05% was studied and evaluated, quantitatively and qualitatively. This was done using zeta potential analysis to assess the likelihood of settling and optical microscope to observe the dispersion quality and evaluate the sizes of cluster at different weight fractions. Along with this, the thermal conductivity data of the nano-fluid samples measured at temperatures of 25 °C, 30 °C, 40 °C, 50 °C, 60 °C and 70 °C was analyzed and compared with predictions of theoretical models. It was found generally that classical models under-predicts the thermal performance of the nano-fluid samples. Moving-particles model namely Rashmi and Kumar models showed conflicting prediction performance. While, Rashmi model can predict thermal conductivity at some temperatures with errors as low as 0.1%, the Kumar model lowest error is found to be around 10% and the highest error is around 56%. A simple empirical modification to the Kumar model is presented which improves the predictions accuracy to that of Rashmi model.

Keywords: Nano-Fluid, DES, Graphene Oxide, Thermal Conductivity, Viscosity.

1. Introduction

Fluids are used as heat carriers in heat transfer systems in many chemical and process industries. The increase of efficiency of these heat transfer systems is strongly related to the thermal conductivity of the heat carrier fluid. It is well known that the suspension of solid particles in a liquid improves the thermo-physical properties such as thermal conductivity of the host fluid. The nano-particles suspension is favored due to their smaller size which overcomes clogging and sedimentation-prone issues associated with micro-sized particles [1]. Fluids in which nano-particles are dispersed are known as nano-fluids, a name which was coined by Choi in 1995 [2]. Though, as time elapses, nano-particles are prone to self-agglomeration due to their high surface energy. The agglomerates size can be as large as micro-sized particles. These large agglomerates are prone to sedimentation which lowers the enhancement of thermo-physical properties [3]. Therefore, the stability of the nano-particles suspension is very critical in evaluating the thermal performance and efficiency of nano-fluids. The suspension can be stabilized through the use of additives such as surfactants, chemical functionalization, homogenization, sonication and many other techniques [3]. However, the use of additives affects the thermo-physical properties of the nano-fluid. Another route to stabilize the nano-particles suspension is to rely on vibration and mechanical means. Nevertheless, agglomerates will form again as the time elapses [4]. Therefore, vibrations and mechanical techniques deal with symptoms by breaking agglomeration rather than addressing the root causes and eliminating them to prevent the formation of agglomerates.

Traditionally, the nano-fluid preparation has been researched on conventional heat carriers such as water and synthetic oil. Adding to their low thermal performance, the stability of nano-suspension in these base fluids is rather limited to the use of additives. New class of fluids has emerged known as ionic liquid which has thermo-physical properties far superior to conventional liquids. It is reported that nano-particles such as graphene and multi-walled carbon nano-tubes can be dispersed in ionic liquids without the use of surfactants [3]. Unfortunately, many reports have pointed out the hazardous toxicity of ionic liquids along with their expensive synthesis [5]. This has led to the emergence of deep eutectic solvents (DES) which are far more environmentally friendly owing to their biodegradability and non-toxicity. Along with that, their synthesis is far cheaper and exhibit similar thermo-physical properties as ionic liquids [5]. This novel class of fluids can be very promising to resolve issues related to the stability of nano-particles suspension. Along with that, the graphene nano-particles have very high thermal conductivity. Therefore, the combination of DES with graphene nano-particles to produce DES based graphene nano-fluid is very promising. In this research, a DES based nano-fluid is produced using graphene oxide as nano-particles. The produced nano-fluid is characterized qualitatively and quantitatively to assess the stability and the dispersion quality. Furthermore, the thermal conductivity data of the DES based fluid used in this research is analyzed, evaluated and compared with predictions obtained from available theoretical models.

2.0 Experimental Procedure

2.1 Chemical

Ethylene glycol and methyl tri-phenyl phosphonium bromide (MTBP) which were used in the DES synthesis were obtained from Merck Millipore at a high purity of > 99%. The DESs were prepared at molar ratios of 3:1, 4:1 and 5:1 of ethylene glycol to MTBP respectively. The graphene nano-particles were purchased from the Graphene Supermarket, United States with high purity of 98%. The graphene nano-powder has an average thickness of 60 nm and a particle size in the range of 3 – 7 microns.

2.2 Analytical and Measuring Instruments

In this research, the Zetasizer Nano device (from Malvern Instruments) was used to characterize the stability of the samples by means of measuring the zeta potential. The Swift M10D Series Digital Microscope was used to characterize the dispersion quality of the graphene oxide nano-particles in DES based nano-fluid. The used thermal conductivity data was measured at different temperatures using KD 2 Pro.

3.2 DES and Nano-Fluids synthesis

In this research graphene nano-particles were dispersed in DES base fluid. DES samples with one salt namely methyl triphenyl phosphonium bromide (MTPB) is to be obtained. MTPB is combined with a hydrogen bond donor (HBD) namely, ethylene glycol in different molar ratios of salt:HBD to produce different DESs. The DES base fluids are to be prepared by mixing the salt with the HBDs in the prescribe molar ratios by a magnetic stirrer at a temperature of 353.15 K and a high rpm until a homogenous and colorless liquid is observed [8]. The rpm value was increased until high vortex was observed. The rpm value which creates vortex is inversely proportional to the size of the magnetic bar.

The GO nano-particles were dispersed at low weigh fraction of graphene nano-particles. Wang et al [9] stated that at weight fractions up to 0.09%, the graphene Ion-Nano-fluid will not be stable and will coagulate in a couple of hours. In their study, the weight fraction of the graphene nano-particles is restricted to the range of 0.03% - 0.06%. In this study, 0.01%, 0.02% and 0.05% weight fractions are used. These weight fractions are similar to that used by Wang et al, and this will make the comparison between the results of the two studies possible and more meaningful. The suspensions then were homogenized using direct probe sonication for 15 minutes using (Branson, SLP-T model). This was followed by water-bath sonication at room temperature for 1 hour using (Elma, ELMasonic-P). (Table 2) shows the composition of DES, GO weight concentrations and the designation for the samples which are used in this research.

Table 1. DES and Nano-Fluid Sample Details

<i>(HBD)</i>	<i>(Salt)</i>	<i>Molar Ratio (HBD/Salt)</i>	<i>DES Sample</i>	<i>NF Sample</i>	<i>GO Wt%</i>
Ethylene glycol	MTPB	3	DES 1	<i>GNF1</i>	0.01
				<i>GNF 2</i>	0.02
				<i>GNF3</i>	0.05
		4	DES 2	<i>GNF 4</i>	0.01
				<i>GNf 5</i>	0.02
				<i>GNF 6</i>	0.05
		5	DES 3	<i>GNF 7</i>	0.01
				<i>GNF 8</i>	0.02
				<i>GNF 9</i>	0.05

2.4 Thermal Conductivity Measurements

The thermal conductivity was measured using thermal properties analyzer KD-2 Pro. Calibration was done using standard glycerin to inspect the accuracy of the probe. A water-bath was used to heat and maintain the nano-fluid samples at different temperature. Three readings were taken at each temperature for each sample. Average values were used to represent the thermal conductivity of the DES based nano-fluid. The readings were taken at temperatures of 25 °C, 30 °C, 40 °C, 50 °C, 60 °C and 70 °C. The measured thermal conductivities were compared with those computed or predicted using the theoretical models in Table 1. This allows evaluating how well the existing theoretical models predict the behavior of DES based nano-fluid.

3. Methodology and Data

3.1 Thermal Conductivity Models

Table 1 shows the thermal conductivity models which are used in this research. The parameters of these models are volume fraction ϕ , thermal conductivity coefficient k of the nano-particle and the base fluid, l particle length, d particle diameter, r particle radius and μ fluid viscosity. The terms n , C and T_0 are constants. The models were selected based on the parameters accessibility through experimental measurements. The subscripts *eff*, *bf*, *p* refer to the effective property of nano-fluid, base-fluid and nano-particles respectively. The symbol k_B represents the Boltzmann constant. The term classification in the right side of the Table 1 shows the basis mechanism based on which the model was derived. The classical models are derived based on the assumption of motionless particles [6]. The Rashmi model is derived from Patel's model [7]. The model was modified to suit application to nano-tube shaped particles. Moreover, the liquid is assumed to be spherical in shape.

The ability of the classical models to predict the thermal conductivity of DES based nano-fluid was examined using the thermal conductivity data obtained at room temperature. For Rashmi's and Kumar's model, the ability for these two models to predict the behaviour of DES based nano-fluid was examined for all the temperatures

since both models are temperature and volume fractions dependant. The two models were attempted to be fitted with the experimental data and the quality of the resulting plot indicated how well each model predicts the behaviour of DES based nano-fluids. This was done by the grouping the unknown sub-variables and constants into one main variable. Accordingly, the Rashmi and Kumar models were simplified to the form shown in Equations 3.2 and 3.3, respectively.

$$k_{eff} = k_f + \frac{k_p \phi C_0}{(1-\phi)} + C_1 \phi (T - T_0) \quad (1)$$

$$k_{eff} = k_f + \frac{\phi}{(1-\phi)} T C_0 \quad (2)$$

In this paper, the author suggests an empirical modification for the Kumar model to include a power variable which controls the volume fraction term in the Kumar model. The inclusion of this variable into Kumar model was found to increase the predictions accuracy for the thermal behaviour of the particular DES based nano-fluid that this research is based on. Equation (3.4) shows the modification made to the Kumar model.

$$k_{eff} = k_f + \left(\frac{\phi}{(1-\phi)} \right)^n T C_0 \quad (3)$$

Table 2. Thermal Conductivity Models

Ref	Model Name & Formulation	Classification
[6]	Maxwell $k_{eff} = \left[\frac{k_p + 2k_{bf} + 2(k_p - k_{bf})\phi}{k_p + 2k_{bf} - (k_p - k_{bf})\phi} \right] k_{bf}$	Classical
	Hamilton and Crosser $k_{eff} = \left[\frac{k_p + (n-1)k_{bf} - (n-1)(k_{bf} - k_p)\phi}{k_p + (n-1)k_{bf} + (k_{bf} - k_p)\phi} \right] k_{bf}$	
	Jeffrey $k_{eff} = \left[1 + 3\beta\phi + \phi^2 \left(3\beta^2 + \frac{3\beta^3}{4} + \frac{9\beta^3}{16} \frac{\chi + 2}{2\chi + 3} + \frac{3\beta^4}{2^6} + \dots \right) \right] k_{bf}$	
	Bruggeman $\phi \left(\frac{k_p - k_{eff}}{k_p + 2k_{eff}} \right) + (1-\phi) \left(\frac{k_{bf} - k_{eff}}{k_{bf} + 2k_{eff}} \right) = 0$	
[7]	Rashmi $k_{eff} = k_{bf} \left[1 + \frac{k_p \frac{2\phi(r_p + l_p)}{r_p l_p}}{k_{bf} \left(\frac{3(1-\phi)}{r_{bf}} \right)} \right] + \frac{C\phi(T - T_0)}{r_{bf}^2 l_{bf}^2 \mu_{bf}} \ln\left(\frac{l_p}{d_p}\right)$	Carbon Nano-Tube
[8]	Kumar $k_{eff} = k_{bf} + c \frac{2 k_p T}{\pi \mu d_p^2} \frac{\phi r_{bf}}{(1-\phi)}$	Brownian Motion

4. Reported Outcomes

4.2 Zeta Potential Analysis

The zeta potential analysis was performed for nano-fluid samples GNF 4, GNF 5 and GNF 6. The zeta potential values for the aforementioned nano-fluid samples were found to generally show an average zeta potential value of 25 mv which indicates a moderate stability [9]. Fig 1 shows a scatter plot for the zeta potential values for the tested nano-samples.

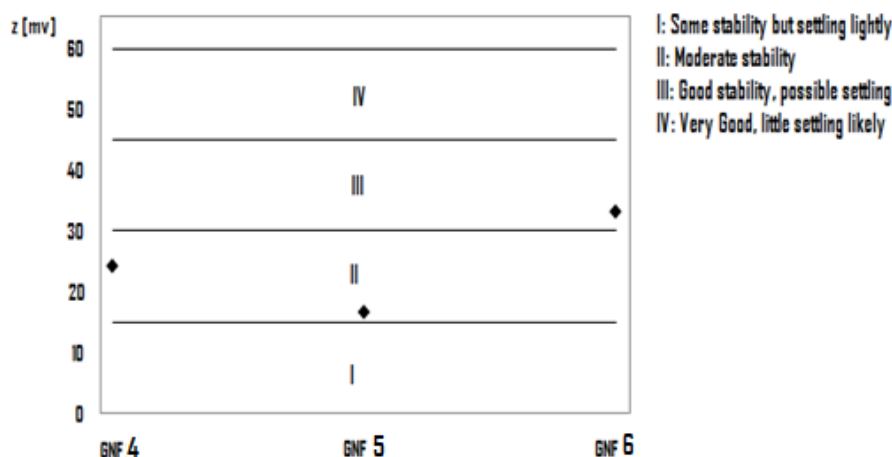


Figure 1. Zeta Potential Values

It can be seen from Fig 1 that the zeta potential value is highest for GNF 6 and lowest for GNF 4. The result indicates that at weight fractions of 0.01% and 0.05%, the stability is higher compared to in-between weight fraction of 0.02%. Moreover, the zeta potential value for GNF 24 falls in the region of good stability. The zeta values of GNF 5 and GNF 6 fall in the region of good stability with the zeta value of GNF 4 being closer to the area of moderate stability and GNF 5 being closer to the area of some stability with light settling. It is to be noted that these readings have been taken after a period of about 3 – 4 months. This shows a high stability for DES based nano-fluids, moreover zeta potential values for fresh samples prepared under the same conditions are more likely to show higher zeta potential values judging from the results shown in Fig 1.

4.2 Optical Microscope Results

Fig 2 shows the dispersion for nano-fluid samples GNF 2 as captured using 40X magnification lens. It can be seen that there is generally a good dispersion of the graphene oxide nano-particles (GONPs) in the DES base fluid. Optical measurements were taken of the clusters observed in each sample. It is to be noted that since this is a normal light microscope, the measurements do not give an exact and accurate sizes of

the cluster in the nano-fluid samples, however it can give an impression or qualitative assessments of the cluster sizes in each nano-fluid sample. In this paper, the cluster sizes are measured and represented by the length size as observed and measured using the optical microscope. In Fig 3, a plot shows the average extent of the cluster size for each samples based on the cluster length.

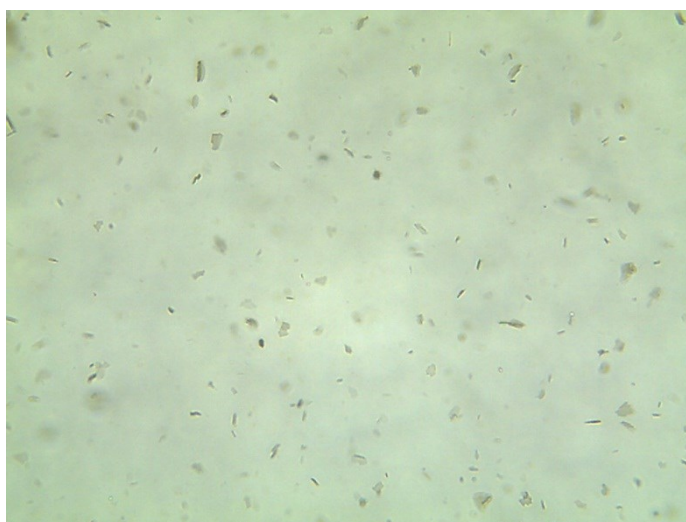


Figure 2. Optical Micrograph of GNF 2

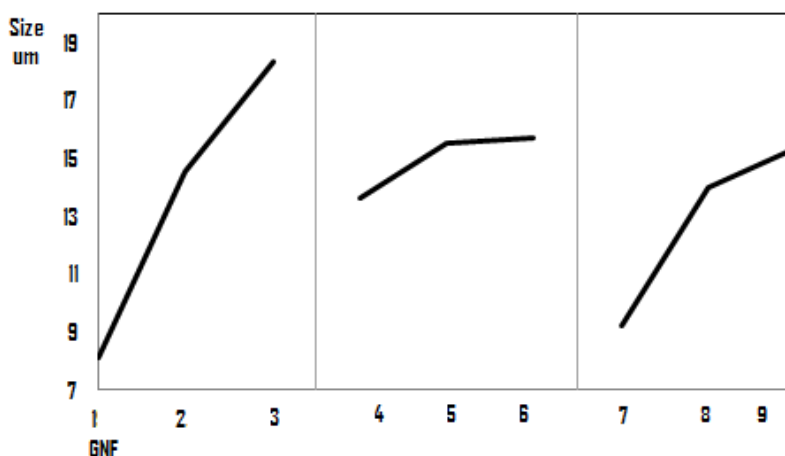


Figure 3. Cluster Size as Measured Using 40X Magnification

4.6 Thermal Conductivity Models Analysis

4.6.1 Classical Models

The classical models were found to have the same prediction for the thermal conductivity of the DES based nano-fluid. The classical models at room temperature generally under-predicted the actual performance of the DES based nano-fluid samples except for samples GNF 7 and GNF 9. The prediction errors or deviation of

the classical models is shown in Table 2. The errors for samples GNF 7 and GNF 9 is quite low which shows that DES 3 based nano-fluid samples do not generally exhibit superior enhancements of thermal conductivity at room temperature as when compared with DES 1 based nano-fluid samples.

Table 2. Classical Model Percentage Errors

Sample	Error%
GNF 1	-22
GNF 2	-25
GNF 3	-31
GNF 7	3
GNF 8	19
GNF 9	-2.5

4.6.2 Moving Particles Models

Fig 4 shows the errors of predictions of Kumar model, Rashmi model and the Kumar modified model for thermal conductivity data at temperature of 50 °C. It can be seen from Fig 4 that the empirically modified Kumar model has the smallest errors as when compared with the other two models. Rashmi model has comparable small deviation as well, but for the pure Kumar model the deviation is relatively large. It is to be noted that the quality of predicting the thermal performance of DES based nano-fluid under research depends on the surrounding temperature and the molar ratio of HBD to salt. Generally, the Rashmi model was found to predict the thermal conductivity of DES 3 better at temperatures of 30 and 60 °C.

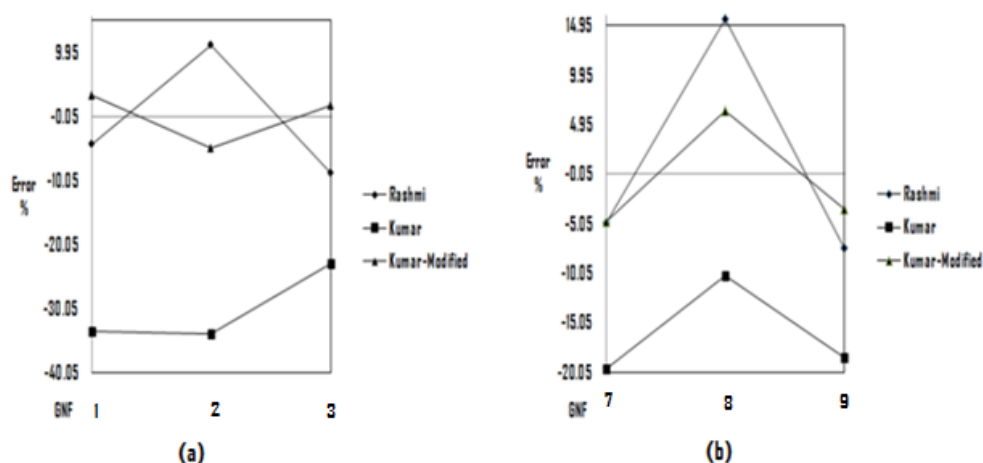


Figure 4. Prediction Accuracy of Brownian-Motion Models At T = 50 °C

6. Conclusions

The DES based nano-fluid was prepared at different molar ratios of the HBD and the salt. The zeta potential values and optical micrographs indicate a good stability and uniform dispersion. The classical models were found to under-predict the actual performance of the DES based nano-fluid. Generally DES 1 exhibit superior performance at room temperature meanwhile the enhancement of DES 3 at room temperature is less significant. The Rashmi and the modified Kumar show better prediction of the thermal performance of DES based nano-fluid.

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Fractionation of Sugar from Hydrolysis of Pretreated Cellulose by Ultrafiltration and Reuse of Enzyme.

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Abstract

Bioethanol process using cellulosic materials have been emerging a interesting field with a high potential of replacing petroleum-based fuel, as a future alternative. This work emphasized on improvement of enzymatic hydrolysis of alkaline NaOH-pretreatment cellulose by applying ultrafiltration membrane 10 kDa cutoff in order to minimise sugar inhibition on enzymes, reuse enzyme in hydrolysis and recover sugar for subsequent fermentation. An improvement in the methodology of enzymatic hydrolysis with ultrafiltration was made that the membrane was installed at the end of tube connecting with a peristaltic pump to continuously remove glucose from hydrolysis reaction hence sugar was unable to inhibit enzyme activity and enzyme was retained inside reactor for reusing purpose. The combination of NaOH 1M alkaline pretreatment, enzymatic hydrolysis of cellulose with the optimum 3% enzyme dosage, ultrafiltration 10 kDa cutoff was evaluated to obtain the highest sugar concentration at 266mg/ml after 6 hour hydrolysis. In comparison between hydrolysis with ultrafiltration and hydrolysis without ultrafiltration, the sugar concentration in hydrolysis with ultrafiltration was very much higher than that in hydrolysis without ultrafiltration in all enzyme dosages (1.5%, 3%, 6%). The hydrolysis with filtration produced time a profile in six hours with continuously significant increase in sugar concentration. Only a small reduction initially for 1.5% dosage and no reduction in sugar concentration in 3% and 6% dosage. Hence the effect of product inhibition in hydrolysis was minimized subsequently. In addition, a direct relationship between sugar concentration inside hydrolysis reactor, enzyme dosage and rate of sugar removal was observed during the hydrolysis process. Higher enzyme dosage in hydrolysis required a higher rate of sugar removal sufficient to avoid inhibition in hydrolysis reaction.

Keywords: enzymatic hydrolysis of cellulose, product inhibition, ultrafiltration, reuse of enzyme cellulase, alkaline pretreatment, Cellic Ctec enzymes.

1. Introduction

Technology of cellulose-based ethanol production has been continuously advanced over the past decades with progressive efforts of making the process more cost-effective and reachable for large-scale industrial production. Hence, nowadays bioethanol is considered as a very potential alternate to conventional fossil fuel usage causing environmental concerns such as green-house effects and global warming. Feedstock containing cellulose to produce bioethanol comes from two main sources, i.e., the first generation (sugar, and starch like corn, wheat, soya, and grains) and the second generation (agricultural crop residues like palm empty fruit bunches, sugar bagasse and corn stovers). However, it was discussed that the first generation feedstock causes a dilemma and a debatable issue on food versus fuel due to its negative impacts on regional water source, biodiversity, soil quality [1, 2, 3, 4, 5]. In contrast, the second generation feedstock from non-food source is able to avoid such issues and create a newly environmental-friendly way to reuse cellulosic biomass by producing a value-added ethanol product.

The production of bioethanol from cellulose consists of sub-processes namely a) pretreatment of cellulose for more susceptibility as well as increase in enzymatic accessibility, b) hydrolysis of cellulose to sugar, c) fermentation of sugar to ethanol to subsequent product purification. Research and development have been on the progress to manage and optimize these sub-process in order to improve its both technological and economic feasibilities [6]. Pretreatment of cellulose plays an important role, which had an impact on hydrolysis later. Without pretreatment, only 20% out of total cellulose are converted to glucose [17]. This is due to the reason that the recalcitrant structure of cellulose was disrupted, results in an decrease in degree of polymorization. Hence cellulose after pretreatment is more susceptible and accessible for enzyme to hydrolyze. [18]. Methods of pretreatment are various and depends on the economic factor, type of feedstock, severity degree and so on. Unlike acid pretreatment causing a severe corrosion on equipment and generating undesirable inhibiting byproducts, alkaline pretreatment is safer to use, minimize corrosion and more preferable in the industry of bioethanol production [15, 16]. In addition, hydrolysis by using enzymes named cellulases is more preferable in cellulosic bioethanol process due to its advantages in term of lower energy consumption, limited formation of inhibiting byproducts in subsequent fermentation, high sugar yield, operating under mild conditions compare to acid hydrolysis [7, 8]. On the other hand, two major disadvantages existing as obstacles in enzymatic hydrolysis of cellulose are accessibility for enzyme to cellulose and sugar inhibition on enzyme activity. These results in an increase in overall production cost.

To overcome the obstacles in the usage of enzyme cellulases in hydrolysis, research and development in two strategies have been conducted firstly to decrease the crystallinity of cellulose with strong solvents hence improve enzyme accessibility and secondly to reduce product inhibition by the removal of sugar from the hydrolysis process [6]. This paper will focus on the second strategy of reducing product inhibition.

The application of membrane separation in hydrolysis to continuously remove sugar was proven to be very suitable and effective in a number of research papers especially, the use of ultrafiltration membrane 10 kDa cutoff (1 Da = 1 g/mol) [6, 9, 10, 11]. Enzyme cellulase as protein with large molecular weight from 35 to 65 kDa

will be retained, whereas glucose molecular (150-180 Da) will be penetrated through membrane barrier [6, 12]. Thus, the high potential of ultrafiltration membrane is applied for reducing sugar inhibition, the recovery of sugar and reuse of enzymes. When sugar product is concentrated after hydrolysis and enzyme is reused, cost saving in subsequent downstream separation and enzyme consumption in hydrolysis will make the overall bioethanol process more cost-effective.

Experiments studied the combination of ionic liquid pretreatment, hydrolysis by a synergy of enzymes, plus different membrane filtration configuration (side membrane reactor, 5kDa or 10 kDa cutoff membranes, nanofiltration, electrolysis) showed very supportive results about the application of membranes in hydrolysis of cellulose [11, 15, 16]. 90% conversion of cellulose to glucose with 98% of enzymes retained were achieved [11]. In addition, testing with a ceramic membrane with higher mechanical strength under the same condition was showed its feasibility to use in industrial scale up [15]. Other research targeted at 50% conversion using 10kDa side membrane reactors managed to reduce inhibition on enzyme and increase conversion [16]. Hence the suitability and effectiveness of membrane filtration was sufficient proven to solve limitations in saccharification of cellulose to sugar by reduce product inhibition, recycle of enzyme and recovery of sugar for subsequent fermentation process.

However membrane filtration has its own disadvantages due to the occurrence of concentration polarization, membrane fouling. This resulted in a decrease in productivity again when a certain permeate flux was exceeded [10]. An explanation to this phenomena is due to the accumulated cellulose on the surface of membrane surface, consequently preventing hydrolysis. Plus the simultaneous loss of cellobiose-an intermediate of sugar into the permeate of membrane as a limiting factor [13]. Moreover, the use of ionic liquid as a pretreatment method is not preferred in industrial production of bioethanol because the very high cost, and being a cost driver taking 33% of total production cost [11]. All of these factors makes the application of ultrafiltration membrane difficult to reach fully commercialization in bioethanol sector, which still prefers acid or alkaline pretreatment because of its low cost and high sugar conversion.

Hence the focus of this research is about combination of alkaline pretreatment, enzymatic hydrolysis with high activity of B-glucosidase and ultrafiltration membrane 10 kDa cutoff to evaluate the performance of hydrolysis and feasibility in applying for industry.

2. Objectives

This research aimed at studying the feasibility of the combination of alkaline NaOH pretreatment, hydrolysis of cellulose with high activity in β -glucosidases, and ultrafiltration membrane 10kDa cutoff to reduce the sugar inhibition on enzyme, recover glucose for subsequent fermentation and reuse enzyme.

3. Methodology

3.1 Materials

Microcrystalline cellulose purchased from R&M Chemical has degree of polymerization 210-270, able to undergo pH 5.5-7.0. Alkaline was sodium hydroxide NaOH dissolving in water to make pH 5.0. The enzyme used in hydrolysis of cellulose was Cellic Ctec from Novozymes, which is a blend of aggressive cellulases, high level of β -glucosidases. Ultrafiltration membrane has molecular weight cutoff of 10 kDa, made of regenerated cellulose.

3.2 Method

3.2.1 Pretreatment

Microcrystalline cellulose (50g) was soaked in aqueous sodium hydroxide (1M) 8% solid loading at 100°C in a water bath. After 3 hours pretreatment, the liquid portion was drained out, left the pretreated cellulose preserved with water. For every subsequent hydrolysis experiment, pretreated cellulose was filtrated by Whatman filter paper to remove water.

3.2.2 Enzymatic hydrolysis and ultrafiltration

Hydrolysis of pretreated cellulose was tested with different enzyme dosages (1.5%, 3%, 6% and 30%) with and without ultrafiltration at 45°C, pH 5.0 citrate buffer under magnetic stirrer for 6 hours at 10% solid loading (mass of cellulose (g)/total volume (ml)). Samples were taken from the hydrolysis reactor and at the permeate for total reducing sugar quantification by dinitrosalicylic acid DNS method for total reducing sugar. Readings of absorbance for each sample were concordant and obtained by repetition of twice for each measurement. From the concordant readings of absorbance, sugar concentrations were converted and considered as preliminary data for this experiment.

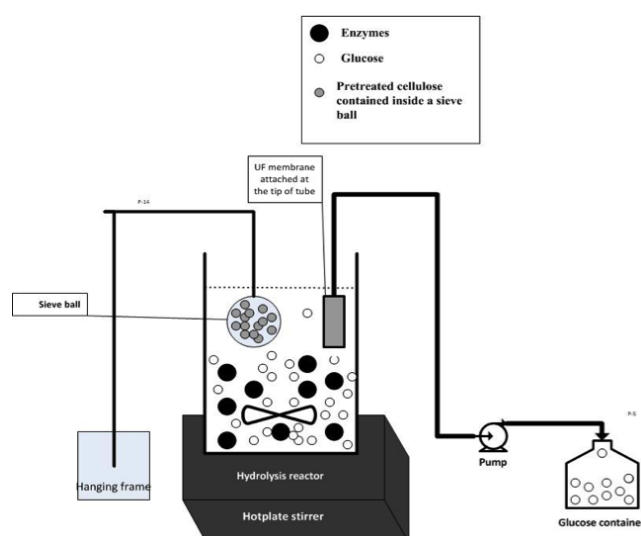


Figure 1: Experimental setup of enzymatic hydrolysis with ultrafiltration

A membrane was attached at the beginning of a tube used to remove sugar solution by a peristaltic pump and thus enzymes and cellulose were retained inside the reactor. After the first 2-3 hours, ultrafiltration was started to perform. Fig. 1 showed the experimental set up of hydrolysis with ultrafiltration.

4. Results and discussion

The experiments were divided into two parts. In part one, hydrolysis of pretreated microcrystalline was carried out without ultrafiltration at four different enzyme dosages (1.5%, 3%, 6% and 30%). In part two, the same hydrolysis experiments were conducted with ultrafiltration membrane 10kDa cutoff. Plus the pretreated cellulose was contained inside a sieve ball, hanging suspended inside the hydrolysis reactor.

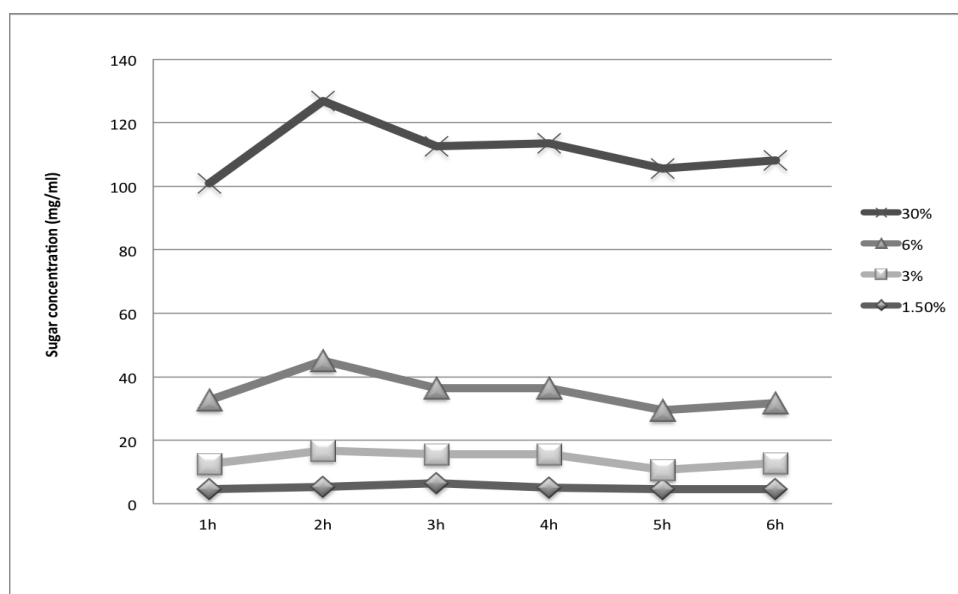


Figure 2. Time profile of hydrolysis for different enzyme dosages without ultrafiltration

Glucose liberated from hydrolysis reaction was measured in term of sugar concentration for every hour inside the reactor. As can be seen in Fig. 2, the sugar concentration is directly proportional to the enzyme dosage. For higher enzyme dosage or enzyme loading, there are more cellulases accessing to polymeric chains of cellulose to release glucose monomers, thus results in higher sugar concentration [8]. However, it is observed that for all four dosages there is the same trend occurring. After the first two or three hours hydrolysis, sugar concentration started to decrease. This trend became obvious with significant reduction in sugar released for hydrolysis with 6% and 30% dosage of enzymes. An explanation for this phenomena is due to the product inhibition on the enzyme. The presence of released glucose causes inhibition on cellulases, or reduces the enzymatic activity of cellulases [9, 14]. Therefore the presence of sugar have an effect on the rate of glucose released and the concentration of sugar dropped after the second hours during hydrolysis (refer to Fig. 2).

To reduce the inhibition effect of sugar on enzyme cellulases, ultrafiltration membrane was applied in the second part of the experiment by means of continuously removing sugar from hydrolysis.

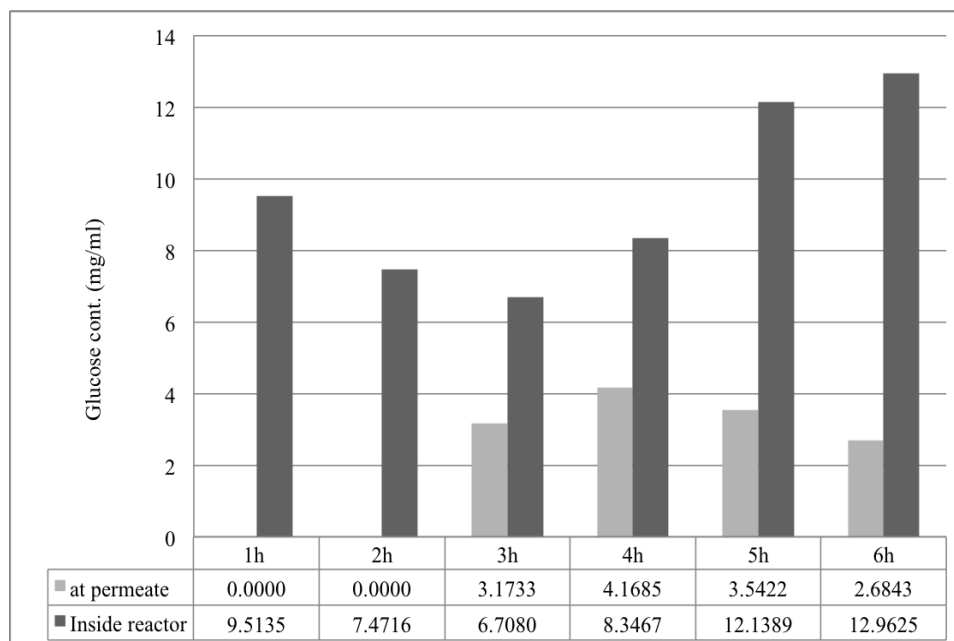


Figure 3. Time profile of 1.5% dosage in hydrolysis with ultrafiltration and 3 ml/min rate of sugar removal.

For the 1.5% dosage hydrolysis experiment (Fig. 3), which ultrafiltration started after two hours, the sugar concentration inside the reactor continuously increased significantly by two folds from 6.7 mg/ml to nearly 13 mg/ml due to the effective removal of sugar by the membrane, thus minimized the sugar inhibition on cellulases.

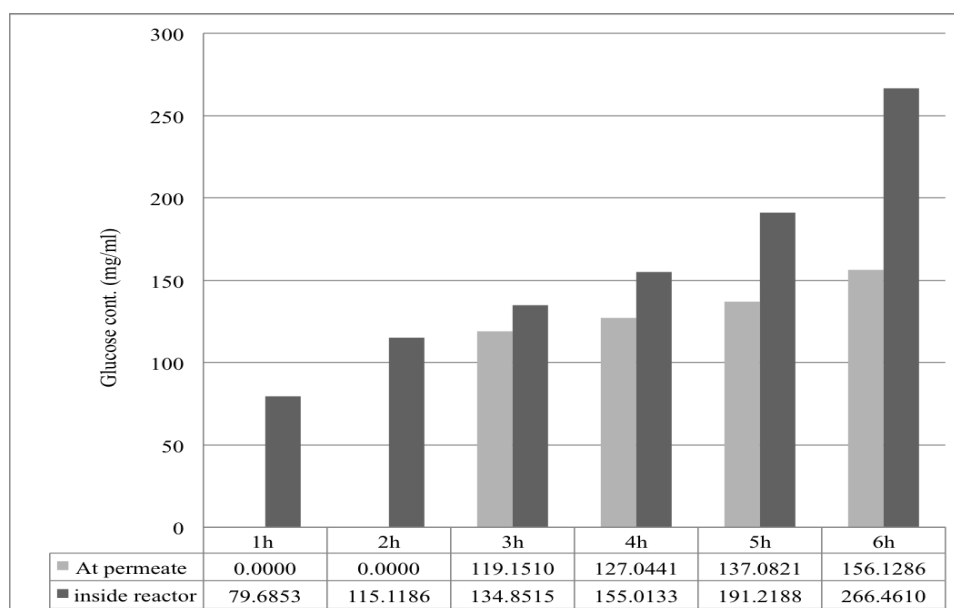


Figure 4. Time profile of 3% dosage in hydrolysis with ultrafiltration and 10-15 ml/min rate of sugar removal.

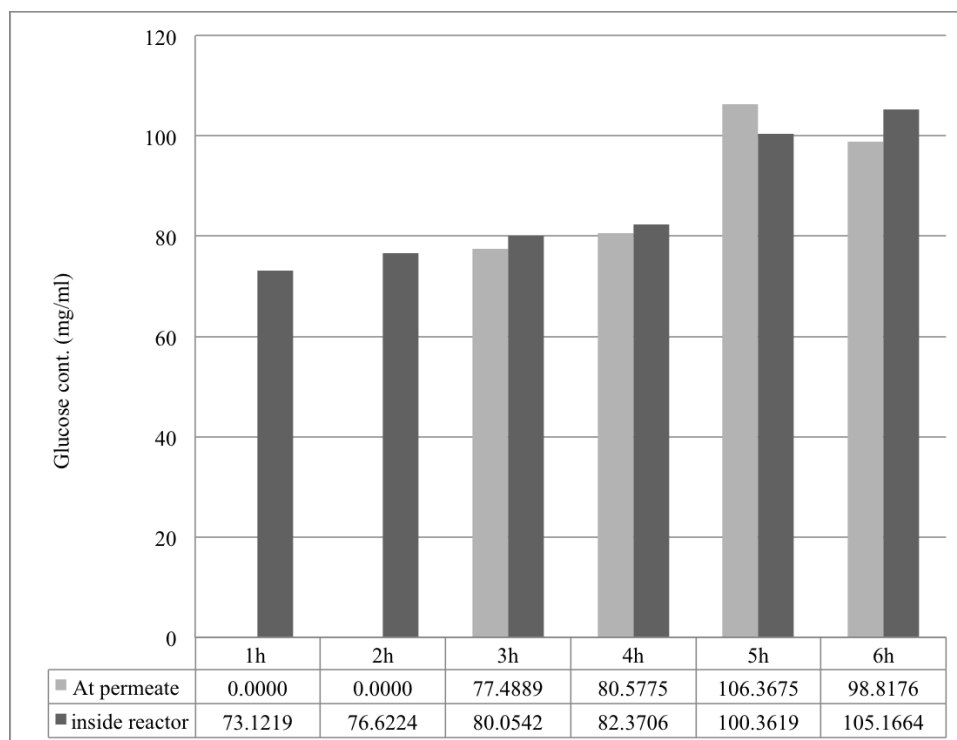


Figure 5. Time profile of 6% dosage in hydrolysis with ultrafiltration and 30 ml/min rate of sugar removal.

The following hydrolysis with ultrafiltration at 3% and 6% enzyme dosage respectively are shown in Fig. 4 and Fig. 5 with increasing rate of sugar removal. No reduction in sugar concentration occurred throughout 6 hours experiments. A rapid increase in sugar concentration inside the reactor from nearly 80 mg/ml up to 266 mg/ml for 3% dosage with a flow rate controlled at 10 to 15 ml/min (Fig. 4). Although hydrolysis with 6% enzyme dosage (Fig.5) showed the same trend with a moderate increase in sugar released with a higher removal rate to 30 ml/min, sugar concentration with 6% dosage at 105 mg/ml was actually lower more than half in comparison to that of 3% dosage hydrolysis at 266 mg/ml after six hours hydrolysis reactions. It was explained that when a certain permeate flux was reached due to a small amount of pretreated cellulose accumulated on the retentate side of the membrane and the loss of cellobiose as intermediate sugar before completely converting to glucose into permeate of membrane [6, 10]. In addition, another hypothesis for this phenomena was that the rate of sugar removal was probably not sufficiently high to avoid sugar inhibition occurring inside the reactor, the amount of sugar inside the hydrolysis reactor was still high enough to cause inhibition on enzyme.

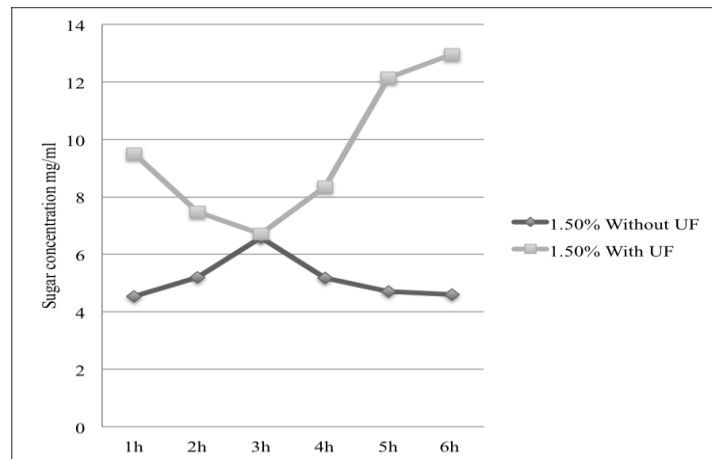


Figure 6. Comparison of hydrolysis with and without ultrafiltration (UF) at 1.5% dosage.

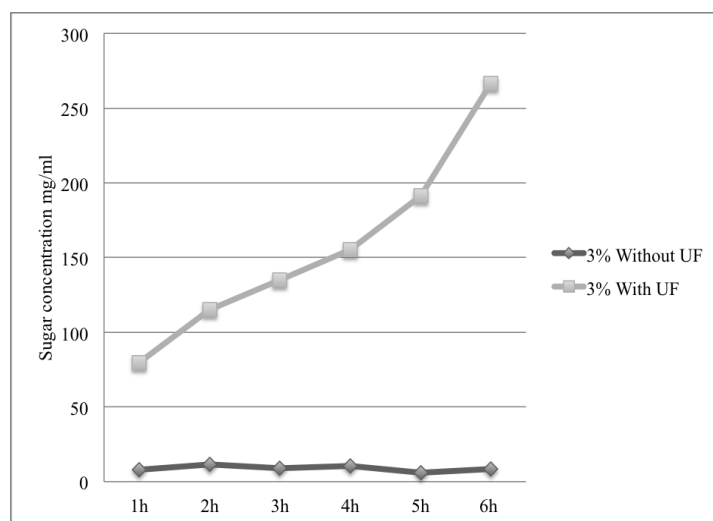


Figure 7. Comparison of hydrolysis with and without UF at 3% dosage.

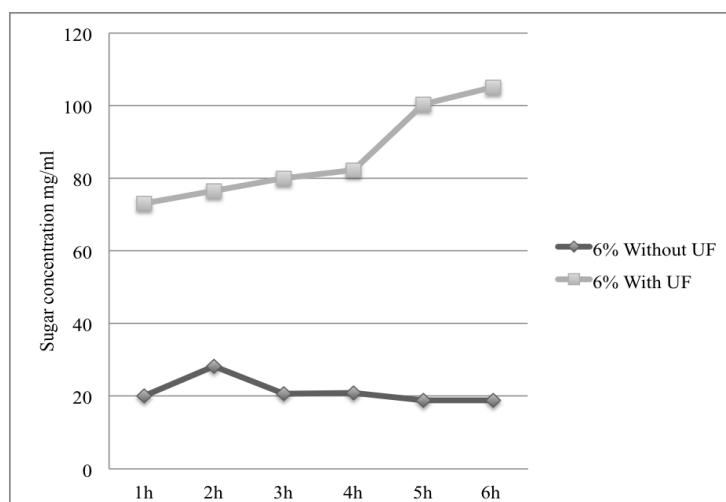


Figure 8. Comparison of hydrolysis with and without UF at 6% dosage.

From Fig. 6 to Fig. 8, a comparison was made for sugar concentration profile during 6 hours between ultrafiltration and without ultrafiltration according to each enzyme dosage at 1.5%, 3% and 6% respectively. Clearly showing in graphs that in

all cases, hydrolysis with ultrafiltration produced more sugar, or showed very much higher sugar concentration without any reduction compared to that without ultrafiltration except for the case of 1.5% dosage which a small decrease occurred during first 2 hours, due to the continuous removal of sugar by the membrane and the ability to retain cellulases inside the reactor.

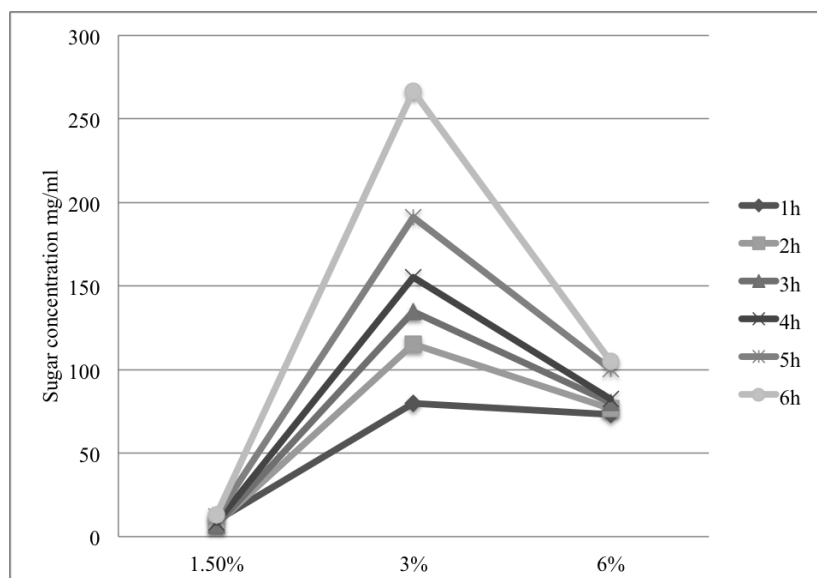


Figure 9. Comparison of hydrolysis at dosages of 1.5%, 3% and 6% with UF.

In these research experiments, among three enzyme dosage 1.5%, 3% and 6% used in hydrolysis with ultrafiltration, the 3% dosage is the optimum enzyme dosage, which always results in a relatively higher glucose concentration during 6 hours hydrolysis of pretreated cellulose compared to 1.5% and 6% dosage (Fig. 9). Therefore, the conditions applied in these experiments (alkaline-pretreated cellulose, hydrolysis at 45°C and pH 5.0, under magnetic stirring, 10% solid loading and membrane ultrafiltration for sugar removal at flowrate 10-15 ml/min), was able to handle low enzyme dosage of 3% as the optimum dosage giving the highest sugar concentration at more than 250 mg/ml compared to 1.5% and 6% at approximate 12 mg/ml and 105 mg/ml respectively after 6 hours.

Comparing the research on enzymatic hydrolysis of cellulose without application of membrane filtration conducted by Rabelo's group, the system could only handle a low solid loading at 3% to give 91% conversion of cellulose to sugar. An decrease by half in enzyme loading in other words, more enzyme dosage resulted in moderate drop in glucose produced and cellulose conversion. When 20% solid loading with same enzyme loading was applied, a significant drop in conversion from 97.9% to 44.4%. This substantial drop was due to the increase in sugar released from cellulose, but the presence of sugar in the hydrolysis reaction itself was a inhibition factor to affect enzyme cellulase activity subsequently [15, 16]. Whereas hydrolysis in this experiment work, was able to handle high solid loading at 10%, with load enzyme dosage of 3% for producing high concentration of sugar by continuously removing sugar product from hydrolysis to avoid inhibition on enzymes.

In comparison with the results of Abels's in 2013 and Lazano's in 2014, in which membrane filtration was applied in hydrolysis, the effect of sugar inhibition

was minimized to give constant concentration of sugar at permeate and retentate at both sides of the membrane to obtain 90% conversion but at quite low solid loading (1% and 2%) and high enzyme loading (700 U/g for cellulase) with an addition of a filtration unit after the hydrolysis reactor. Whereas for this research, the ultrafiltration membrane was directly installed at the end of the tube connected with a peristaltic pump to fractionate sugar released from hydrolysis.

It is predicted that there is probably a direct relation between sugar concentration inside hydrolysis reactor, enzyme dosage and rate of removal sugar in hydrolysis with ultrafiltration membrane. In the experiment of 1.5% dosage, sugar removal rate 3 ml/min (Fig. 3), the sugar concentration decreased initially and quickly increased again when filtration started after two hours. Furthermore, with double enzyme dosage 3% (Fig. 4) and an adjusted flowrate to 10-15 ml/min, an continuous rise without dropping in sugar concentration and applied for 6% dosage. Thus, there should be an improvement space to further study the relationship between these three parameters with the purpose of finding a minimum rate of removing sugar, hence maximizing glucose released from cellulose or conversion of cellulose to glucose and minimizing sugar inhibition in hydrolysis of cellulose.

In this research work, there were still some errors and uncertainties during the experiments. Firstly cellulose loss occurred when primary filtration after pretreatment using Whatman filter paper. However, the dosage of enzyme as well as the percentage of solid loading in hydrolysis for each experiment was totally based on the initial quantity of microcrystalline cellulose before undergoing pretreatment. Secondly the measurement of sugar concentration after every hour was by using DNS method in the reaction of sugar and DNS reagent to give a brown to black color intensity through spectrophotometer. The darker the color, the higher sugar obtained in hydrolysis. During the sugar measurement step, the method did not give a stable reading, whereas the reading will drop slightly. Hence double measurements and an average reading was taken to obtain concordant reading. This can probably give some softs of inaccuracy in preliminary data obtained. The very high sugar concentration like in the case of 3% and 6% dosages, resulted back color samples were obtained, a notice in spectrophotometer showed “out of the range of 540 nm wavelength”. Hence a dilution of sample with dilution factor of 10 was used in order to take reading. The dilution by water might result in slight inaccurate compared to original one during the pipetting of water for the dilution task.

5. Conclusion

This work highlighted the suitability of applying ultrafiltration membrane in hydrolysis process to remove glucose product continuously, thus minimize the product inhibition on cellulases. The combination of industry-preferred alkaline 1M sodium hydroxide pretreated microcrystalline cellulose, hydrolysis using cellulases Cellic Ctec from Novovymes and ultrafiltration membrane 10 kDa cutoff was effective to work together in a whole integrity. Based on the result, it was proved that concentration of sugar in hydrolysis with ultrafiltration was much higher than that in hydrolysis without filtration with insignificant reduction in sugar produced (1.5% dosage) and no sugar drop observed for 3% and 6% dosages. In addition, this method was able to handle low enzyme dosage (3% as optimum) to obtain the highest sugar

concentration plus high solid loading (10%) in hydrolysis. The significant difference of this research compared to others, was that the direct attachment of ultrafiltration membrane material at the end of the tube connected with a pump to remove sugar produced in hydrolysis reactor, this method is potentially a new way of applying membranes to fractionate sugar in hydrolysis, and considered to be very effective to reduce product inhibition, increase conversion of cellulose to sugar, able to retain enzymes for reuse as a way of cost saving. A direct relationship between enzyme dosage and the rate of removing sugar was found. Higher enzyme dosage, increase sugar removal rate is necessary to ensure concentration of sugar inside reactor not sufficiently high to cause product inhibition on enzyme. Hence a further study on this relationship in order to clarify would be suggested for improvement.

Acknowledgement

I would like to express my deep gratefulness and thanks to two of my supervisors Dr. Rajesh and Ms. Masni, who have guided me through the research successfully with a contributive result. A deep thank to the Mr. Douglas as module coordinator of my final year project subject for providing me all necessary skills to conduct research, identify research gap and how to contribute to the body of scientific knowledge through research activity, sharing results for improvements.

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***Hibiscus Sabdariffa* as a Coagulant for Treating Dye Wastewater**

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Abstract

Coagulation process has been very important in wastewater treatment industry including dye wastewater. It has been reported as one of the best pre-treatment in wastewater treatment because of its low cost and high efficiency in color removal. Coagulant aid used in this process, helps to neutralize the suspended charged particles in dye synthetic wastewater. The coagulant aid utilized widely in the industry is the conventional chemical-based coagulant. The objective of this study is to investigate the impacts of natural-based coagulant as a coagulant aid in synthetic dye wastewater treatment using the coagulation process and to compare its performance as an alternative to the conventional chemical-based coagulant, aluminium sulphate. The natural-based coagulant used in this study is *Hibiscus Sabdariffa* and *Jatropha Curcas* and the dye used in dye synthetic water is Congo Red dye. It has been found that the quality of color removal using natural coagulant is comparable to the chemical-based coagulant. Hence, could be a good substitute for aluminium sulphate. Highest color removal was recorded at 98.86% for the combination of both the natural coagulant at 50:50 volume ratio at its best working condition of pH 2, coagulant dosage of 50 mg/l and initial dye concentration of 200 mg/l. Color removal using aluminium sulphate at pH 10 was found to be at 99.24%.

Keywords: Natural coagulant, Coagulation, Wastewater treatment, Dye.

1. Introduction

Dye wastewater is one of the most produced industrial pollution mainly contributed by the textile industry and posed as a threat to the environment because of its aromatic and bio-recalcitrance properties [1]. Treatments recommended for the removal of dye color is the physico-chemical treatment which has its advantages and disadvantages. One of the important processes in the wastewater treatment is coagulation. During coagulation, coagulant neutralizes electrical charges of fine particles such as color producing organic substances in the water to assemble microflocs. Microflocs also known as impurities come to rest at the bottom and separated via water suspension. Microflocs may not be visible to the eye but by comparing before and after coagulation treatment, water after treatment should have less color or clearer compared to the untreated water. Generally there are two existing types of coagulant, which is conventional chemical-based coagulant and natural organic coagulant. The most utilized chemical-based coagulant is ferric and alum based. Ferric-based normally utilized in a range of pH from 4 to 11 and consequently utilized for color removal at high and low pH [2]. Alum-based coagulants that are widely used, namely, alum chloride ($AlCl_3$), and aluminium sulphate is the most extensively used coagulant and also has been used in wastewater treatment for many decades [3]. It is widely used in the industry because of its effectiveness, low cost and availability. Nevertheless, conventional chemical-based coagulant has been indicated to be the cause of neurological diseases such as Alzheimer, dementia and other bad effects on human wellbeing such as irritable bowel, amnesia, seizures, abdominal cramps, energy loss and learning impairment. Hence, the huge interests on natural coagulant's properties as a coagulant to treat wastewater and to further improve and increase its efficiency. The research will be done to find the suitability of *Hibiscus Sabdariffa*, *Jatropha Curcas* or the combination of both to treat dye wastewater and enhance its performance in the treatment process and the possibility of its usage as a substitute for the conventional chemical-based coagulant in the future. Based on previous research *Jatropha Curcas* has been reported to be a successful coagulant and limited studies were found on *Hibiscus Sabdariffa* efficiency as a natural coagulant [4].

2. Methodology

2.1 Coagulating Agent Preparations

Jatropha Curcas commonly known as Roselle and *Hibiscus Sabdariffa* are both locally grown in Sabah and Negeri Sembilan, Malaysia. Coagulation mechanism that works with soluble organic pollutants that exists in the wastewater depends upon the electrostatic attraction of pollutants to the cationic coagulants in the solution. This clearly shows that coagulation process is dependent on pollutants charged state [3]. Several previous studies showed that organic coagulants commonly are efficient in the removal of dye and shows the ability to act as a coagulant when used to remove anionic nature of dyes [5]. The positive charged acid amino in the protein from seeds is important in neutralizing charges of particles in synthetic dye wastewater [1, 6]. The approximate compositions of seeds are shown in (Table 1). Mature seeds were washed with tap water and again with distilled water, dried in the oven at 60 ± 2 °C for 24 hours to remove the moisture. The dried seeds then were pulverized using Fanda JE-116 blender to powdery form and will be used with distilled water as its

protein extraction agent. 5g of powdered seeds and 100ml of distilled water are blended together at room temperature for 5 minutes and filtered with muslin cloth. These solutions are advised to be used on the same day for the best stability. Syafalni's research stated the best result in coagulation activity of combined coagulants is at the ratio of 50:50 due to the increase in any dosage may result in self-coagulation [7].

Table 1. Proximate composition of *Jatropha Curcas* and *Hibiscus Sabdariffa* seed.

	% composition	
	<i>Jatropha Curcas</i>	<i>Hibiscus Sabdariffa</i>
Moisture	8.14 ± 0.10	5.00 ± 0.19
Crude fat	20.83 ± 0.55	46.24 ± 0.20
Crude Protein	27.32 ± 0.39	29.40 ± 3.00
Ash Content	4.47 ± 0.11	4.90 ± 0.40
Carbohydrate	39.24 ± 0.19	16.89 ± 2.00

2.2 Synthetic Dye Wastewater Preparation

Stock solution for synthetic dye wastewater will be prepared by adding congo red dye (C.I. No. 22120, Direct Red 28) with chemical formula of $C_{32}H_{22}N_6O_6S_2Na_2$ directly into distilled water without further purification. Precisely weighed quantity of dye will be dissolved with distilled water to make up 250mg/l stock solution. Stock solutions will be diluted with distilled water for different concentrations of dye wastewater in jar test and the required pH can be achieved by adding hydrochloric acid or sodium hydroxide.

2.3 Jar Test

Jar test basically consists of a few beakers filled with dye water solution dosed with coagulant solution. The mixture then would be stirred at 100 rpm 4 minutes after the coagulant was dosed and then stirred at 40 rpm for 25 minutes to give time for flocculation. The samples then stand for half an hour to allow flocs to settle and the suspended flocs to be observed. The overhead stirrer used in jar test experiment is R50D Precision Overhead Stirrer from CAT Scientific with an adjustable speed from 50 to 1600 rpm.

2.3.1 Preliminary Experiment

Jar test of all three coagulants, *Hibiscus Sabdariffa*, *Jatropha Curcas* and combination of both extracts at 50:50 volume ratio was done at constant temperature, same pH of 4, dosage of 50 mg/l and concentration of dye wastewater of 50 mg/l and 200 mg/l. Coagulant with highest coagulation activity then will be used to determine the suitable working condition. [8].

Table 2. Working Condition for natural coagulant performance.

Parameters		Value
pH		4
Coagulant dosage		50 mg/l
Temperature		20
Rapid mixing	speed	110 rpm
	Time	4 minutes
Slow mixing	speed	50 rpm
	Time	25 minutes

2.3.2 Experimental Run

The experiment of the optimization of parameters will be done using each selected range of parameters; pH (2-7), coagulant dosage (20-70 mg/l) and the effect on different concentration of dye stock solution (50-300 mg/l). Values for fix parameters of pH, initial concentration of dye wastewater and coagulant dosage will be 4, 50 mg/l and 50 mg/l respectively. All the values were predetermined based on optimum parameters for coagulation activity in previous studies [5]. Optimum parameters from this jar test then will be used as the parameters in the jar test experiment to compare selected natural coagulant with aluminium sulphate.

Table 3. Experimental parameters.

Varied parameters	pH	Coagulant dosage	Wastewater concentration
Fixed parameters	temperature	temperature	temperature
	coagulant dosage	pH	coagulant dosage
	wastewater concentration	wastewater concentration	pH
	mixing speed and time	mixing speed and time	mixing speed and time

2.3.3 Natural Coagulants Performance

Jar test of *Jatropha Curcas*, *Hibiscus Sabdariffa* and combination of both at 50:50 volume ratio was done again at the optimized parameters for the best working condition at constant room temperature, pH of 2, dosage of 50 mg/l and concentration of dye wastewater of 200 mg/l. Coagulant with highest coagulation activity then will be used in the performance comparison to chemical-based coagulant jar test experiment.

2.3.4 Performance Comparison of Natural-based and Chemical-based Coagulant

Jar test of coagulants, selected natural coagulant and chemical based coagulant was done by using the best working condition. The result shows the natural coagulant

either comparable or incomparable to the conventional chemical-based coagulant based on the percentage of color removal. Aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3$ from Sigma-Aldrich was the chemical-based coagulant used.

2.4 Coagulation Activity

Samples before coagulation (S_0) and after coagulation process (S_i) that has stand for half an hour, was tactfully collected without disrupting settled flocs to measure the turbidity and light absorption values. The coagulant activities from the coagulation process were then calculated using the values from the measured absorbed light using Eq. (1);

$$\text{Coagulation activity} = \frac{(S_0 - S_i)}{S_0} \times 100 (\%) \quad (1)$$

2.5 Analysis of Data

Physical and chemical properties of the wastewater need to be evaluated before and after each coagulation treatment for the results of this experiment.

2.5.1 Water Characteristic Test

The removal of colour is determined by turbidity and colour removal (clarity). Physical properties such as changes of turbidity, colour and sludge produced can be observed. Turbidity of water is inversely proportional to clarity of water. Turbidity of water will be measured using Eutech Instruments Turbidimeter TN-100 in Nephelometric Turbidity Units (NTU) with the range of 0 – 1000 NTU accuracy of $\pm 2\%$ for 0 – 500 NTU and $\pm 3\%$ for 501 – 1000 NTU. Removal of the dye colour from the wastewater can be evaluated using the HALO RB-10 with the maximum absorbance wavelength of 549 nm and wavelength accuracy of $\pm 0.5\text{nm}$. Pictures of wastewater should be taken before and after coagulation process to easily be compared and evaluated.

2.5.2 Chemical Analysis

Chemical analysis that will be done in this research is pH measurement and COD test. The pH values of wastewater will be taken using Hanna Instruments HI98127B pH meter with the accuracy of ± 0.01 . COD is a test to measure the oxygen required to oxidize nearly all compounds that can be chemically oxidized. Unlike BOD, that only measures the amount of organic compounds that can be oxidized [9]. This can be done with titration method of wastewater with potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) bought from Sigma-Aldrich (product number: 207802). This test can be done by using $\text{K}_2\text{Cr}_2\text{O}_7$ in boiling concentrated sulphuric acid at the temperature of 150°C , in the presence of a silver catalyst (Ag_2SO_4) to facilitate the oxidation. After digestion, the remaining unreduced $\text{K}_2\text{Cr}_2\text{O}_7$ is titrated with ferrous ammonium sulfate to calculate the amount of $\text{K}_2\text{Cr}_2\text{O}_7$ consumed. The amount use in the titration is proportional to the amount of organics that exists in the wastewater.

3. Result Outcomes & Discussion

3.1 Preliminary Experiment

Both seed extracts has been reported to possess the positive electrical charges amino acids that will be the main component in neutralizing pollutants in dye wastewater [10, 11]. Dye particles in water exist as colloids and as a result of their polar molecules, these particles keeps an electrical equilibrium point also known as the isoelectric point. Coagulation activity depends a lot on the percentage of cationic protein in seeds as the dye particles are negatively charged.

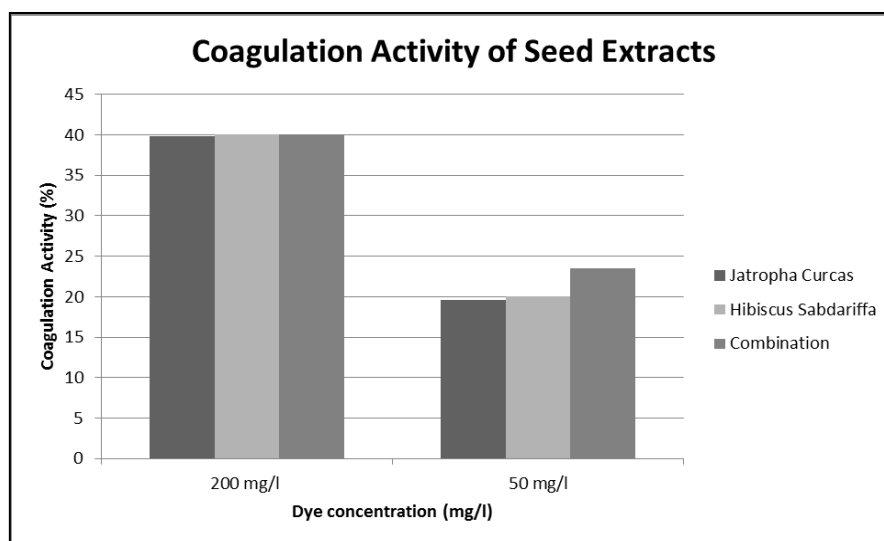


Figure 1. Coagulation Activity of Different Type of Seed Extracts.

Based on Fig. 1, it is found that concentration of dye at 200 mg/l shows that the combination of both seed extracts works the best at 40.08% of coagulation activity. The experiment was repeated at dye concentration of 50 mg/l to further investigate its effectiveness. It is shown again that the combination works the best at 23.51% of coagulation activity. From the results, we can conclude that the behavior of both seeds is similar to each other in coagulation process as the percentage coagulation activity is close to each other. This was caused by the similar chemical composition and acid amino content. It also shows that combination of different type of coagulants could work as efficiently or even better in wastewater treatments using coagulation process [7].

3.2 Parameter Optimization

Different types of coagulant give different efficiencies of removal and works at different operating conditions such as pH, dosage, concentration and temperature. Hence, the combination seed extract's best working condition as a coagulant was also done in order to increase its efficiency. Natural coagulants were reported to perform the best under acidic condition since dye wastewater mainly consists of negative charge particles. The surface charge of coagulants, solubility of particles and matter and the stabilization of its suspension can be affected by pH level of dye wastewater [12].

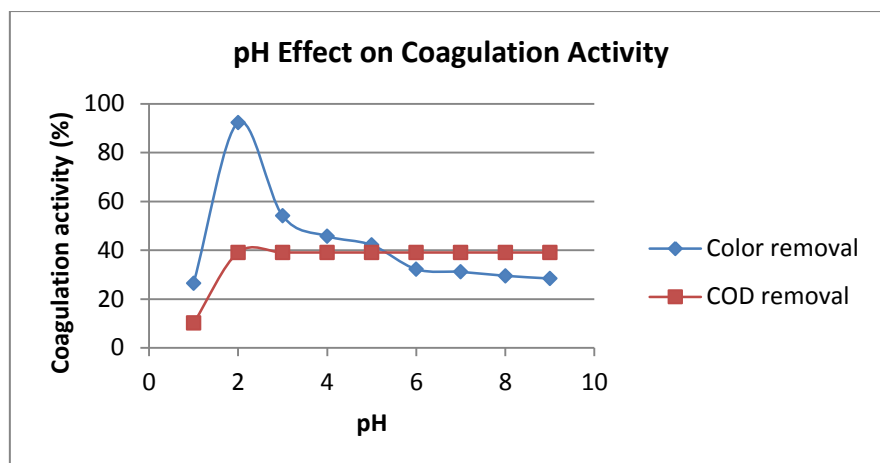


Figure 2. Effect of pH on Coagulation Activity.

Fig. 2 shows the highest percentage colour removal is at pH 2 with the value of 92.32%. It is also shown that the removal of colour decreases significantly at pH value of 3 to 9. This shows that the removal of colour is higher in acidic condition. Similar results were also reported by some researches [12]. The protein amino acid in the combination of natural coagulant is positively charged which in result acts as a cationic polyelectrolyte. Dye wastewater particles exist negatively charged and both H. Sabdariffa and J. Curcas are attractive to be used as a coagulant. Cationic polyelectrolytes acts as a coagulant aid in treatment of wastewater [12]. The decrement of colour removal may also be caused by partial denaturation by the attack of the hydroxyl group (OH-) [5].

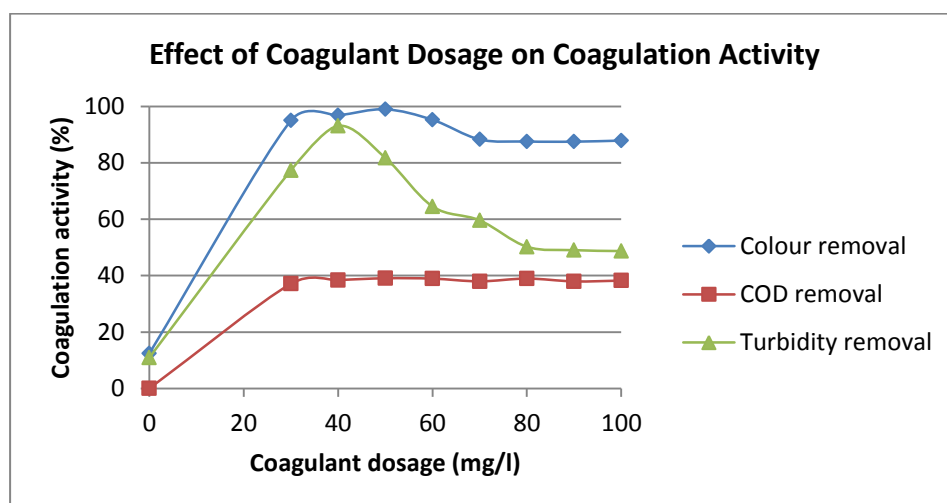


Figure 3. Effect of Coagulation Dosage on Coagulation Activity.

Shown in Fig. 3, increasing amount of dosage up to 50 mg/l leads to the increments on the colour removal. Removal percentage of dye colour was also shown to be above 95% at the coagulant dosage range of 30 to 60 mg/l and highest coagulation activity at dosage of 50 mg/l for 98.96% colour removal. The decreasing percentage of colour removal may be caused by overdosing of coagulant. This decrement can be caused by the solid re-suspension. It was reported that at higher

coagulant concentration, the coagulant positive charges on the particle surface cause the particles to re-disperse [8]. At lower dosage or no dosage of coagulant was a result of the dosage is too low to initiate coagulation process [5]. Similar results of coagulant overdosing were also reported by other researches [5, 12].

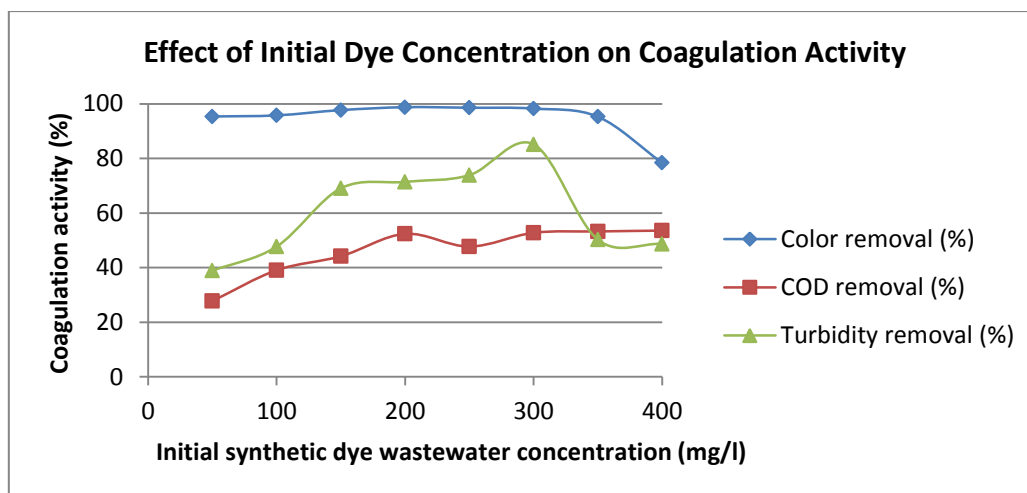


Figure 4. Effect of Initial Dye Concentration on Coagulation Activity.

Fig. 4 shows that the percentage color removal increases with the increments of initial dye concentration only until the concentration of 200 mg/l. It is also shown that the coagulation activity is all above 95% except for initial dye concentration of 400 mg/l. It can be deduce that coagulant dosage needs to be increased after the concentration of 200 mg/l. This can be due to not enough charges in the coagulant to neutralize all the charged particles [12]. With the coagulant dosage of 50 mg/l, it is clearly shown that it can remove 98.78% from the synthetic dye wastewater with the initial concentration of 200 mg/l.

3.3 Natural Coagulant Coagulation Performance

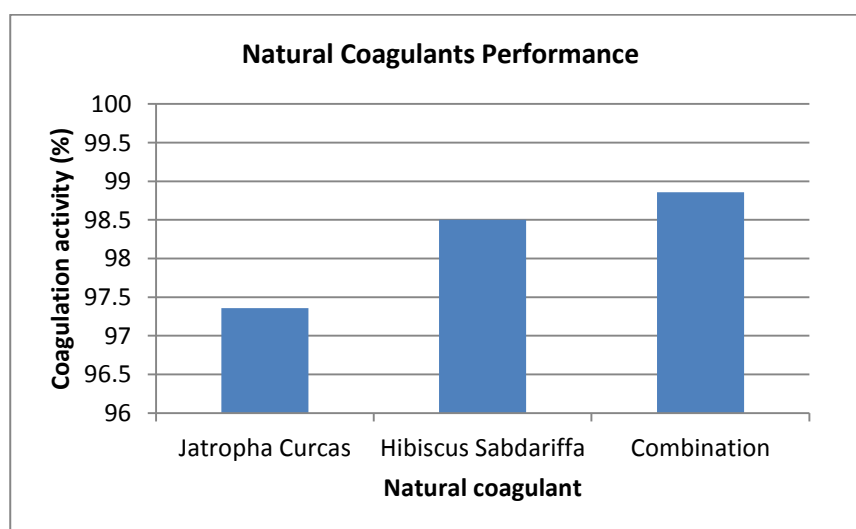


Figure 5. Natural Coagulants Performance.

Based on result shown in Fig. 5, it is found that all three coagulants work similarly at the percentage above 95% colour removal. This was caused by the similar chemical composition and acid amino content in both seeds. The combination of both seed extracts still the best coagulant in coagulation treatment because of its higher colour removal percentage at 98.86% compared to *Jatropha Curcas* and *Hibiscus Sabdariffa* individual extracts. It has been reported that combination of different type of coagulants could work as efficiently or even better in wastewater treatments using coagulation process [7].

3.4 Performance comparison of natural-based coagulant and chemical-based coagulant.

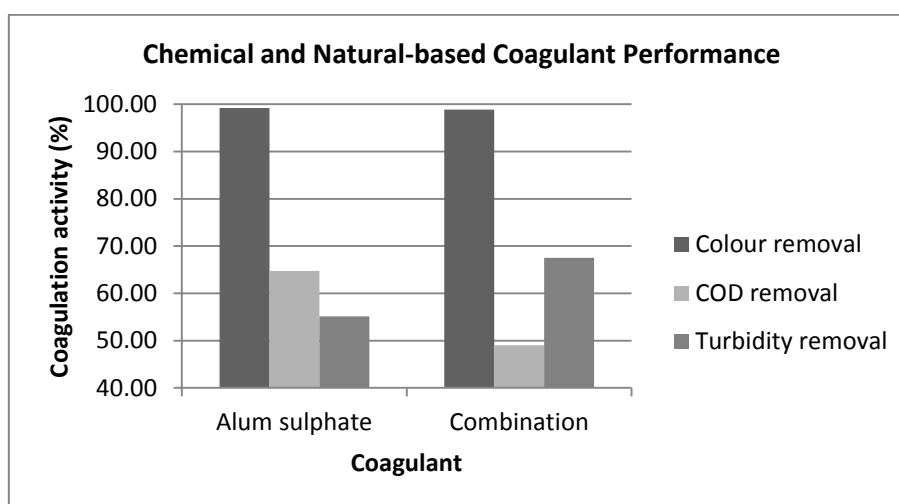


Figure 6. Chemical and Natural-based Coagulant Performance.

From Fig. 6, it was found that the natural combination of both seed extracts is comparable to chemical-based coagulant, aluminium sulphate in terms of percentage colour and turbidity removal. It was reported in other researches that natural coagulants can work at par or even better compared to chemical-based coagulants. *Moringa Oleifera* was reported to work better than chemical-based coagulant [13]. Similar results were also reported [8, 14].

4. Conclusions

The best working condition for the combination of both seed extracts was determined to be at the pH value of 2, coagulant dosage of 50 mg/l and works significantly well for concentration of dye wastewater upto 200 mg/l. It is also concluded that at higher concentration of dye wastewater more dosage of coagulant needed in the coagulation process as more cations needed to neutralize the particle charges in the wastewater. Experimental result shows that at these working conditions, percentage of colour removal is at 98.86% for the combination of seed extracts. Meanwhile percentage colour removal of *Jatropha Curcas* and *Hibiscus Sabdariffa* 97.36 and 98.5% respectively. Result shows that all three extracts works very well as a coagulant but combination of both extract at 50:50 volume ratio was used in performance comparison with chemical-based coagulant, aluminium sulphate because

of its highest coagulation activity. Test on COD and turbidity analysis was also done and percentage removal for both is 49.02% and 67.49%. This research also shows that coagulation process for synthetic dye wastewater using natural-based coagulant is comparable to the quality of synthetic dye wastewater treated with conventional chemical-based coagulant. Hence, it can be used as a substitute for aluminium sulphate as the commercial coagulant in the industry.

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Removal of Residual Catalyst from Palm Oil-Based Biodiesel Using New Ionic Liquids Analogous

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Abstract

Biodiesel is produced through transesterification of triglyceride and methanol in the presence of alkali catalyst to form glycerol and biodiesel. A number of purification methods are used to remove undesired products that are retained inside the biodiesel. The purified biodiesel grade should adhere to the international standard specifications EN 41214 and ASTM D6751. Residual potassium hydroxide (KOH) catalyst is one of the impurities in biodiesel that has to be removed after transesterification reaction. Deep eutectic solvents (DESs) were introduced in order to remove residual KOH catalyst from palm oil-based biodiesel. All the DESs were formed by one salt and two hydrogen bond donors (HBDs). In this work, choline chloride (ChCl) was used as the salt while glycerol and ethylene glycol were used as the hydrogen bond donors. Six DESs based on choline chloride were synthesized with various compositions of salt and HBDs to remove the catalyst. All the DESs (DES1, DES2, DES3, DES4, DES6 and DES7) were successful to reduce the KOH content in biodiesel. The results of the experiment demonstrated the removal efficiency of KOH increase with the increase of DES:biodiesel molar ratios and the mole fraction of HBD in mixture of DES. DES2 and DES4 in this work had performed their outstanding efficiency in removing KOH content in palm oil-based biodiesel. All tested DESs were able to decrease KOH content in biodiesel below the specification limit set by the international standards EN 14214 and ASTM D6751 (5 mg/kg). The optimum DES to biodiesel molar ratio for each DES was determined. The result shown indicated DES4 was the best solvent for removal of KOH from biodiesel.

Keywords: Removal, Catalyst, Biodiesel, Transesterification, Deep eutectic solvent.

1. Introduction

It has been expected that the transportation energy use increases from year 2005 to 2035 with an overall percentage of 1.8% per year around the world. The industrial sector and transportation sector have been classified as the first and second largest energy consumption sector in global. At the same time, it has been accounted that the transportation sector could cover up 60% of the oil in the world thus resulting in substantial growth of oil demand. There are approximately 97.6% of oil is used as the fossil fuel for transportation sector with traces amount of natural gas. Figure 1 shows the production and consumption of oil around the world between 1965 and 2009 [1].

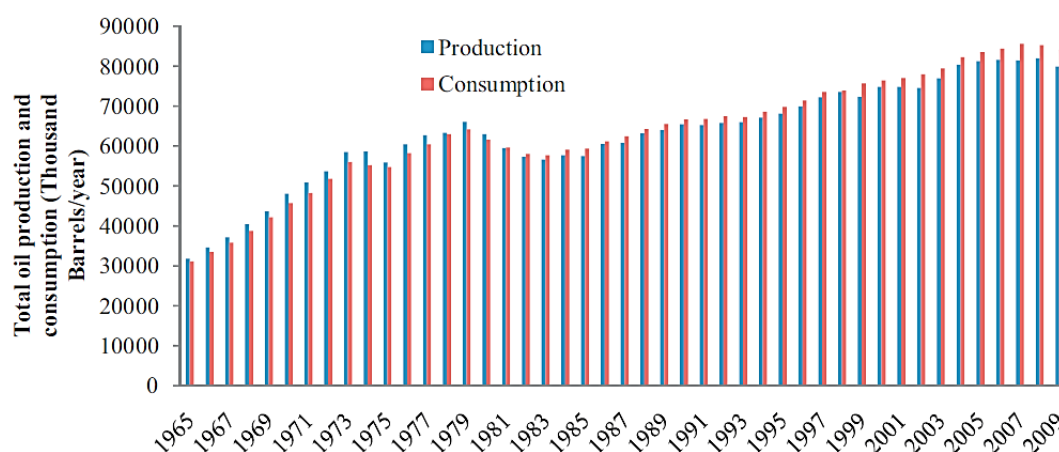


Figure 1. Total production and consumption of oil between 1965 and 2009.

Biodiesel as a renewable energy has been receiving much attention to overcome these problems due to its environmental benefits and its sources which derived from animal fats, plant oils, wastes or renewable sources such as cooked vegetable oils. It has several advantages over biodiesel to fossil fuel as being biodegradable, renewable, emit slight amount of carbon dioxide (CO_2) with no net addition to atmospheric CO_2 level thus decreases global warming issues. Besides, biodiesel has high combustion efficiency due to its properties likely the same with fossil based biodiesel which has high cetane number and flash point. Biodiesel has low sulfur and aromatic content yet it possesses high energy content [2-4].

Four major methods are used to produce biodiesel, for example direct-use or blending of oils [5, 6], microemulsion [7], thermal cracking [8, 9] and transesterification [10]. Figure 2 shows the most common method in biodiesel production, which is transesterification of triglyceride and alcohol in the presence of alkali catalyst to form glycerol and fatty acids alkyl esters (FAAE). Triglycerides are the main components in vegetable oils. Methanol is the common alcohol utilized by the industries due to low cost and good chemical properties which helps in producing low viscosity of biodiesel [11]. Potassium hydroxide (KOH) is used as the alkali catalyst due to its high conversion rate in transesterification reaction [12]. The viscosity of triglycerides is generally reduced after transesterification reaction; as a result improve the physical properties of biodiesel [13].

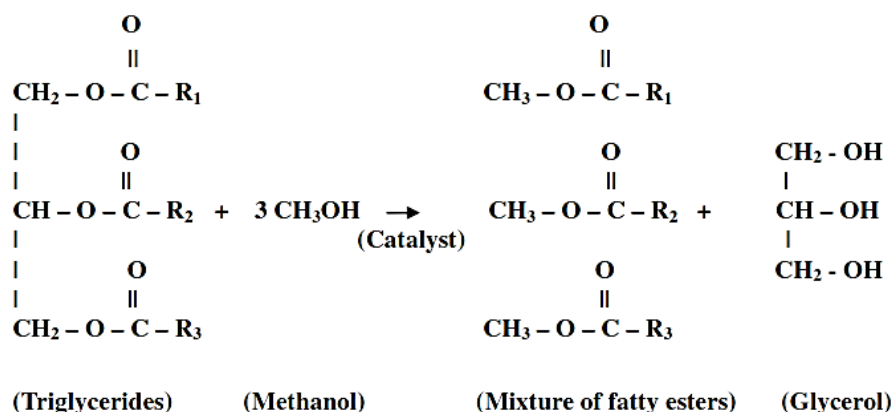


Figure 2. Transesterification reaction.

Transesterification reaction can be categorized into acids, alkalis and enzymes catalytic transesterification. Enzyme-catalyzed transesterification has its own advantages. It is able to produce high yield of methyl esters, absence of side reactions and ease up glycerol recovery to produce high grade of glycerol [14, 15]. Moreover, enzyme-catalyzed transesterification is applicable for feedstocks with free fatty acid (FFA) ranging from 0.5% to 80% [16, 17]. Nevertheless, enzyme-catalyzed transesterification is not commercialized due to high lipase catalyst's production cost, longer reaction time as compare to alkali-catalyzed transesterification reaction as well as limitation of regeneration and reuse of biocatalysts within a long operating time [10, 14]. Acid and alkali catalyzed transesterification are utilized in biodiesel production typically. The acid-catalyzed transesterification reaction is sensitive to the presence of water. Canakci and Gerpen et al. [18] revealed that concentration of water at 1 g kg⁻¹ presence in the reaction mixture can affect the yields of ester in the transesterification of vegetable oil. When the water concentration reaches to the point of 50 g kg⁻¹, transesterification reaction is completely inhibited. More disadvantages of homogeneous acid catalytic transesterification include equipment corrosion, produced wastes from neutralization process, difficult to recycle, formation of secondary products, higher reaction temperature, long reaction times, slow reaction rate, weak catalytic activity and elaborate engineering process [19].

The best biodiesel production is achieved by using homogeneous alkali catalyst [20]. Sodium hydroxide (NaOH) and potassium hydroxide (KOH) are common catalysts used in the alkali-catalyzed transesterification [21]. This method produces high yield of fatty acid methyl esters (FAME) from triglycerides at high conversion rate within a short reaction time (30-60 min) [1, 14]. Alkali-catalyzed transesterification can be carried out at ambient pressure and moderate temperature range of 40-60°C with low catalyst concentration range of 0.5-2.0 wt%. Alkaline catalytic method is the most efficient and economical catalytic method than other method. The conversion rate of an alkaline catalyst is approximately 4000 times faster by comparing it with same amount of acid catalysts use in transesterification reaction [22, 23].

On the other hand, alkali-catalyzed reaction has its disadvantages as well. These drawbacks include the high consumption of energy, difficult to have recovery of glycerol, requirement of treating alkaline wastewater after reaction, interference of

FFA and water during the reaction as well as occurrence of undesirable side reaction due to low selectivity [14, 15, 24]. Homogeneous base catalytic transesterification requires post reaction separation of catalyst, by-product and product at the end of the reaction which increases biodiesel cost. During transesterification process, saponification will occur if significant amount of FFAs found in the vegetable oils react with the alkali catalyst. As a result, separation of final product into biodiesel and glycerol becomes more difficult. Subsequently, wastewaters produce from purification of biodiesel (water washing) increase [21]. The presence of water content in vegetable oils also contributes to the happening of saponification. Soap produced consumes some of the alkali catalyst thus reduced the efficiency of catalyst in the transesterification reaction. The formation of gels from the soap decreases the yield of methyl ester (biodiesel) and makes the separation of glycerol more difficult [25].

Impurities contain in produced biodiesel include free glycerol, residual KOH catalyst, methanol, water and soap. These impurities can decrease the performance of the car engine. Thus, several stages of purification method for example evaporation of residual methanol, neutralization reaction and water washing are require to remove the impurities in biodiesel before commercializing the biodiesel to market.

The presence of residual KOH catalyst in produced biodiesel can cause carbon residue deposited in fuel injection system. Consequently, these carbon residues could poison the emission control system. Besides, residual KOH catalyst induces engine filter blockages therefore reduce the engine performance in general [26]. In addition, the presence of residual KOH catalyst reduces the quality of biodiesel.

Therefore, biodiesel purification process is an essential. Biodiesel purification methods can be categorized into three major methods, i.e. water washing, dry washing and membrane extraction [26, 27]. In general, water washing method uses water as the medium to dissolve impurities in biodiesel. Washing step is repeated a few times until clear water phase is observed. Water washing has several disadvantages which are high production cost, high energy consumption, long production time, production of polluting liquid effluent, also considerable loss of desired product due to retention in water phase [28]. On the other hand, dry washing method used ion exchange resin or magnesium silicate powder as an adsorbent to remove impurities. Unfortunately, the purified biodiesel grade after dry washing cannot accomplish specification limit set by the international standard EN 14214. Dry washing method increases the production cost due to the expenses of added material in purification process. Another purification method is membrane extraction. Membrane extraction performs a liquid-liquid extraction to remove impurities. However, cost of material used in membrane extraction is expensive, also high flow rate of material stream causes fouling effect in the membrane.

Deep eutectic solvent (DES) is characterized as a mixture of two or more inexpensive and benign components that associated by hydrogen bond interactions to form eutectic mixtures [29]. They exit as liquid phase below 100°C due to the large freezing point depression resulted from strong hydrogen bond [30] In general, DES can be synthesised from organic halide salts and hydrogen bond donors [2].

Shahbaz et al. explored another application of DES in removing residual catalyst KOH from palm oil-based biodiesel. His team demonstrated DESs that are

made from ChCl and glycerol are successfully in removing residual KOH and water content lower than the limit set by the EN 14214 and ASTM D6571 [31]. Besides, the researcher also discovered that new combination of DESs from ammonium salt: ethylene glycol at 1:2.03 molar ratio has higher efficiency in eliminating total glycerol compared to conventional ammonium salt: glycerol. It is projected that the new ternary DESs composed of ChCl, glycerol and ethylene glycol have the capabilities to remove both glycerol and residual KOH in produced biodiesel. Also, some ternary DES exhibits lower freezing point than binary DES of the similar components which is more advantageous in industrial application [32]. In this project, the new DESs (ChCl: glycerol: ethylene glycol) are investigated as solvent to remove KOH catalyst to below the permissible level set by EN 14214 and ASTM D6751 biodiesel international requirement.

2. Experimental section

2.1. Materials

Palm oil is widely available in Malaysia, also, it is found abundant in South East Asian countries [33]. Palm oil-based biodiesel possess highest cetane number among other vegetable oils could provide better ignition quality for diesel engine [14, 34, 35]. For these reasons, palm oil is chose as the raw material in transesterification reaction to produce biodiesel. RBD palm oil is utilized in this work due to trace amount of impurities that contain inside the RBD palm oil. RBD palm oil (Yee Lee Sdn Bhd) was obtained at the local mart.

Chemicals such as methanol and potassium hydroxide pellets with purity of 99.8% and 98.9% respectively were purchased from Merck, Malaysia mainly for biodiesel production. For synthesis of DES, choline chloride salt ($C_5H_{14}ClNO$) and glycerol ($C_3H_8O_3$) and ethylene glycol ($C_2H_6O_2$) as two hydrogen bond donors (HBDs) with high purity (>99%) were purchased from Merck, Malaysia. These three chemicals are used to synthesize DESs without further purification. Mass fraction of water in these chemicals is $< 10^{-4}$ as per the guide from the manufacturer.

2.2. Production of palm oil-based biodiesel

500 g of RBD palm oil was added into a beaker and was heated up by using water bath (Daniel DNP 9051) to carry out alkali catalyzed transesterification reaction. Potassium hydroxide as a catalyst (1wt% of palm oil) was mixed with methanol to form potassium methoxide. The homogeneous potassium methoxide solution was added into the beaker which operating at a reaction temperature of 333.15 K. Molar ratio of palm oil to methanol was 1:10 (methanol in excess) was prepared in this experiment to increase yield of product. The mixture was stirred by an agitator at a constant speed of 400 rpm. After the mixing for 2 hours, the mixture was cooled to room temperature and was then poured into a separation funnel. Two layers of liquids will be formed after overnight settling. The biodiesel phase at the upper layer was separated from the rich glycerol phase at bottom layer.

2.3. Deep eutectic solvents (DESs) synthesis

In this work, choline chloride (ChCl) was used as the salt while glycerol and ethylene glycol were selected as the HBD to synthesize seven ternary DESs with various compositions. 20 g of ChCl was prepared and the mass of HBDs were varied based on the specified molar ratios in each synthesized DES. The mass of each chemical was measured precisely by using weighing balance Shimadzu TX423L. DES mixture was added into screw cap vial and a magnetic stirrer was put into the vial to homogenize the mixture. The screw cap vial was sealed with parafilm to prevent moisture from surrounding air contacting with DES in the vial. DES mixture was heated up to 80 °C on a hot plate stirrer (IKA C-MAG HS 7) and was stirred at 300 rpm for one hour until a homogeneous colourless liquid phase was obtained. Table 1 shows the molar ratios of salt and HBDs in different DES.

Table 1. Molar ratios of salt and HBDs in each synthesized DES.

Abbreviation	Molar ratio		
	ChCl	Glycerol	Ethylene glycol
DES1	1	1	1
DES2	1	2	1
DES3	1	1	2
DES4	1	2	2
DES5	2	1	1
DES6	2	2	1
DES7	2	1	2

2.4. Characterization of deep eutectic solvents

2.4.1. Freezing temperature

Mettler Toledo Differential Scanning Calorimeter (DSC 1 STAR[®] System) is used to measure the freezing points of all the samples of DES. The instrument is first calibrated against known standards using water and 2-propanol to assure the accuracy of measurement before carrying out the experiment.

2.4.2. Water content

Karl Fisher titration method is employed to determine the water content of all the DESs. The instrument is calibrated against the known standard using Hydranal-water standard 1.00 mg/g to ensure the measurement accuracy of the Karl Fisher coulometer.

2.5. Extraction of residual KOH catalyst using DESs

Liquid-liquid extraction process is performed in removal of KOH catalyst in biodiesel phase. Each synthesized DES was added to the biodiesel phase which separated from glycerol-rich phase at different molar ratios (ranging 0.5, 1.0, 2.0, 2.5 mole DES per 1 mole biodiesel). The samples were agitated at 200 rpm using an orbital shaker for 1 hour at ambient temperature. After 2 hours of settling, the upper layer of purified biodiesel is removed from the used DES for KOH content analysis using inductively coupled plasma-optical emission (ICP-OES).

2.6. KOH content analysis

The residual KOH catalyst in final product (after extraction process) was measured using the PerkinElmer Optima 7000 DV ICP-OES instrument (PerkinElmer, Inc., Shelton, CT, USA). ICP-OES instrument is equipped with WinLab 32 utilizing argon (99.99%) as the carrier gas to measure the content of potassium in biodiesel. Table 2 shows the ICP-OES analytical condition while doing the sample analysis. The wavelength is set at 766.486 nm for the analysis of potassium content. The oil standard for potassium (500 mg/kg) was diluted in xylene solution (Merck, >99%) at five various concentrations (0.1, 0.25, 0.5, 0.75 and 1 ppm). The oil based in this work was supplied by Conostan Company. The solutions of different concentrations were inserted into the ICP-OES to conduct the calibration. Linear correlation coefficient (R^2) was obtained and the result show a good linearity of 0.998. All purified biodiesel samples were injected into ICP-OES to determine the potassium content after the determination of potassium peak area. The potassium content in all biodiesel samples was calculated with reference to calibration.

Table 2. ICP analytical conditions.

Plasma gas flow	15 L/min
Auxiliary gas flow	1.5 L/min
Nebulizer gas flow	0.45 L/min
RF power	1450 W
Pump flow rate	1 mL/min
Read delay	90 s
Processing	Peak area
Replicates	3
Torch	Quartz for axial view

3. Results and discussions

3.1. Biodiesel synthesis

The palm oil-based biodiesel was synthesized through alkali catalyzed transesterification of triglycerides with methanol in the presence of alkali catalyst which is potassium hydroxide (KOH). The produced biodiesel was not purified in the washing column; it is then analyzed by ICP-OES directly. Table 3 shows the results of ICP-OES for the analysis of KOH content in produced biodiesel before extraction using the DESs. 69.978 mg/kg of KOH content was detected in unpurified biodiesel which has over the limitation set by the international standards EN 14214 and ASTM D6751 (5 mg/kg).

Table 3. KOH content of unpurified biodiesel.

Attributes	KOH content (mg/kg)
Produced biodiesel	69.978
EN 14214	5
ASTM D6751	5

3.2. DESs synthesis

Choline chloride (ChCl) was mixed with two different hydrogen bond donors: glycerol and ethylene glycol at seven different molar ratios to form seven ChCl based DESs (DES1 – DES7). The chemicals combination ChCl: glycerol DES was chosen due to its high removal efficiency of KOH catalyst; on the other hand, ChCl: ethylene glycol DES can eliminate high amount of glycerol from palm oil-based biodiesel [31, 36]. DES molar ratios were used based on lowest freezing point attained for the combination of salt to HBD. During the synthesis of DES, salt:HBD mixture had formed a white viscous gel during the first 20 minutes of mixing process. A clear liquid phase with some undissolved salt was then formed after another 30 minutes of mixing. A continuous of mixing process was required until a homogeneous liquid phase of DES was observed. Colourless liquid was appeared in all the newly synthesized ternary DESs at the ambient temperature except for DES5. DES5 appeared as a cloudy white liquid phase or a colourless mixture of solid and liquid based on the temperature of the mixture. The existence of solid sediment at the bottom of the mixture revealed that the quantity of salt was in excess corresponding to the HBDs (2:1:1 ChCl:glycerol:ethylene glycol). This condition also expressed that DES5 does not reach to the eutectic point at that given salt:HBD:HBD molar ratio. Stronger hydrogen bonding was achieved between salt and hydrogen bond donors by increased the amount molar ratio of hydrogen bond donors as described in DES2, DES3, DES4, DES6, and DES7. All DESs had complete dissolution except DES5 thus DES5 was not studied further and was not taken as extraction solvent in this work.

Table 4 shows the freezing point for all synthesized DESs. It has been reported that all synthesized DESs have lower freezing points than their constituting components. The freezing temperatures of synthesized DESs are basically below the room temperature. This property has in turn indicated the normal behavior of DES. In addition, it can be observed that hydrogen bond donors had shown its large contribution in lowering freezing point of DES by strengthens salt: HBD hydrogen bonding interactions and by decrease its lattice energy. This can be observed where freezing temperature of DES significantly decreases as the hydrogen bond donors' molar ratio increase. Besides, water content of all synthesized ChCl based DESs was studied. As shown in Table 4, the water content of all newly synthesized DESs are slightly higher than 0.1 wt% except for DES 1 and DES 6 which has water content of 0.0908 wt% and 0.0959 wt% respectively. The average water content of all synthesized DESs was 0.1 wt% which was consistent with the physical properties of deep eutectic solvents (1 wt%).

Table 4. Freezing point and water content of all DESs.

DES	Freezing temperature (°C)	Water content (mg/kg)
1	8.36	908
2	-4.28	1018
3	-18.06	1158
4	-23.75	1303
6	12.25	959
7	22.77	1189

3.3. Removal of KOH residues from biodiesel

Synthesized DESs were added into produced biodiesel at four different molar ratios of DES to biodiesel (0.5:1, 1:1, 2:1 and 2.5:1) to determine maximum removal efficiency of residual catalyst in biodiesel. DES: biodiesel were mixed for one hour. The extraction process was then carried out at room temperature. After two hours of settling, two layers are formed due to the density difference where the upper phase was purified biodiesel and bottom phase was spent DES. It was detected that the DES layer is immiscible with biodiesel phase so it can be wholly separated from the biodiesel. The purified biodiesel phase was analyzed by using ICP-OES for its KOH content through measuring the concentration of potassium element in the biodiesel. Calibration for ICP-OES was done before injecting the sample for analyzing. The result had indicated a perfect linearity as the linear correlation coefficients (R^2) has shown a value which was greater than 0.99.

Figure 3 and Figure 4 demonstrate the results for KOH content in biodiesel after extraction using all studied DESs. The KOH content in biodiesel before extraction was 69.98 mg/kg which was incredibly higher than maximum concentration specified by EN 14214 and ASTM D6751 (5 mg/kg). All studied DESs were able to reduce KOH content below the standard at low DES: biodiesel molar ratio (1.0) except for DES1, DES3 and DES7.

In general, the increase of DES: biodiesel molar ratio up to 2.5 shows excellent KOH extraction for all DESs except for DES1. All DES: biodiesel molar ratios for DES1 could not meet the EN 14214 and ASTM D6751 standard. Figure 3 has shown all DES:biodiesel molar ratios for DES1 were failed to remove KOH content in biodiesel. Same condition goes to low DES:biodiesel molar ratios (0.5:1 and 1:1) for DES3. On the other hand, all DES:biodiesel molar ratios of DES2 were successfully reduce the KOH content in biodiesel below EN 14214 and ASTM D6751 standard test limit. It was also detected that higher molar ratios of DES:biodiesel in DES3 (2:1 and 2.5:1) had successfully reduced KOH content from biodiesel. The removal efficiency of KOH using DES1, DES2 and DES3 were above 93.33%. It can be observed in Figure 3, the optimum KOH removal was attained by DES2 which removed all KOH content at lowest DES: biodiesel molar ratio of 0.5:1.

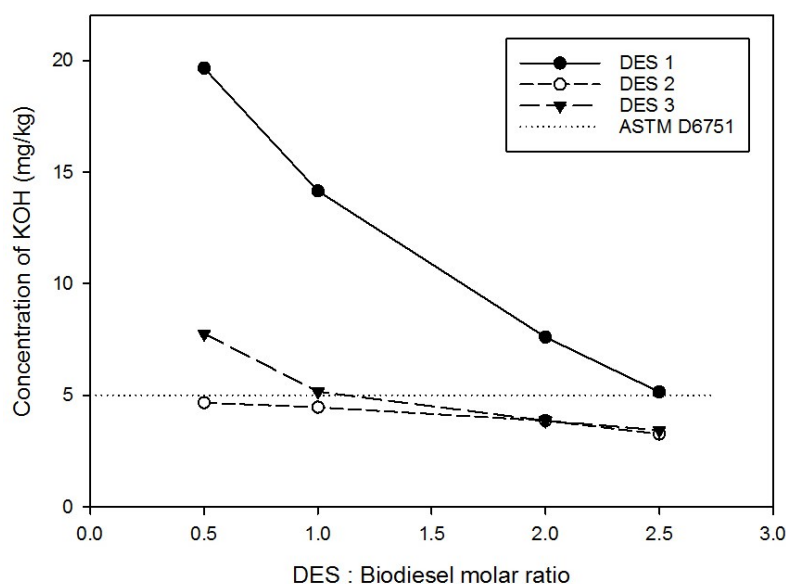


Figure 3. KOH removed after extraction by [ChCl:glycerol:ethylene glycol] DES1, DES2 and DES3.

ICP results for KOH removal by ChCl: glycerol: ethylene glycol DES (DES4, DES6 and DES7) were shown in Figure 4.2. All DES4:biodiesel molar ratios (0.5:1, 1:1, 2:1 and 2.5:1) were perfectly reduced KOH content in biodiesel below the standard limitation. Low DES: biodiesel molar ratio (0.5) in DES6 did not provide a good KOH removal efficiency. However, it is noticeable that removal efficiency of KOH was improved with the increase of DES: biodiesel molar ratio. Hence, higher DES: biodiesel molar ratios from DES6 (1:1, 2:1 and 2.5:1) and two higher DES: biodiesel molar ratios from DES7 (2:1 and 2.5:1) could reduce KOH content below EN 14214 and ASTM D6751 specifications. The maximum removal efficiency of KOH content in biodiesel was found at 2.5:1 DES: biodiesel molar ratio in all studied DES. DES2, DES3, DES4, DES6 and DES7 have a maximum removal efficiency of 95.34%, 95.09%, 98.61%, 96.00% and 97.48%, respectively.

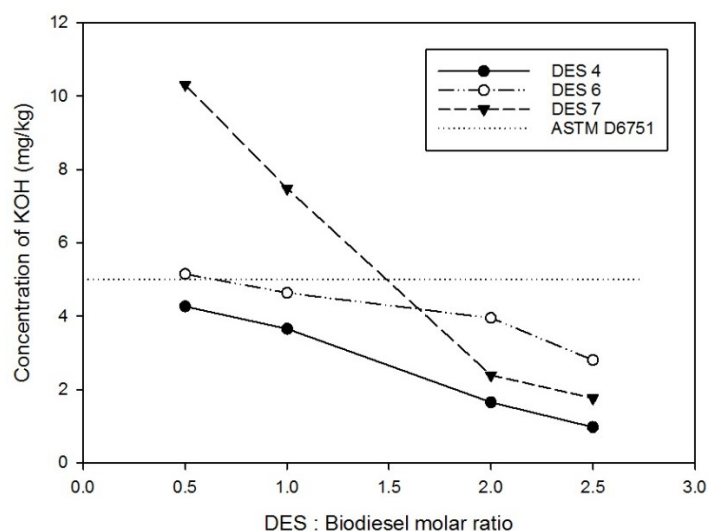


Figure 4. KOH removed after extraction by [ChCl:glycerol:ethylene glycol] DES4, DES6 and DES7.

Apart from the increase of KOH removal efficiency by the increase of DES to biodiesel molar ratio, one of the elements which can affect the extraction performance is the composition molar ratio of DES. When the mole fraction of glycerol in DES increases from 0.33 to 0.50 (DES1 and DES2 in Figure 4.1), the removal efficiency of KOH increases. This outcome is reinforced by the research work completed by Shahbaz et al. [31] in which glycerol-based DESs have larger impact in removal of residual catalyst. Besides that, increase of the mole fraction of ethylene glycol had resulted in an incremental improvement of KOH removal in biodiesel. KOH removal efficiency increases when the mole fraction of ethylene glycol in DES increases from 0.25 to 0.40 (DES 2 and DES 4 in Figure 5). In this research work, the average removal efficiency of KOH using ternary DES is 92.14 %.

As shown in Figure 5, all DES: biodiesel molar ratio of DES2 and DES4 were successfully reduced KOH content in biodiesel to the permissible level. DES2 has molar composition ratio of 1 mole of salt, with 2 moles of glycerol and 1 mole of ethylene glycol while DES4 has molar composition ratio of 1 mole of salt, with 2 moles of glycerol and 2 mole of ethylene glycol. It is not difficult to discover that both DESs have similar glycerol molar composition ratio. Because KOH has high solubility in glycerol, it resulted in increase of DES capability to dissolve more KOH in DES. Hence DES2 and DES4 can easily remove large amount of residual catalyst from biodiesel at very low DES: biodiesel molar ratio.

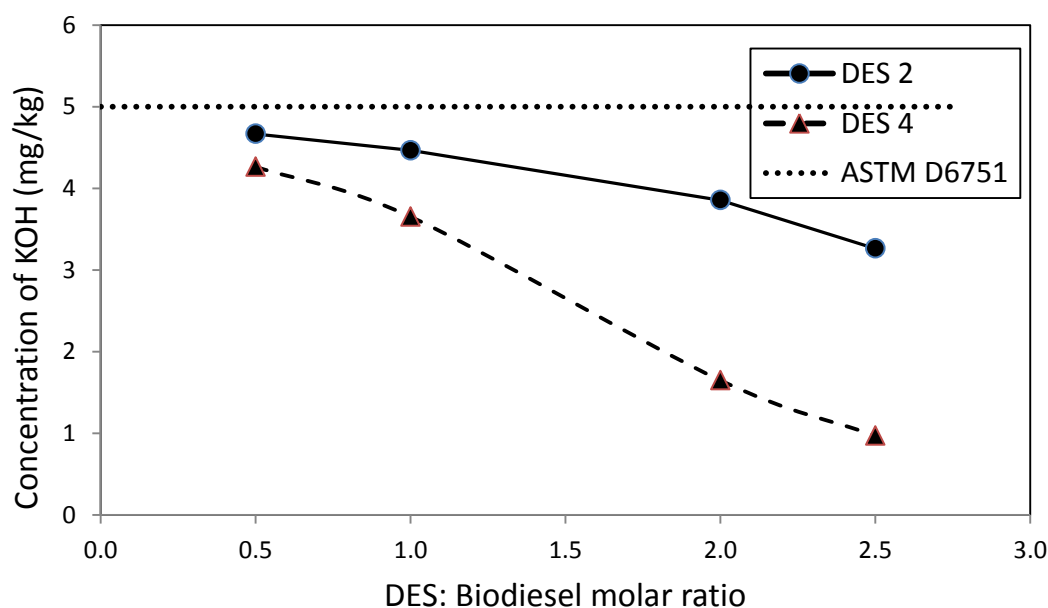


Figure 5. Comparison of removal efficiency of DES2 and DES4.

0.5: 1 up to 2.5:1 DES: biodiesel molar ratios were used in this project. In fact, the use of higher DES: biodiesel molar ratios (e.g. 3.0 to 10.0) can be used in order to increase the removal efficiency of KOH catalyst in biodiesel. However, by observing the exponential trends in Figure 3 and Figure 4, the increment of removal efficiency of KOH using higher DES: biodiesel molar ratio may be little or no increment at all. In addition, DES will be present in excess corresponding to biodiesel when more DES molar ratios are added. According to Figure 3 and Figure 4, all studied DESs were

successfully to reduce KOH content below the international standard specification using DES: biodiesel molar ratios of 2.0. Hence, it is not necessary to increase DES: biodiesel molar ratio since this molar ratio had given good removal efficiency. In addition, it is not cost effective to increase DES: biodiesel molar ratios to higher values with little increment of KOH removal efficiency as higher DES: biodiesel molar ratio will require higher amount of CHCl_3 , glycerol and ethylene glycol when synthesizing DES. As a result, capital cost of project increases.

Intermolecular attraction took place between solvent (DES) and solute (KOH). Intermolecular attractions include hydrogen bonding, ion pairing, dipole and Van der Waals interactions. High removal efficiency of KOH using DES is basically due to the polarity of ternary DES to form hydrogen bonding between hydrogen bond donors with chloride anion in ammonium salt. Because of the polarity of DESs and the presence of hydroxyl group in both DES and KOH as well as the solvation force of KOH in biodiesel, DESs have high affinity to the attraction of KOH as dipole-dipole attraction and hydrogen bonding was took place during extraction process [36].

According to the research work done by Atadashi et al. [37], the author had revealed that the KOH content in biodiesel had been reduced by 96.25% after the separation process using ultra-filtration membrane technology. The initial content of KOH in palm oil-based biodiesel before membrane separation was 9.607 mg/kg. After the separation process, the KOH content was then reduced to 0.36 mg/kg. However, there was formation of saturated membrane after a few cycles run of biodiesel through ultra-filtration membrane. Removal efficiency of KOH was decreased along with repeated membrane separation process. This result had in turn contributed to the use of DES as extraction solvent where spent DESs did not decreasing much efficiency to extract KOH catalyst for few cycles of extraction process continuously [31].

DES2, DES3, DES4, DES6 and DES7 were able to reduce KOH content to below the ASTM and EN standard at the minimum DES usage. Table 5 shows the optimum molar ratios for all used DESs with the corresponding removal efficiency of KOH. DESs which have similar optimum DES: biodiesel molar ratio was compared in terms of KOH removal efficiency. The comparison result had finalized DES4, DES6 and DES7 as the three best DESs to remove residual catalyst from biodiesel. The optimum DES in this project was rule by the DES performance which gave high KOH removal efficiency with the minimum usage of DES. Hence, it can be concluded that the optimum molar ratio of all studied DESs in removal of KOH catalyst was undertaken by DES4 at 0.5:1 DES to biodiesel molar ratio as it removed residual catalyst below the standard specification at the minimum usage of DES.

Table 5. Optimum molar ratios for KOH removal using DESs.

DES	Optimum molar ratio (DES:biodiesel)	Removal efficiency (%)
1	-	-
2	0.5:1	93.33%
3	2.0:1	94.49%
4	0.5:1	93.91%
6	1.0:1	93.38%
7	2.0:1	96.59%

4. Conclusion

In this work, we had presented and examined a new purification method for the removal of residual KOH catalyst from palm oil-based biodiesel by using ammonium-based DESs. Seven ChCl-based DESs with different compositions of HBD were synthesized and were examined as new solvents to remove KOH catalyst.

Synthesized DESs were added into palm oil-based biodiesel at different molar ratio of DES: biodiesel at room temperature. Shahbaz et al. [31] who employed binary DES to eliminate residual catalyst reported that ChCl: glycerol and ChCl: ethylene glycol DESs have certain impact on the removal of residual KOH catalyst. All studied DESs in this work have an average removal efficiency of 92.14 % where the highest removal efficiency was achieved at the highest DES: biodiesel molar ratio (2.5) in each synthesized ternary DES. The experimental KOH removal efficiency obtained was also higher than ultra-filtration membrane separative technology contributed by Atadashi et al. [37]. This outcome has supported the advantages of new ternary DESs as potential extraction solvent to eliminate residual catalyst from palm oil-based biodiesel.

In addition, all tested DES: biodiesel molar ratio of DES2 and DES4 demonstrated excellent removal of KOH in biodiesel. Both DESs were successfully reduced the amount of catalyst to permissible level set by EN 14214 and ASTM D6751 international biodiesel standards. DES: biodiesel molar ratio (2.5: 1 for DES6), (2.5: 1 for DES7) and (2.5: 1 for DES4) were disclosed as the most effective extraction solvent which has removal efficiency of 96.00%, 97.48% and 98.61% respectively. The optimum molar ratio of all studied DESs in removal of KOH catalyst was undertaken by DES4 at 0.5:1 DES to biodiesel molar ratio as it removed residual catalyst below the standard specification at the minimum usage of DES.

Acknowledgements

The author would like to express her utmost gratitude to her final year project supervisor, Dr. Kaveh Shahbaz for exemplary guidance and constant monitoring throughout the project work. The author would also like to offer her sincere appreciation to the Centre for Ionic Liquids (UMCiL) from University of Malaya for their cordial support which helped the author in completing the research work on time.

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An Investigation on the Relationship between Activated Carbon Micropore and CO₂ Adsorption

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Abstract

Carbon dioxide (CO₂) which is emitted in abundance is harmful to the environment and therefore various methods and techniques have been done to capture CO₂ for a better and cleaner environment. Carbon adsorption is one of the up-coming methods used in capturing CO₂ however this method is not considered to be the most sustainable approach. There is a need for a cheap adsorbent in the carbon dioxide adsorption industry. Activated carbon is commonly used as an adsorbent for this process as it's porous like structure would be suitable medium for the capturing of CO₂. The significant characteristics of activated carbon would be that it is reusable, cheap and environmentally friendly. Currently, extensive research has been done in regards with the characterization of activated carbon, however these researches has not been done using spent tea leaves obtained from restaurants for CO₂ adsorption. This study focuses on different activating agents, carbonization temperature as well as different heating rate of the raw material. The initial stage would consist of the chemical activation of the material using Potassium Hydroxide (KOH) and Potassium Carbonate (K₂CO₃) and the second stage would include carbonization of the material in at 800⁰C, 600⁰C and 500⁰C and a heating rate of 5⁰C/min and 10⁰C/min for 2 hours. The final stage would be the characterization analyses of the material using Proximate Analysis, Ultimate Analysis, Fourier Transform Infrared Spectrophotometer (FTIR) and Brunauer- Emmett- Teller (BET) analysis. The FTIR analysis shows that there is significant difference the strength of the C-H and C=C bond at 500⁰C for KOH at 10⁰C/min compared to the other samples. As for the BET analysis a higher surface areas of 731m²/g as well as smaller micropore size of 1.93nm of was found in sample impregnated with K₂CO₃ at 600⁰ compared to the 500⁰C and 800⁰C.

Keywords: Activated carbon, Spent tea leaves, Micropores, Adsorption, Carbon dioxide

1. Introduction

The extensive use of fossil fuel as an energy source has caused the formation of greenhouse gas mainly carbon dioxide has been a contributing factor towards global warming [1]. In 2005, Malaysia itself emitted approximately 138.04 million metric tons of carbon dioxide into the environment [2]. The major source of this CO₂ emission would be from the combustion of fossil fuel, industrial emission, and transportation sector and energy usage in residential areas. The effect of high concentration of this gas has cause global climate changes and decline in human health [3]. Thus, it is important for us to contain this gas before it leads to further destruction to our environment. However, it is important for us to remember that carbon dioxide plays significant role in the growth of plants in our earth mainly for the photosynthesis process. This gas is much needed to help plants to grow faster, larger as well as live in drool conditions [4]. So, the main aim would be to control the emission and not to eliminate it completely.

Currently, in the market there are many techniques and equipment used for the separation and capture of CO₂. Carbon sequestration is one of the most matured and common method used to control carbon dioxide emission yet this technique is not considered to be the most sustainable approach. There are many other techniques that e.g. cryogenics, adsorption technique, absorption technique and membrane separation that are also used to capture carbon dioxide [1]. However, the adsorption process outstands other technologies in terms of cost saving, high CO₂ adsorption capacity and high CO₂ selectivity [4]. In the adsorption process the emitted gas molecules is captured by the solid substance, which would cause the gas molecule to either disappear into the solid substance or either stick at the outer surface of the substance [5]. Silica gel, zeolites, , activated carbon, ion-exchange resins ,activated alumina, metal oxides, meso-porous silicates and other surface-modified porous media are some examples of conventional solid absorbents. Absorbents like carbon fibers and their composites as well as metal organic frameworks, in recent years, have been developed for gas separation [6]. Currently, there are still a wide range of optimization products available to improve the performance of these materials and a large range of new sorbent can still be investigated even though there is already a vast variety of sorbents available for CO₂ separation. Besides that, another advantage of the adsorption process is that this technology enables product recovery and no chemical pollutants are needed for the capture of CO₂, making it a more environmental friendly [8, 9]. The current commercial activated carbon available in the market mainly produced from coal is said to be unsustainable and expensive, thus there is an urgent need to obtain a new substitution for the product [7]. To date many researches have been conducted in the field of carbon dioxide adsorption using activated carbon as an adsorbent. Though much research has been done in this area, there is always room for improvement as well as further exploration in this area. The most common area that can be exploited would be the base of the raw material used. In this 21st century the focus on a clean and greener environment can be widely seen. Thus, the utilization of waste materials as the base of activated carbon is highly encouraged. The natural activated carbon can be produced from coconut shell, saw dust, agriculture waste, old tires and many more [10]. The greatest properties of natural activated carbon that makes it a suitable adsorbent would be its porous structure, its availability in abundance, its reusability, cost of the raw material and most importantly environmental friendly [11].

Activated carbon is a carbonaceous material that contains many porous like surface which is a good adsorbent for the capture of small particles. Due to their porous structure, it has expansive surface area which has a lot of holes and tunnels over their surface. This surface allows materials and particles to fill up these holes with the respective materials. The carbon content is said to be between the ranges of 87% to 97% [11]. However, the surface area, hardness and other properties may vary according to the type of raw material used [8]. Some of the natural raw material that can be used to develop activated carbon would be coconut shell, industrial waste and bamboo [10]. The greatest properties of natural activated carbon that makes it as a suitable adsorbent would be its porous structure, its availability in abundance, its reusability and most importantly environmental friendly [11]. The selection of raw material as the base of the activated carbon is very important as different raw materials can produce varied amount of micropore and mesopores during the thermal and chemical activation process [12]. The existence of these mesopores structures does not allow effective adsorption to occur thus during activation the presence of this structure will not allow more channels for the creation of micropore structure. In addition, to the amount of macropores structure, mesopores structure, the percentage of carbon, cellulosic and lignin components in the materials contributes in the formation of micropores in the material [13]. The conversion of the raw material to activated carbon requires two main activation processes which are chemical activation and thermal activation. The chemicals normally used are either an acid or strong base such as phosphoric acid, potassium hydroxide, zinc chloride and sodium hydroxide [14]. Phosphoric acid and zinc chloride are activating agents usually used for the activation of lignocellulosic materials which have not been previously carbonized, while alkaline metal compounds usually KOH are used for activation of coal precursors or char. The positive aspect in the chemical activation method in comparison with the thermal activation would be that in this method the activation of the raw material is done in room temperature as well as shorter activation time [15]. Besides that, it is stated that chemical activation produces higher surface area in terms of pores formation and also higher yield of carbon. This is because the chemical agents used in this process are substances that contain dehydrogenation properties that prevent formation of tar and reduce the production of other volatile products [14]. Where else for the thermal activation the raw material will be carbonized at high temperature with the absence of oxygen gas [15, 16]. For complete oxygen free carbonization, an inert gas normally nitrogen gas will be purged into the furnace. During this carbonization period only 80 percent of the carbon content will be attained. Besides that, this thermal activation process also removes most of hydrogen, the non-carbon elements and oxygen in gaseous form by means of pyrolytic decomposition causing the formation of organized crystallographic [17, 18]. Both this activation process are done to increase the surface area and develop porous of the raw material. The effectiveness of the activated carbon to adsorb gasses depends on the number of carbon elements in the material as well as the pore size [19].

Therefore this research project will be focusing on carbon dioxide adsorption using spent tea leaves. The reason for the selection of this raw material would be its availability in abundance, cost effective and its carbonaceous physical properties [9]. In the process of preparing tea beverage, once the essence of the tea leaves has been extracted, it will then be discarded into the dustbin as waste. Hence, spent tea leaves are considered to be a contributing factor towards the production of solid waste [11]. Currently, there are many researches conducted using waste tea leaves but very limited study were conducted using the spent tea leaves from hawker stalls and restaurants as

most of the leaves used are from the tea factories itself. Besides that, in the project the effect of carbonization temperature, heating rate and activating agent on activated carbon characterization will be studied. It is believed that these three parameters strongly affect the micropore structure of the activated carbon which in directly lead to the efficiency and the development of the micropores of the activated carbon. Thus it is important to identify whether the efficiency and structure of an activated carbon changes with carbonization temperature, carbonization heating rate and the type of activating agents. The research question for this project is 'Does the carbonization temperature, carbonization heating rate and type of activating agent affect the micropore structures formed on used tea leaves-derived activated carbon ? In addition the purpose of using two different activating agents, KOH and K_2CO_3 would be to study whether a similar effect on micropore structure of the activated carbon can be obtained from these chemicals. It is also well known that carbon surface area and micropore volume has adhesive effect on CO_2 adsorption rate. The bigger the surface area and micropore volume, the higher the carbon dioxide adsorption rate [10]. Besides that, when selecting the raw material for the activated carbon it is important to take pore volume, composition, particle size, chemical structure, mineral content, pore size distribution and specific surface area into consideration as these properties has an effect on the volume of mesopores and micropore structur [9]. In this project another angle that can be focused on would be does the changes in surface area and micropore structure of an activated carbon have an effect on the CO_2 adsorption rate? For, gas adsorption due to its molecular structure large micropore volume is required for efficient CO_2 adsorption.

2. Research Methodology

The main objective of conducting this study would be to develop an efficient activated carbon and study its relationship between the adsorption rate and micropore structure. The parameter that would be manipulated in this project is carbonization temperature, carbonization heating rate and the type of chemical activating agents.

2.1 Materials

The raw material used for the production of activated carbon is spent tea leaves. An average of 4 kg spent tea leaves were obtained from each restaurant around the Subang Jaya area everyday. The spent tea leaves obtained form the restaurant has a mixture of all types of tea leaves however majority of the tea leaves are fermented black tea. Besides that, this study will be focusing on the three parameters rather than the types of the spent tea leaves. The collected sample were washed several times with distilled water for the removal of impurities and dried in a forced air convection oven (FAC -50) at $110^{\circ}C$ for 24 hours. The two chemical activating agents used were anhydrous Potassium Carbonate (R&M Chemicals) and Potassium Hydroxide (R&M chemicals). For the neutralization process 1% Hydrochloric Acid (R&M Chemicals) was used [10, 22, 24, and 25].

2.2 Preparation of Activated Carbon

This section was divided into three main sections which are chemical activation, thermal activation and neutralization process. For the chemical activation, Potassium Hydroxide (KOH) and Potassium Carbonate (K_2CO_3) will be added into

the raw material for the initial activation process. The equation used for preparation of the material based on the impregnation ratio would be as follows:

$$\text{Impregnation ratio} = \frac{\text{Mass of Alkaline}}{\text{Mass of Raw Material}} \quad (1)$$

The selected impregnation ratio for Potassium Carbonate (K_2CO_3) was 1.5 and for Potassium Hydroxide (KOH) it was decided that an impregnation ratio of 2.0 would give the most effective results [22, 24]. Thus, 500 gram of K_2CO_3 is mixed with 400 ml of distilled water and 333 gram of tea leaves to give a ratio of 1.5. The similar method will be used to prepare Potassium Hydroxide activation only this time a ratio of 2.0 was used to prepare the sample. Both the samples were stirred at 200 rpm for 3 hours and left overnight for complete impregnation. Once the chemical activation is complete all the sample will be placed in the oven again and dried at 110°C for 24 hours [22,61]. The dried impregnated spent tea leaves was then transferred into a ceramic crucible, covered with an aluminum foil and inserted into a high temperature furnace (KSL-1100X) for 120 minutes. The thermal activation is conducted at constant carbonization period at three different temperatures and heating flow rate. The selected temperatures would be 500°C , 600°C and 800°C , where else for the heating rate would be $5^\circ\text{C}/\text{min}$, and $10^\circ\text{C}/\text{min}$. Once the samples have been carbonized, it will then be left at room temperature to be cooled. Cooled samples will then need to be neutralized to remove the remaining chemicals on the samples. A pH meter with a probable calibration error of 5% (Hanna pH Meter HI 110 series) was used to measure the pH of the sample. Initially 1% of Hydrochloric acid was added onto the carbonized sample for the removal of organic salt. The samples will be washed and filtered repeatedly with distilled water until it reaches the required pH of 6.5-7. The washed sample was then placed in the forced air convection oven (FAC - 50) and dried at 110°C for 24 hours [10, 11, 24, and 25].

2.3 Structural characterization and Analysis of Activated Carbon

There will be three major analysis conducted on the activated carbon samples. Those analysis include Proximate and Ultimate analysis, Fourier Transform Infrared Spectrophotometer (FTIR) and Brunauer- Emmett- Teller (BET)

2.31 Proximate and Ultimate analysis

A Proximate thermogravimetric method on the spent tea leaves to identify the, major components, carbon content, ash content, volatile matter and moisture level of the raw material by means of comparing the percentage of weight change with the temperature for each TG chart (ASTM D7582 standard method). Where as for Ultimate analysis a CHNS analyzers was used to determine the structural content in the material

2.32 Fourier Transform Infrared Spectrophotometer (FTIR)

An analysis on the surface functional group of the raw material, impregnated samples and the final activated carbon was done using Perkin Elmer Fourier Transform Infrared Spectrophotometer. The first step in conducting this FTIR analysis would be by adding 1:99 ratio of the activated carbon sample with KBr powder.

This mixture was grinded using a pestle and mortar until a perfectly mixed powder is formed and a small amount of it was placed in a cylindrical bore in between two dies. The assembled cylindrical bore was then placed into a hydraulic press to pelletize the mixture. The force was set at 10 tons at a vacuumed pressure state for 20 seconds. The third step was to remove and dismantle the cylindrical bore from the hydraulic press. A disc like shaped sample mixture was then removed from in between the dies and placed onto a disc holder and molded into the FTIR Spectrophotometer. This analysis would produce a graph comparing the Wave number vs. Transmittance and can be used for sample with covalent bond. The spectra range recorded would be from 4000cm^{-1} to 450 cm^{-1} [22]. Last but not least, before running the analysis it is important to make sure that the activated carbon samples are dried in the oven for few hours before the analysis to prevent any moisture build up in the sample. Another precaution that needs to be taken into consideration would be to ensure that the polished surface of the die is wiped clean and is free from any dust or finger prints.

2.33 Brunauer- Emmett- Teller (BET)

To calculate the pore size distribution, surface area, micropore and mesopores structure for each sample a Brunauer- Emmett- Teller (BET) method was used. In this method the specific area (degassed at 110°C for 12 hours) was obtained from the application of multipoint N_2 adsorption isotherm with the BET equation at a pressure of $p/p_0 = 0.5-0.3$. As for the pore distribution a cylindrical pore model using Non Local Density functional Theory (NTDFT) method was used to calculate the total mesopores and micropore volume. The relative pressure used for the calculation of total pore volume was 0.95 bars. A fitting error at a range of 0.03 to 0.35% varied throughout the whole experiment. Estimation on the micropore volume as well as the micropore surface area was estimated using a t-plot method of the BET model [25].

3.0. Results and Discussion

This section is divided into main four sections. The first section would discuss the structural analysis of the raw and pretreated material using proximate and ultimate analysis. The second section would be focusing of the effect of activating agent, carbonization temperature and carbonization heating rate on the BET analysis. The third section is about the structural bond of the samples using FTIR analysis. The final section focuses on the relationship of the activated carbon micropore with the carbon dioxide adsorption capacity

3.1 Characteristics of Raw Material

3.1.1 Proximate Analysis

The initial moisture in the raw spent material is 7.5% and after carbonization the percentage of moisture decreased to around 5%. This shows that carbonization of raw material reduces the moisture level by 2.5%. Only slight amount of moisture was reduced because the initial raw sample was already dried in an oven at 110°C for 24 hours, during this period most of the water content in the sample would have already vaporized. For storage purposes a moisture level of less than 3% is much preferred because the presence of high moisture will result in fungal growth and multiplication which could cause carbon blockage [48]. The higher moisture level in the raw spent

leaves and carbonized sample compared to the recommended value is due to the longer period taken to send the sample for the proximate analysis thus, a slight amount of moisture may have entered the sample bottles [27, 30]. From table 3.1 it is seen that the raw spent tea leaves sample has volatile matter of 70% and after carbonization the amount reduced to 17.5%. At high temperatures the organic substances in the material would degrade causing instability in the carbon matrix which will result in formation of gas and liquid tar as well as high carbon content [10, 30]. For the raw tea leave sample the amount of fixed carbon was 22% and after carbonization it increased to 68%. The fixed carbon content specifies the amount non volatile in the sample which would be in the form of pure carbon. However, high fixed carbon gives a more friable texture of the carbon where as high volatile matter and lower fixed carbon content gives higher carbon strength [30]. Lastly for the ash content, the raw material has extremely little ash content of 0.5%, on the other hand the carbonized sample has 10%. The increase in ash content is due to the residual remain of the inorganic substances in the material. This inorganic material when exposed to high temperature it would turn to ash as it is unable to convert itself to carbon molecules. The range of ash content is generally between 2% to 10%. High ash content can cause catalytic effect and increase hydrophilic structure during regeneration process [10, 27,30]

Table 3.1: Proximate Analysis of raw sample and carbonized sample.

	Moisture level (%)	Volatile matter (%)	Fixed Carbon (%)	Ash Content (%)
Raw spent tea leaves	7.5	70	22	0.5
Carbonized sample at 600°C	5	17	68	10

3.1.1 Ultimate Analysis

Ultimate analysis of the raw tea leaves has a reasonable amount of carbon content of 46.40% and after carbonization the amount of carbon increased to 71.91%. Higher carbon content in the sample produces better activated carbons quality which also related to the adsorption capacity of the activated carbon [29]. As for the amount of hydrogen, the percentage of hydrogen decreases when exposed to high temperature because hydrogen element has a very low molecular weight of one thus, the hydrogen content is easily vaporized from the hydrocarbon formation during carbonized. Lastly, the sulphur content in the raw material is around 1 % and after carbonization it increases to 2.3%. Low sulphur content is preferred as high sulphur content in the activated carbon can cause corrosion, clinking and slugging in the equipment [29,33].

Table 3.2 Ultimate Analysis of raw spent tea leaves and carbonized sample

	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulphur (%)
Raw spent tea leaves	46.40	6.809	3.830	1.019
Carbonized tea leaves at 600°C	71.91	2.415	4.070	2.303

3.2 Structural Characteristics of the Activated Carbon

As shown in table 3.3 the maximum surface area obtained is $732\text{m}^2/\text{g}$.which falls under the minimum range of the typical surface area range of $700\text{m}^2/\text{g}$ to $1800\text{m}^2/\text{g}$. As for the micropore size the smallest diameter of the pores obtained is 1.93nm and the largest is 3.55nm . For effective carbon dioxide adsorption ultramicropore ($<1\text{nm}$) is much preferred. However, in this project only two samples has fallen under the micropore category. This could be due to the fact that the dehydration and elimination reaction was incomplete thus more mesopores structure was formed. The range on micropore in this project lies between $0.35\text{cm}^3/\text{g}$ to $0.446\text{cm}^3/\text{g}$. [31,34].

Table 3.3: Surface area and porosity of the activated carbon at different parameters

Activating agent	Parameters	Surface Area (m^2/g)	Micropore Volume (cm^3/g)	Micropore Size (nm)
KOH	800°C at 10°C/min	654.33	0.404	2.47
	600°C at 10°C/min	710.99	0.346	1.95
	500°C at 10°C/min	608.28	0.478	3.14
	600°C at 5°C/min	478.29	0.393	3.28
K_2CO_3	600°C at 10°C/min	732.82	0.360	1.93
	600°C at 5°C/min	501.39	0.446	3.55

3.2.1 Effect of different activating agents on BET analysis

Based on the BET analysis obtained in table 3.3 it is seen that K_2CO_3 shows more promising results compare to KOH in terms of surface total surface area , micropore area and micropore size. At carbonization temperature of 600°C and heating rate of $10^\circ\text{C}/\text{min}$, a difference of 4% is obtained for the surface area both the activating agent and as for the micropore size a difference of 0.02nm was achieved. The similar relationship was also found at a heating rate of $5^\circ\text{C}/\text{min}$, with a difference of 5% in surface area and 0.2nm in micropore size. The reason of K_2CO_3 being a better chemical activating agent could be that carbonates has better catalytic reactivity towards the dehydration of spent tea leaves compared to hydroxides [35,36]. In addition, it can also be said that K_2CO_3 has better ability to decompose the lignocellulosic biomass of the tea leaves compared to KOH. Thus , for a more efficient and environmental friendly activated carbon the use of K_2CO_3 as an activated carbon is much encouraged [22,35,36].

3.2.2 Effects of different carbonization temperature on BET analysis

The BET results shows that 600°C gives the highest surface area , highest micropore volume and the smallest micropore size followed by 800°C and the least is 500°C . This is because at low temperature of 500°C the reaction between the chemical

activating agent and the carbonization heat is taking place slowly hence an improper pore structure is formed. As temperature from 500°C to 600°C the surface area and porosity of the activated carbon increases due to high reaction between the chemical activating agent of KOH and K₂CO₃ with the thermal activation process which produces tar from the crosslink framework generated by the chemical activating agent. However, for 800°C the reason the surface area and porosity of the activated carbon decreases could be that during combustion and chemical activation large amount of the volatile matter has been released making the sample more friable. Another reason for the decrease in surface area at 800°C could be due to high breakdown of micropore wall at high temperature [10,15,18, 22].

3.2.3 Effects of different carbonization heating rate on BET analysis

As for the heating rate it is seen that 10°C/min is a more suitable carbonization heat rate as higher surface area, higher micropore volume and smaller micropore size is obtained. At carbonization temperature of 600°C and heating rate of 10 °C/min the KOH impregnated samples has a surface area of 710.29m²/g, a micropore area of 679.73m²/g and a micropore size 1.95, whereas when comparing with 5°C/min the surface area is only 478.29m²/g, micropore area is 327.95cm²/g and finally micropore size of 3.28 which is already a mesopores. A similar relation was also found in samples impregnated with KOH, the higher heating rate of 10°C /min had better porosity structure compared to 5°C/min. This difference in porosity value is because at lower heating rate the volatile product removed per unit time is higher compared to a higher heat rate. At lower heating rate a longer time is taken to the complete carbonization process, allowing complete removal of the volatile matter in sample thus, allowing complete breakdown of the micropore wall. This reaction would also contribute in the reduction of micropore volume, and increase the formation of mesopores in the sample [23, 37].

3.4 FTIR Analysis

When comparing all the spectra values it is seen that all the samples have similar stretching vibration of hydroxyl compound from 3500-3200 cm⁻¹. This indicates that all the samples have strong links of hydrogen bond. In comparison with heating rate samples carbonized at 5 °C/min have stronger O-H bonds. In addition, KOH samples has slightly stronger O-H bonds compared to the K₂CO₃ sample, this indicates that KOH activating agents has more dehydration properties compared to K₂CO₃. The spectrum shown in K₂CO₃ and KOH at 500°C at 10 °C/min has an extremely very weak asymmetric C-H stretching compared to all the other samples. This difference could be due to the existence of high moisture level in the sample. The reduction in the C-H level also indicates that the particular activation has reduced the hydrogen value in the samples. Similar wavelengths and peaks is seen at the C=C bonds at 1623 cm⁻¹ K₂CO₃ at 600°C at 10 °C/min and 5 °C/min. For samples impregnated in KOH for the C-H asymmetric bending disappears at 10 °C/min. lastly, the formation of C-C stretching bond of K₂CO₃ for 500°C at 10 °C/min has disappear from the sample. Thus, based on the peaks and spectrum lines obtained from the FTIR analysis it is seen that sample carbonized at 500°C at 10 °C/min forms weak carboxyl bonds [17, 22, 28].

3.5 The performance of carbon dioxide adsorption based on activated carbon micropore size

For an effective gas adsorption processes the pore size of an adsorbent to capture the gas has to be maximum 5 times the adsorbents molecular size thus with CO₂ having a molecular size of 0.209nm the pore size of an activated carbon has to be lesser than 1nm for effective adsorption [17,31]. However too small pore sizes (<0.26nm) also can prevent carbon dioxide adsorption [31]. In this study the range of micropore sizes are in between 1.93nm to 3.55nm. Based on theoretical analysis the carbon dioxide adsorption for the activated carbon samples in this study is considered to be less effective, however based on similar pore sizes it is seen that a higher range of micropore size still has the ability to adsorb CO₂ [17,31,38,39]. In comparison, with other studies it is seen at a micropore size of 2.47nm the CO₂ adsorption is 2.98 mmol/g whereas for micropore size of 1.95nm CO₂ adsorption is 4.10 mmol/g [24]. In another study, for the micropore size of 3.14nm the CO₂ adsorption is 2.25 mmol/g and for 3.28nm the adsorption is 1.93 mmol/g [38]. Besides that, when comparing this results with a commercial activated carbon there is a difference of only 2.6 mmol/g with the sample activated at 600°C at 10°C/min with KOH [24]. Thus, this shows that these activated carbon samples have the abilities to absorb carbon dioxide even with larger micropore sizes. Further more it is also seen that smaller micropore sizes gives better CO₂ adsorption [17, 31]. The results of the CO₂ adsorption is only limited to certain parameter as most of the adsorption rates given in other journals are conducted in different temperature and pressure. Thus, only a limited amount of results can be obtained.

4.0 Conclusion

In this study, a low cost and environmental friendly activated carbon adsorbent can be developed from spent tea leaves. Based on the proximate and ultimate analysis obtained it is found that the raw spent tea leaves has a good carbon content, low ash and moisture content making it a suitable raw material for activated carbon. Besides that it was also seen that the carbonization process increases the carbon content and reduces the moisture content in the sample. This proves that the carbonization process increased the carbon content in the raw material. However, it was also seen that during carbonization process the % yield decreases with respect to increasing temperature and decreasing heating rate. As for the effect of activating agent towards the micropore structure and surface area it was found that K₂CO₃ produced higher surface area 732m²/g and smaller micropores size of 1.93nm compared to KOH. In addition for the effect of temperature towards the surface area and micropore size it was found that the optimum temperature is 600°C as higher amount of surface area was obtained compared to 800°C and 500°C. As for the heating rate it was found that samples carbonized at 10C/min have better porous structure compared to the samples heat at 5°C/min. Hence, it was found that sample chemically activated by K₂CO₃ at 600°C at 10°C/min produced the most porous structure compared to other parameter but still is not the most efficient activated carbon.

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Performance of POME blended Nano-lubricant

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Abstract

POME derived from palm oil transesterification process possesses quality including high viscosity and lubricating properties which enables it to form protective boundary layer to reduce wear properties on metal surfaces. Graphene nanoparticles on the other hand possess high thermal conductivity and small morphology which enables it to reduce friction and withstand high pressure. By adding the POME and graphene into conventional bio-lubricant, it is believed that their combined properties will lead to a breakthrough in nanolubricant research field. The study aims to produce a stable nanolubricant blended with optimum proportions of POME and graphene oxide. Surface modification of graphene was conducted by simplified Hummers method. The presence of peaks from FTIR spectroscopy at 3409.18 cm^{-1} and 1627.24 cm^{-1} indicates the presence of OH and COOH groups and successful oxidation of graphene nanoparticles. Graphene oxide with 0.01 to 0.03 wt% was blended with POME of 1 to 5wt% in TMP ester base oil to obtain different proportion of nanolubricant. After a two weeks of visual observation, GO with 0.01wt%+1wt%POME, 0.025wt%+2.5wt%POME and 0.03wt%+2.5wt% POME was selected to be the most stable nanolubricant. The lubricant sample was then analysed zeta potential to characterize the stability of particles. The thermal conductivity and viscosity measurement was also made to study the thermophysical properties. It is observed that with the increase in graphene concentration, an increase is observed in thermal conductivity and viscosity of the sample.

Keywords: Nanolubricant, Palm oil methyl esters, graphene oxide.

1. Introduction

In today's world, high amount of energy output is provided by fossil fuels. However with increasing demand and decreasing supply, the need to look for alternative sources increases [1]. Almost all of the daily life process requires fossil fuel, from generation of electricity up to machine lubricants. Apart from the threat of insufficient fossil supply, the pollution and hazard created from fossil fuel emission also leads to strict restriction to be imposed, which ultimately leads to interest in alternative sources [1]. Lubrication plays major role in environmental pollution. In fact, a big fraction of lubricants contributes to the ecological damage during or after its usage.

Lubricant purposes to inhibit progressive wear, reduce friction at the same time enhance efficiency and durability in engine components [2]. Mineral oil based lubricants have been ruling the market since 20th century. With much cheaper option, the market has outshined the production of plant based lubricants [3]. However, mineral oil based lubricant contains high amount of sulphur and phosphate which adversely affects the environment. With enforcement of environment regulation to minimize release of heavy metals such as Sulphated Ash, Phosphorus and Sulphur (SAPS), plant based lubricant is gaining more and more attention [2].

As mentioned, plant based lubricant or commonly termed biolubricant is in limelight as alternative for mineral oil based lubricant due to better lubricating performance. Biolubricant derived from vegetable oil offers added advantages over mineral oils with biodegradability, less emission of carbon dioxide and highly renewable [4]. Palm oil methyl ester (POME) is a type of methyl ester derived from palm oil which has good potential to be used as bio-lubricant. POME is prepared by means of transesterification process where palm oil is reacted with methanol in presence of catalyst (usually alkali) to form methyl or ethyl esters. POME is suitable material for it has high oxidative values that increases the lubricity, combustion and reduces the emission [5]. Apart from that, esters are polar lubricants where they form physical bonds with surface oxide layer when transferred to metal surfaces [6]. The suitability of palm oil methyl ester as lubricants have been widely discussed and proven. The paper on palm oil methyl esters and its emulsion effect on lubricant performance and engine wear have shown how POME has better resistivity against wear compared to ordinary diesel [7]. Similarly the research on wear prevention characteristics of a palm oil based TMP (trimethylolpropane) ester as an engine lubricant how addition of POME has improved the tribology properties of lubricant to perform better compared to mineral oils [8].

Trimethylpropane (TMP) as base stock for biolubricant is highly preferred in the study of alternative lubricant. This is due to its benefits of having low melting points, which allows it to react at lower temperature and being available at cheaper price which reduces the cost of the process [9]. Using vegetable oil by itself as lubricant cannot provide best performance, especially at higher temperatures [10].

Therefore, the use of polyol incorporated with methyl ester was investigated. Reportedly, the transesterification of polyol and methyl ester would result in polyol esters that contribute to better performing biolubricants [11]. This is proven as transesterification removes the hydrogen molecules from the beta carbon position of substrate consequently improving oxidative and thermal stability of the ester [11]. Zulkifli and co-workers [8] have shown how TMP esters improved coefficient friction and wear preventive properties. Study by Resul and co-workers on properties of modified jatropha biolubricant by means of transesterification with trimethylolpropane also showed improved viscosity, wear, pour point and oxidative stability [9].

New research trend shows that addition of nanoparticles has the tendency to enhance the property of lubricating oil by creating a protective layer [5]. Nanoparticles mixed with lubrication oil have the ability to decrease the friction coefficient and increase pressure which improves the anti-wear and anti-friction properties [12]. The use of nano diamonds and SiO₂ in liquid paraffin oil in minute concentration has reportedly improved anti-wear and antifriction properties [13]. The exceptional tribology, self-mending and eco-friendly nature of Cu nanoparticles results in many research published in area of nanolubricant [14]. With the emerging study on the potential nanoparticle for lubrication purpose, the potential of graphene for the synthesis of nanolubricant is questioned. Graphene is a thin layer of carbon, where the carbon atoms are connected in hexagonal honey comb lattice, with one carbon atom covalently bonded to another three carbon atoms. Graphene sheets are extremely thin, with one atom thick and flat in shape. For a very thin material, graphene is very strong with high mechanical strength, thermal stability and charge mobility [15]. The use of graphene is considered in lubricant preparation is due to the fact that addition of this nanoparticles eliminates the need to use anti-wear and extreme pressure additives which are highly toxic and hazardous to the environment [15].

Nanoparticles despite its excellent tribology properties cannot be used directly due to its high surface energy. This may result in the particles to agglomerate and settle down [5]. Therefore, to produce a uniform colloid of nanoparticle infused lubricant, surface modification of the particles became necessary. Many have reported that the modified nanoparticles have good dispersion in lubricating oils [15]. Only when nanoparticles uniformly dispersed in the lubricant, it is able to perform to its fullest. Luo et al. [12] reported that modified Al₂O₃ shows excellent dispersion stability and is difficult to agglomerate in lubricating oil. Li and Zhu [16] also proved that the modified SiO₂ particles in hydrocarbon can disperse stably in lubricating oils. Extensive research on Cu as nanoparticle results in outstanding anti-wear and friction reducing properties with its modified surface. Apart from that, test conducted by Ingole et al. [13] on the dispersion of TiO₂ nanoparticles shows that, TiO₂ particles settles and agglomerates faster when no surfactants or dispersion agents is introduced. However when the dispersion is achieved, high wear and friction resistance is shown.

In this study, a breakthrough is intended to develop potential nanolubricant with enhanced friction and wear resistance utilizing the properties of POME, TMP and graphene oxide nanoparticles. The objective of the paper is to produce a well dispersed, and stable homogeneous lubricant blended with different proportions of POME and graphene which subsequently improves thermophysical and tribological properties of blend at the end of this research.

2. Methodology

2.1 Materials

The main component of the experiment includes TMP esters, POME and graphene. Trimethylolpropane (TMP) used as base stock was obtained from Emery Oleochemicals. POME was obtained from Sime Darby. Graphene of 98.7% purity was obtained from Graphene Supermarket, United States. Hydrochloric acid (HCl), potassium permanganate (KMnO₄), phosphoric acid (H₃PO₄) and hydrogen peroxide (H₂O₂) for synthesis of functionalized graphene were obtained from Sigma-Aldrich.

2.2 Preparation of Graphene Oxide

The graphene powders were first functionalized using Simplified Hummer's method. A total net mass of 0.8g of graphene was weighed and added into solution containing strong oxidizing agent namely sulphuric acid and phosphoric acid. The acids were prepared at a ratio of 4:1 whereby 320ml of sulphuric acid and 80ml of phosphoric acid were measured. As soon as the graphene was added into the acid, 18g of potassium permanganate were gradually added into the mixture. The mixture was left to stir for 3 days. The oxidation process comes to a halt when the addition of 300ml of deionized water and 50ml of hydrogen peroxide. Upon adding hydrogen peroxide, the brown suspension turns bright yellow. Next with a ratio of 1:10 hydrochloric acid and deionized water were added into the suspension. The suspension was decanted and centrifuged at 8000rpm to isolate the paste samples from the remaining solution. The paste collected was then dissolved in deionized water. The suspension was washed for 5-7 times until its pH value becomes 7. To ease this step a few drops of sodium hydroxide was added to fasten the neutralization process. The suspension was further filtered and the paste was collected and kept in a petri dish. Finally, the collected sample was put into an oven (FAC 350) operating at 60°C±1°C until the sample becomes completely dry.

2.3 Characterisation of Graphene Oxide

The characterisation of graphene oxide particles were recorded using Fourier Transform Infrared Spectra (FTIR) on a Perkin Elmer Spectrum 100 spectrophotometer using Potassium Bromide (KBr) as mulling agent. Sample to KBr

ratio of 1:99 was transferred to mortar and grinded homogeneously with a pestle. Cylinder bore was assembled with provided die, shiny surface facing upward. A small amount of ground sample mixture was added just enough to cover the surface of the die. The plunger was inserted and lightly swivelled to obtain a flat and even surface. Once even surface was obtained, the second die was inserted into the bore, with shiny surface facing the sample and followed by plunger. The assembled die was then placed to the hydraulic press. The die was ensured to be held firmly and tightly in the hydraulic press. At vacuum condition, force of 10 tons was applied by pulling the pump handle downwards. The die was left under pressure for 20 seconds. After 20 sec, vacuum was slowly released and die was removed from the press. Sample was removed from the dismantled die and placed in a disc holder, which was then placed in the spectrophotometer for analysis.

2.4 Preparation of nanolubricant

Two set of lubricant oil was prepared for the experiment purpose, one set containing graphene and POME and another without POME. Graphene with concentration of 0.01, 0.025 and 0.03 wt% was carefully measured in closed weighing balance. Similarly, POME with concentration of 1, 2.5 and 3 wt% was measured. The measured values of graphene and POME were added to the TMP ester to make up total lubricant of 20g. The prepared sample was sonicated in an ultrasonic bath (Sonica Ultrasonic Cleaner) for 4 hours at 25°C to obtain a well dispersed nanolubricant sample. The sample was then kept for monitoring of the stability for a period of a week. At the end of the week, most stable sample from all three different concentrations will be analysed using Malvern Zeta Potential Analyser from University of Nottingham, Semenyih.

2.5 Thermophysical Properties of Nanolubricant

2.5.1 Thermal Conductivity

Thermal conductivity measure the ability of the sample to conduct heat. Thermal conductivity of lubricant samples was measured using the KD2-pro equipment (Decagon,USA), which is a portable thermal analyser. Before usage, the thermal portable analyser was first calibrated with provided standard glycerine to ensure validity and accuracy of the data [11]. The study of thermal conductivity was conducted with a single needle probe of 6 cm. The thermal conductivity of prepared nanolubricant was measured for temperature of 25-60°C as specified by Gupta et al. [8] for this experiment.

3.5.2 Viscosity Measurement

Viscosity being an important parameter for lubrication is also measured in this experiment. The viscosity of the nanolubricant sample defines its characteristics by determining the formation of a film between a moving and stationary part [10]. The samples were tested using the enhanced Brookfield UL Adapter, which consists of

precise cylindrical spindle rotating inside accurately machined tube, attached to the standard Brookfield DVII+ Pro Viscometer for small sample size (16ml) measurement. Brookfield Rotary Method ASTM D2893 was used to measure the dynamic viscosity.

3. Results and Discussion

3.1 Characterisation of Graphene Oxide

Graphene oxide by means of simplified Hummers method was synthesised using graphene in concentrated acid with strong oxidizing agent. This method was opted as it appears to be utmost effective and less harmful for graphene oxidation as well as being the most common method of graphene synthesis [17, 18]. Simplified Hummers method is productive in making of graphene oxide as the surface of graphene oxide are highly oxygenated, bearing hydroxyl, epoxide, diol, ketone and carboxyl functional group which has the ability to modify the van der Waals interaction significantly and allow solubility in water and organic solvent; in this case TMP ester [15, 19]. With the presence of additional carbonyl and carboxyl at the edges and both sides of plane, thin sheet of graphene oxide can be obtained as described in literature [15, 17].

FTIR is opted to identify the structure and functional group in synthesized graphene oxide. Based on fig.1, it is clearly observed that functionalization method opted is successful in oxidizing graphene. As the peaks highlight components in higher concentration, the peaks at 3409.18 cm^{-1} and 1630 cm^{-1} show the adsorption of hydroxyl (-OH) from water molecules on graphene oxide, which concludes the strong hydrophilicity of the sample [17]. The presence of peaks at 1627.24 cm^{-1} and 798.41 cm^{-1} can be ascribed to the stretching vibration of C=C and C=O of carboxylic acid and carbonyl groups that exists at the edges of graphene oxide [20]. Finally the peaks at 1376.67 cm^{-1} and 1087.46 cm^{-1} relates to the stretching vibration of C-O of carboxylic acid and C-OH of alcohol respectively [17].

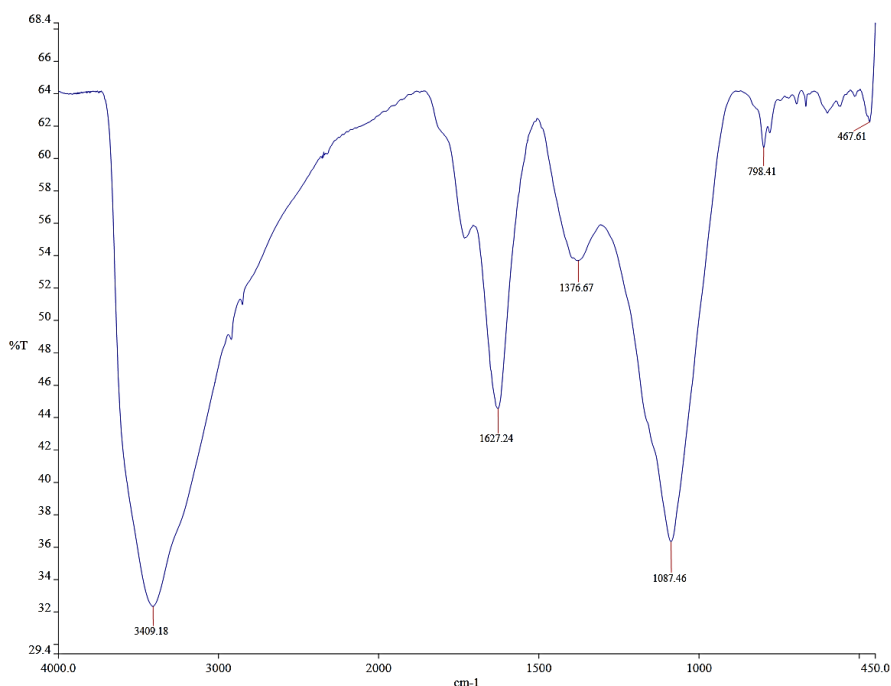


Fig.1: FTIR spectrum of graphene oxide

3.2 Preparation and Stability of Nanolubricant

The samples were prepared in three different concentrations of 0.01wt%, 0.025wt% and 0.03wt%. The concentration was chosen based on literature that proves that lower concentration provides good improvement to friction and wear as the nanoparticles improves the properties of base oil by deposits on rubbing surface [14]. Similarly, concentration of POME were kept between 1 to 5wt% to study the performance of anti-wear characteristics with 5wt% is expected to provide the best anti-wear characteristics as reported in literature [11]. Table 1 shows the nanolubricant sample preparation according to weight percentage. As the work was done with digital precision unit, the error is taken to be half of the precision unit. In this case, as the weighing balance smallest precision is 0.001g, the error to be considered is ± 0.0005 g.

To ensure the stability of the sample and graphene well dispersed within the mixture, dispersion using ultrasonic bath was chosen. After dispersing for 4 hours under room temperature condition, it can be seen that the lubricant are uniformly dispersed. Fig 2 shows the well dispersed nanolubricant sample for 0.01wt%, 0.025wt% and 0.03 wt% of graphene oxide. Due to the high surface energy of nanoparticles, graphene oxide has the tendency to agglomerate and settle down. Hence to ensure the prepared samples are stable and homogeneous, the prepared solution was monitored visually for duration of two weeks to see if there is phase separation or agglomeration. When no such occurrences observed, the sample can be analysed further for stability with Zeta Potential Analyser and Optical Microscopic Images.

Table 1: Amount of graphene, POME and TMP used for preparation of nanolubricant

Graphene		POME		TMP
(wt%)	(g)	(wt%)	(g)	(g)
0.01	0.002	0	0	19.998
	0.002	1	0.2	19.798
	0.002	2.5	0.5	19.498
	0.002	5	1	18.998
0.025	0.005	0	0	19.995
	0.005	1	0.2	19.795
	0.005	2.5	0.5	19.495
	0.005	5	1	18.995
0.03	0.006	0	0	19.994
	0.006	1	0.2	19.794
	0.006	2.5	0.5	19.494
	0.006	5	1	18.994
TOTAL		0.052	5.1	234.848

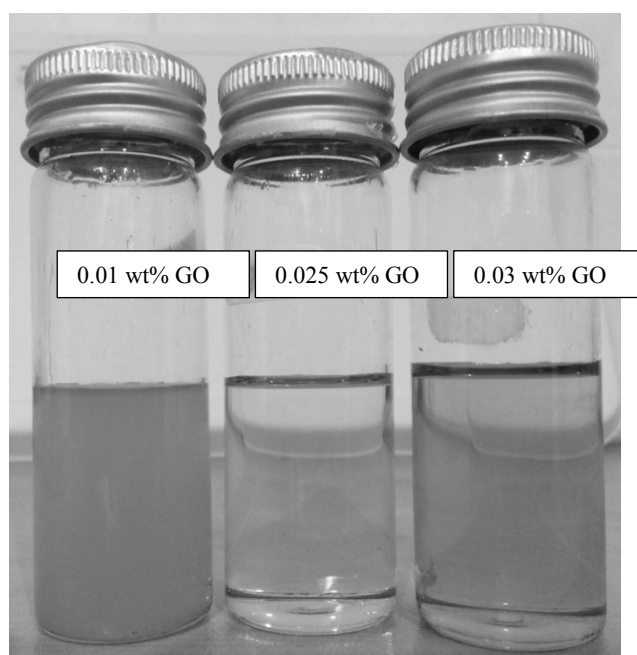


Fig 2: Dispersed nanolubricant sample after 5 days.

After a period of two weeks of visual observation, it is noticed that the samples with 0.01wt%GO+1wt%POME, 0.025wt%GO+2.5wt%POME and 0.03wt%GO+2.5wt%POME has the highest stability compared to other samples where sedimentation is observed. It is also observed that higher the concentration of GO, darker the colour of the solution as the solution turns from clear yellow to brown, which indicates that more graphene oxide particles are dispersed in the solution. As for the POME addition, it is observed that the samples with POME have higher

stability compared to the one without POME. This is due to the presence of oleic acid in POME that acts as stabilizer for the graphene and TMP ester for well distributed and stable nanolubricant.

3.3 Validation of Stability of Nanolubricant

The Zeta Potential absolute value is selected to describe the agglomeration of nanoparticles. Zeta potential values describe the potential difference between dispersion medium and the stationary layer of fluid attached to the dispersed particles. Basically it is a representation of surface charge repulsing between particles to avoid agglomeration [21]. In zeta potential, the higher the absolute value, the more will the dispersion resist agglomeration and the longer the duration of stability [22]. In short, the zeta potential values between 0 mV to ± 5 mV shows strong agglomeration of dispersed particles, ± 10 mV to ± 30 mV shows incipient instability and values above ± 30 mV shows overall good stability [22, 23]. In this research, the zeta potential values are expected to exceed ± 30 mV for highly stable and dispersed nanolubricant. Figure 3 below shows the zeta potential graph against total counts along with the zeta potential values. It is clear that the values are above ± 30 mV for all three samples stated earlier which implies that the nanolubricants prepared are highly stable. However, it is to be noted that the values are not completely accurate. In order to conduct the zeta potential test, it is vital to have the refractive index, viscosity and dielectric constant of the dispersed solvent. Although the refractive index and viscosity was measured, the dielectric constant was assumed from the palm oil dielectric constant as there was no reported literature on the dielectric constant of TMP ester. Hence, slight variation in the result is expected.

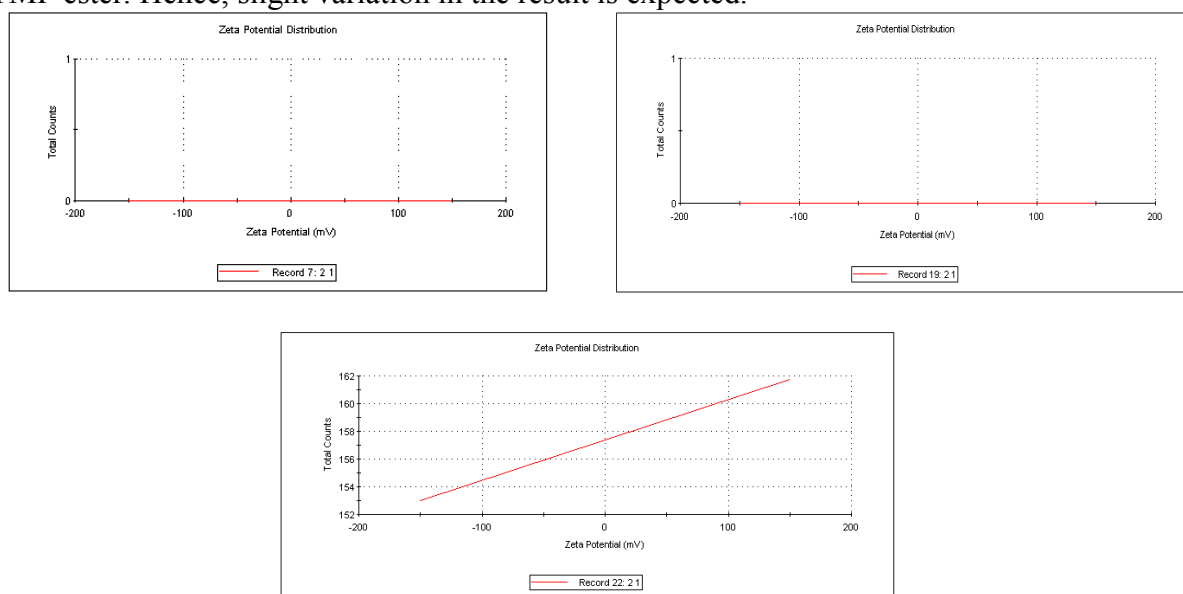


Figure 3 (a): Zeta Potential of 0.01wt% GO+1wt%POME, -30.2mV, (b) Zeta Potential of 0.025wt% GO+2.5wt%POME, -251mV, (c) Zeta Potential of 0.03wt% GO+2.5wt% POME, -41.7mV

3.4 Thermal Conductivity

The thermal conductivity of stable nanolubricant samples were measured at temperature varying from 25°C to 60°C. Fig 4 below shows the plot of thermal conductivity of nanolubricant with respect to change in temperature.

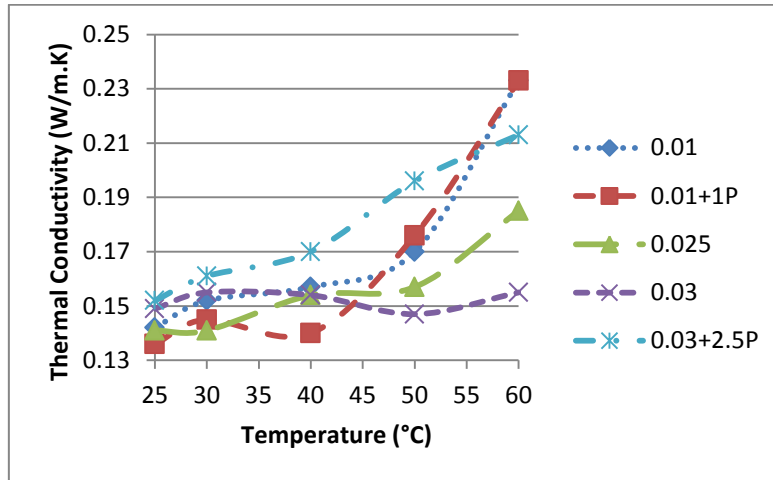


Figure 4: Thermal Conductivity vs. Temperature

Based on the result, it can be seen that as the concentration of graphene oxide increased, the thermal conductivity increased. This is due to the properties of graphene nanoparticles that are relatively high compared to base oil. From the fig 3 above, it can be observed an increment from 1% at 25°C and 5.3% at temperature of 60°C. This is due to the Brownian motion and outstanding thermal conductivity properties of nanoparticles [24]. As the temperature increases, nanoparticles gain high energy which in turn increases the kinetic energy and bombardments of nanoparticles [11].

Increase in thermal conductivity is highly regarded for lubricants as they allow hydrodynamic film formation especially under high slip and high load conditions [25]. Also, high thermal conductivity increases the amount of energy transferred from the lubricant to the contacting material and fluid, whereby decreasing the temperature in the contact zone and subsequently increase the viscosity and reduce the friction and wear properties.

3.5 Viscosity

The viscosity of samples was measured according to Brookfield Rotary Method ASTM D2893. Dynamic viscosity measures the fluid's resistance to flow when is subjected to force. The dynamic viscosity of the stable nanolubricant sample is measured at 40°C which is a standard temperature used to measure efficiency of lubricant. The measured values are as shown below.

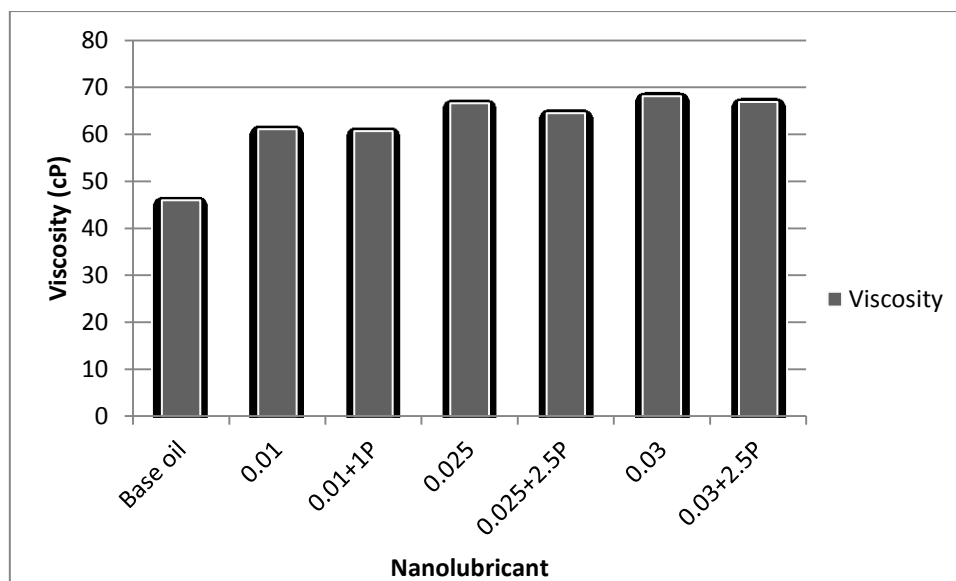


Figure 5: Dynamic Viscosity of Nanolubricant Sample

Based on the observation it can be seen that viscosity increases with the increase of graphene oxide concentration. Compared to TMP ester base oil, there is an increment of 32-48% in overall viscosity of lubricant. When spherical or tubular nanoparticles are introduced to base oil in a low concentration, it is a common phenomenon to observe a decrease in viscosity. This is due to the structure that enables the nanoparticle to settle between oil layers that lead to ease movement of fluid, i.e. lower viscosity. However graphene due to its flat structure has the opposite impact. The structure allows agglomeration to take place where when concentration is increased, large particles are created, which prevents the movement of oil layer and thus resulting in increase of viscosity [26]. Still, is also observed that the nanolubricant with addition of POME has slightly lower viscosity compared to the one without POME. This might be due to the presence of double bonds in POME that reduces the viscosity by 1.7-3.25%.

4. Conclusion

In this work, graphene oxide was successfully modified by oxidation via Simplified Hummers Method. The presence of functional groups like hydroxyl (3409.18 cm^{-1} and 1630 cm^{-1}), carboxyl (1627.24 cm^{-1} and 798.41 cm^{-1}) and carbonyl further proves the surface modification of graphene oxide. Nanolubricant with different proportion blend were prepared and monitored for stability. After duration of two weeks of visual observation, it is seen that the blend of 0.01wt%GO+1wt%POME, 0.025wt%GO+2.5wt%POME and 0.03wt%GO+2.5wt%POME has the highest stability compared to all the samples. Zeta Potential Analysis for all three samples shows high stability values with values exceeding $\pm 30\text{mV}$. The thermal conductivity measured for all blends of graphene with and without POME blending shows that, the thermal conductivity increases with the

increase of temperature. This is deduced to be the effect of graphene oxide that allows in energy gain of nanolubricant with respect to temperature that increased the kinetic energy and bombardness of nanoparticles. Higher viscosity is also observed in the nanolubricant compared to the base oil shows the impact of graphene oxide in enhancing viscosity at high temperature which is suitable for tribology blend that would contribute to the breakthrough in nanolubricant field with the usage of biolubricant as base oil.

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Wastewater Treatment by Immobilized Algae in Membrane Bioreactor

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Abstract

Today, heavy metal contaminations are one of the main environmental concern in the world. In the near future, the availability of fresh clean water will be limited due to contamination of water. Metal removal using combinations of biological process and membrane separation process have become more popular. From the previous studies, several methods have been developed for the removal of heavy metal ions from aqueous wastes like biosorption, ion exchange, electroplating, membrane process, etc. An immobilized algae, *Nannochloropsis Oculata* was used to remove three heavy metals, cadmium, lead and arsenic ions by biosorption and membrane separation in membrane bioreactor (MBR) because of its high metal removal capability and economically feasible. The capability of *Nannochloropsis Oculata* in removing heavy metals were assessed based on different parameters which are the effects for initial concentration of metal ions, pH solution and contact time of metal ions. The Langmuir and Freundlich models were studied to identify the relationship between the amount of the metal ions adsorbed by the algae at a specific time and the equilibrium concentration of the solution. Two kinetic models, Pseudo first order and Pseudo second order reaction were used to analyse the rate of sorption of metal ions into the biomass. Initial studies have shown that removal of the particular three heavy metals using *N. Oculata* from aqueous solution in membrane bioreactor shows a potential in the application of wastewater treatment.

Keywords: membrane bioreactor, heavy metals, *Nannochloropsis Oculata*, biosorbent, wastewater

1. Introduction

Water is an important resource, for the growth of social, economic as well as the entire ecosystem [1]. The rising standard of living, increasing population growth, industrial or agricultural activities are the main concerns that impacting the availability of clean water. The wastes that are discharged into the environment from industries or sanitation system are the main causes in contamination of water supply and even threaten the health of human being.

The presence of heavy metals in wastewater has become major focus of environmental pollution. With the rapid development of industries from various sectors, wastes are uncontrollably discharge into the environment [2]. Mining and construction industries eventually produce and release large amount of wastes containing heavy metals into nearby ground water sources. Hence, it can be directed into drinking water and accumulate in human body once polluted water is being

consumed. Other industries including electroplating, photography, electric appliance manufacturing, metal surface treating and others [2] are tending to discharge wastewater containing toxic metal ions. There are few heavy metals that are very hazardous and most often to human poisoning such as lead, mercury, arsenic and cadmium whereas other heavy metals like copper, zinc and chromium are required by body in small amount but toxic in big doses.

Amongst the heavy metals mentioned, cadmium and lead are the leading toxic heavy metals that have been paid much attention in the field. These heavy metals pose the greatest hazard to human health or to the environment or may cause corrosion. Exposure to lead may cause liver and kidney damage or even mental retardation. The major sources of this metal release into the environment are coal burning, automobile emission, painting, etc [3]. On the other hand, cadmium was chosen in this study as it is a commonly used metal in industrial processes which is very dangerous. It may cause kidney damage, bone fracture, infertility and damage to immune system [3]. Arsenic is another heavy metal which is known to be carcinogen that apparently affecting the central nervous system, causing skin and lung [3].

2. Methodology

2.1 Materials and Equipments

In this research study, the chemicals used in preparing synthetic wastewater were cadmium nitrate tetrahydrate, $(\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O})$, R&M Marketing), lead nitrate, $\text{Pb}(\text{NO}_3)_2$, R&M Marketing) and sodium hydrogen arsenate heptahydrate ($\text{NaHAsO}_4 \cdot 7\text{H}_2\text{O}$, R&M Marketing). Sodium alginate, $\text{C}_6\text{H}_7\text{O}_6\text{Na}$ and sodium chloride, NaCl were purchased from R&M Marketing too. The microalgae, *N. Oculata* strain and F/2 medium used in the growth of microalgae were purchased from Algaetech International Sdn. Bhd., Kuala Lumpur, Malaysia. A piece of ultrafiltration membrane sheet (14650-47-D, Satorius Germany) were used in determining the permeate flux.

Autoclave (WAC-60, Daihan Scientific Co. Ltd., Korea) was used to sterilize the instruments and solutions whereas the cultivation of algae was carried out using Laminar Flow Cabinet (AHC-4D1, ESCO Micro (M) Sdn. Bhd.). Atomic Absorption Spectrophotometer (Z-2000, ChemoPharm, Hong Kong) was used to analyse the final concentration of the solutions. Besides that, the absorbance of microalgae was measured using UV Spectrophotometer (Hasa RB10, Malaysia) while centrifuge (Universal-32R, Hettich, Germany) was used in harvesting the microalgae. Different concentrations of the solutions were used and shaken in Digital Orbital Shaker (LM400D, Yihder Technology, Taiwan). Preparation of arsenic solution was carried out under fume hood with respirator and chemical resistant gloves for safety measures.

2.2 Experimental Procedures

2.2.1 Preparation of biosorbent

F medium is used as a medium for algae growth. The medium was prepared by adding 3 ml of F medium into 1L of seawater. The solution was then transferred into the bottle and autoclaved at 121°C for 15 minutes. The apparatus and solutions used such as measuring cylinder, distilled water and conical flask were also sterilized in autoclave. The cultivation of microalgae was carried out in Laminar Flow Cabinet to minimize the assays contamination. Two sets of solutions containing mixture of 20ml of microalgae in 100 ml medium were prepared. The growth of *N. Oculata* was carried at room temperature with the light intensity of 1800 lux. The parameter was

being monitored to ensure the growth of algae. UV spectrophotometer was used in determining the absorbance of microalgae in every five days. Harvesting of microalgae was carried out after the microalgae reached its optimum growth. It is filled into the centrifuge bottle to separate the microalgae from the medium by centrifuge. The harvested microalgae was rinsed and collected. It was then suspended with 2% of sodium alginate solution to obtain a mixture of algae-alginate solution and hence it was immobilized. Alginate beads were formed when sodium alginate solution was titrated into 2% calcium chloride solution. The immobilized microalgae was left in the solution for it to be harden then rinsed with saline solution and stored in the refrigerator at 4°C.

2.2.2 Preparation of Metal Ions Solution as Synthetic Wastewater

The synthetic wastewater containing cadmium, lead and arsenic ions will be prepared in the chemical laboratory. The synthetic wastewater solution was prepared by mixing and diluting different metal ions solution into 1L of distilled water. Lead nitrate with 63% weight of lead dissolved in 1L of distilled was used to produce wastewater containing Pb ions [5]. Cadmium solution was prepared using 0.125g of cadmium nitrate tetrahydrate dissolved into 1L distilled water while arsenic solution was using sodium hydrogen arsenate heptahydrate diluted in 1 L of distilled water [6]. Different concentration of lead, arsenic and cadmium ions (100, 175, 200, 225 mg/L) were prepared for further testing.

2.2.3 Determination of metal ions uptake by microalgae with different parameters

The effects of different parameters on three heavy metals removal by microalgae were assessed. To determine the effect of initial concentration of the solution, the concentration of metal ions will be carried out in the solutions that are ranging from 100-225 mg/l in every 25 mg/l interval at a constant pH. About 1g of alginate bead was added in each conical flask with different concentration. For the pH testing, the synthetic solutions were adjusted to the desired pH by adding 0.1M of hydrochloric acid (HCl) or 0.1M of sodium hydroxide (NaOH) solution. Experiment was carried out in pH 4,5,6,7,8. Each conical flask containing 100 ml of synthetic metal ion solution with different pH value was added with 1g of alginate beads. The time required for the biosorbent to reach the equilibrium was determined by taking samples at certain intervals with standard volume of solution. Samples were taken from 10-60 minutes in every 10 minutes interval until reached the equilibrium. 1 g of alginate beads was added into 100 ml of metal ion solution. For the measurements of permeate flux, different concentrations of stock solution were prepared. 200ml of prepared solution was fed into filtration cell with the pressure of 2 bar.

2.2.4 Data Analysis

Before determining the concentration of the stock solution, the absorbance value of each sample was measured using UV spectrophotometer. Before analysing, beakers were shaken at 100rpm using Digital Orbital Shaker. The samples with varying variables were filtered using a filter paper and analysed by Atomic

Absorption Spectrophotometer (AAS). The amount of metal ions adsorbed will be calculated using the Eq. (1) below:

$$q_o = \frac{V}{S} (C_i - C_f) \quad (1)$$

where q_o is the sorbate uptake (mg sorbate/g biomass), C_i is the initial concentration of metal ion (mg/l), C_f is the final concentration of metal ion (mg/l), V is the volume in aqueous solution (L) and S stands for the amount of the biosorbent solid (g).

Two simple kinetic models, pseudo first order reaction and pseudo second order reaction are the most commonly used kinetic models in biosorption process to analyse the rate of adsorption of metal ions onto the microalgae [7]. The kinetic rate constant (k_2), the R^2 and q_e of the model were aimed to have the highest value in which it indicated a good correlation for the adsorption of metal ions.

Langmuir and Freundlich models are used for modeling of biosorption equilibrium in the presence of one metal ion with constant pH. The linearized form of Langmuir isotherm for single metal sorption by algae can be described in the following equation.

$$\frac{C}{q} = \frac{1}{K \cdot q_m} + \frac{1}{q_m} \cdot C \quad (2)$$

Where , q is the amount of metal ions adsorbed per specific amount of adsorbent (mg/g) and C is equilibrium concentration (mg/L); q_m is the amount of metal ions required (mg/g) and k stands for Langmuir equilibrium constant.

For fitting the model into experimental data, Freundlich definitely provide better fit for higher equilibrium metal concentration in the solution [8]. Freundlich model is an empirical model that describes monolayer or multilayer adsorption of metal ions on the surface of adsorbent. In fact, this model provides a more realistic description of the adsorption of metal ions because the sorption is attached to heterogeneous surface or surfaces that attached to affinity sites. The equation of Freundlich model in linearized form can be expressed as below.

$$\log q = \log K_f + \frac{1}{n} \cdot \log C \quad (3)$$

Where K_f is the biosorption equilibrium constant, which indicated the sorption capacity while n is the Freundlich equilibrium constant indication of biosorption capacity. The possible errors that could have affected the results were the imperfect surface of the cuvette cell. Scratches and fingerprint adhering the wall should be removed to obtain more accurate data. Parallax error could be avoided by taking readings perpendicular with the eye level.

3. Results and Discussion

3.1. Biosorption Isotherm

From the results shown, it was found that the equilibrium data satisfied both the Langmuir and Freundlich isotherm models. Freundlich equation seems to fit better as the values of R^2 were found to be 0.9586, 0.9948 and 0.9901 because it has higher correlation factor. On the other side, the R^2 value of Langmuir equation was found to be 0.9117, 0.9291 and 0.9891 for cadmium, lead and arsenic ions. However, the

limitation of Freundlich isotherm is that it failed at higher pressure. The results and parameters obtained are shown in Tables 1 and 2.

Table 1: Data collection of Langmuir model

Parameters	Metal ions		
	Cadmium	Lead	Arsenic
q_m (mg/g)	4.08	6.41	4.62
K (L/mg)	0.005	0.002	0.005
R^2	0.9117	0.9291	0.9891

Table 2: Data collection of Freundlich model

Parameters	Metal ions		
	Cadmium	Lead	Arsenic
n	0.55	0.73	0.57
K_f	50.22	74.66	45.24
R^2	0.9586	0.9948	0.9901

3.2. Kinetic Study

From the graph, the rate constant, k_1 and k_2 , amount of heavy metal adsorbed, q_e and the linear regression correlation coefficient, R^2 can be obtained. Pseudo second order equation seems to fit better as the values of R^2 were found to be 0.991, 0.9856 and 0.9963 because the correlation factor is closer to 1. An R^2 value of 1 is a perfect fit. For Pseudo first order equation, the R^2 value was found to be 0.9127, 0.8548 and 0.8908 for cadmium, lead and arsenic ions.

Table 3: Data collection of Pseudo first order model

Parameters	Metal ions		
	Cadmium	Lead	Arsenic
k_1 (min ⁻¹)	0.089	0.070	0.087
q_e (mg/g)	11.76	4.36	7.36
R^2	0.9127	0.8548	0.8908

Table 4: Data collection of Pseudo second order model

Parameters	Metal ions		
	Cadmium	Lead	Arsenic
k_2 (min ⁻¹)	0.029	0.041	0.047
q_e (mg/g)	2.83	2.67	2.97
R^2	0.991	0.9856	0.9963

3.3. Relationship Study on the Effect of Different Parameters

Figure 1 shows the graph of three metals uptake by biosorbent at different contact time. It is clearly shown arsenic has comparably higher metal uptake compare to the lead and arsenic ions. It can be explained that algal species are more likely to absorb metal ions with greater electronegativity and smaller ionic radius [11]. As refer

to the periodic table, arsenic ion has the largest electronegativity followed by lead ion and lastly cadmium.

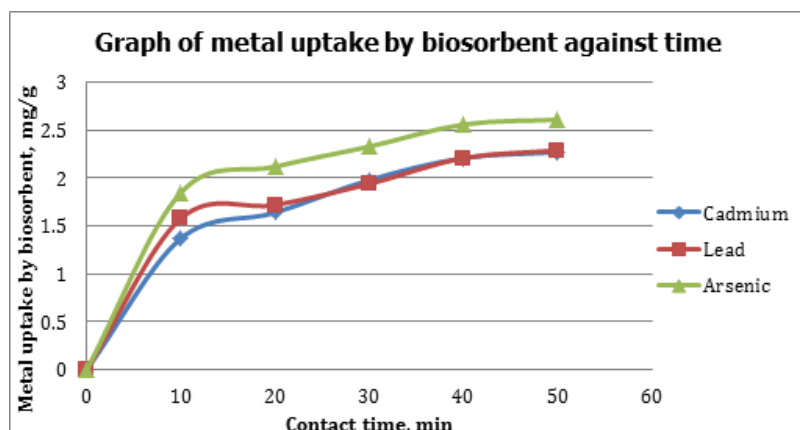


Figure 1: Effect of contact time with different metal ions

In the study of effect of the initial concentration of the metal ions in the synthetic solution, five different concentrations are used to investigate the effect sorption capacities which are 100, 125, 175, 200 and 225 respectively. Initially, metal sorption increased with increase in initial concentration of metal ion in the solution. However, it will become saturated after a certain concentration. In contrast with sorption, the removal of metal decreases as concentration of the solution increases. The graph of the amount of metal uptake by immobilized *N. Oculata* against initial concentration was plotted in Figure 2.

The sorption of the metal ions on immobilized microalgae is highly depending on the pH of the solution. The sorption of metal ions was determined at the pH ranging from 4 to 8. The results were tabulated in the following table. The maximum percentage removal was found at the pH range of 6-7. Very low removals of metal ions are found at pH below 4. It can be justified that the metal uptake is highly dependent on the functional groups on the surface of microalgae. At low pH, the charge on the surface of microalgae is associated with H^+ ions, thus it repulses the positively charged metals ions from binding. As pH increases, high pH value which is in alkaline phase, the biomass surface has become more negatively charged and allows the metal cation to bind together [12]. However, there is high repulsion of electrostatic between cations and surface sites and precipitations of metals tend to occur at high pH which results in decreasing of metal uptake by *N. Oculata*.

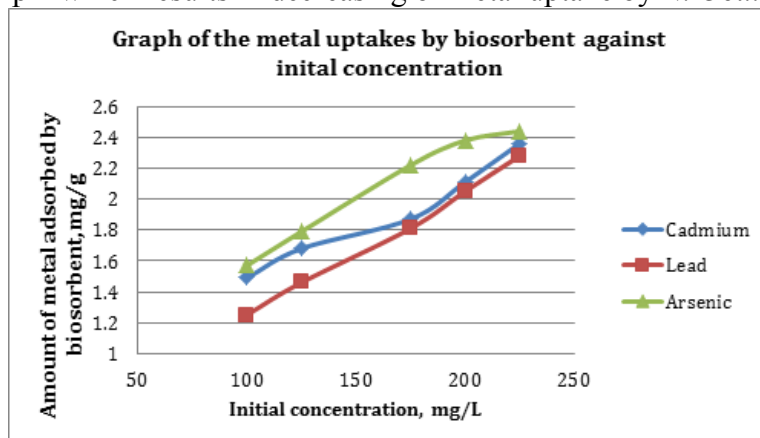


Figure 2: Effect of initial concentration with different metal ions

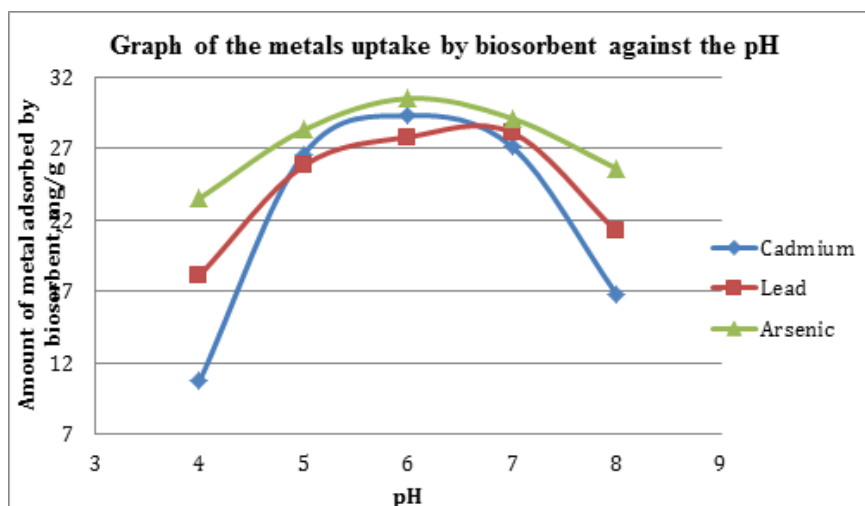


Figure 3: Effect of pH with different metal ions

4. Conclusion

There are three main targets to be achieved in this research paper. In order provide access of clean water as a final outcome, the high percentage removal of cadmium, lead and arsenic ions are expected by using *Nannochloropsis Oculata* as biosorbent in the application of membrane bioreactor. Batch experiments were conducted to investigate the efficiency of metal ions removal. The optimum contact time of removing three metal ions are approximately 50 minutes. It was observed that the contact time work its best to reach the maximum removal is attained after an hour of contact time. By taking the initial concentration of the range of 100-225 mg/L of the aqueous solution, the removals of metal ions are the highest at the initial concentration of 100mg/L. It calculated that removal of 14.9% for cadmium ion, 12.5% for lead ion and 15.7% for arsenic ion. For the study of pH the optimum pH occur at the pH range of 6-7. For the equilibrium modeling for sorption study, Freundlich model fit better for the modeling of biosorption equilibrium in the presence of one metal that showed multilayer of adsorption. The kinetic study of metal sorption by *N. Oculata* followed Pseudo second order reaction best from the experiment results. This research shows the immobilized microalgae, *Nannochloropsis Oculata* a potential biosorbent for the removal of heavy metals in wastewater using MBR.

In future work, various types of heavy metals could be used to analyze the performance and capability of immobilized *N. Oculata* in membrane bioreactor. Other than that, other performance characteristic such as COD removal, nitrogen removal and total phosphate removal can be used parameters that affect that performance of immobilized microlage.

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Case Study: Analysis of Water Quality in Sungai Batu Ferringhi

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Abstract

A patch of black water the size of a football field has been spotted at Ferringhi beach. The black water stretching for about 100m from the Sungai Batu Ferringhi, which believe is the source of the pollution. The aim of this study is to investigate the current water quality index of Sungai Batu Ferringhi and classify it in accordance to the Water Quality Index (WQI) Malaysia. WQI is a very useful tool to determine the water quality of the surface water through the means of water quality assessment from the determination of physico-chemical parameters. The chemical parameters tested include Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Dissolved Oxygen (DO) and Ammoniacal Nitrogen (NH₃-N), while physical parameters include pH, temperature and Suspended Solids (SS). An external biological parameter, Escherichia Coli (E-coli) has been tested to investigate the current concentration of bacteria from Sungai Batu Ferringhi. The concentration of E.coli has been reduced from 16,000 cfu/100ml to 900 cfu/100ml. All the laboratory of physico-chemical parameters are in accordance to American Public Health Association (APHA) and United States Environmental Protection Agency (USEPA) standard methods. The WQI will be calculated using DOE-WQI based on the following parameters which include pH, DO, SS, BOD, COD and NH₃-N. Therefore, 6 parameters were being focused throughout the whole analysis. Based on the result findings, the WQI determined from Location A to C is 84.12, 85.00 and 79.73. Location C is considered slightly polluted while Location A and B are considered clean. But according to DOE Water Quality Index Classification, Location A and B are classified as Class I and Location C is Class II. The overall WQI obtained is 82.95 and Sungai Batu Ferringhi is classified as Class II.

Keywords: Water Quality Index (WQI), Sungai Batu Ferringhi, Surface Water Analysis, Physico-Chemical Parameters, Biological Oxygen Demand (BOD).

1. Introduction

The access to clean water is a basic essential requirement or needs of human life. More than 70 percent of the Earth's surface is covered by water, 97.5 percent out of 70 percent is saltwater, leaving only 2.5 percent as fresh water [1]. The remaining is saline and ocean-based. This means that the competition for a clean, copious supply of water for drinking, cooking, bathing, and sustaining life intensifies increasing dramatically every year. In Malaysia, the most tapped raw water sources are rivers [2]. There are total 180 rivers whereby 150 of them are the major river systems while 97 percent of Malaysia's water supply comes from those rivers and streams [3]. According to the Department of Environmental, in the Environment Quality Report 2009 showed that 46 percent out of the total river in Malaysia is polluted when compared to the previous years [4]. The accessibility of clean water will be more challenging if pollution continues to occur. Fresh water is not only vital for protecting public health, it also play some important roles especially in providing ecosystem habitats. Therefore, it is important to determine the water quality to determine the classification of the current river. It is important to have a good water quality for a healthy river.

The water quality is judged or classified based on evaluating the water quality index (WQI). Water quality index serves as a mean indication of water quality assessment through determination of physico-chemical parameters of surface water. Furthermore, WQI can be used as an indicator of water pollution by providing feedback on the quality of water to the policy makers and environmentalist. Water quality index is important to be measured in order to determine health of the river before consuming or safe to use in other purposes. In order to develop these water quality indexes, several parameters have to be considered. The parameters are physical, chemical, biological and radioactive. Each of the parameters has significant impact on the water quality [5]. The physical parameters include temperature, pH, turbidity, total dissolved solids and total suspended solids. In terms of chemical, the parameters involve Dissolved Oxygen (DO), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), nitrates and total phosphate. Fecal coliform such as *Escherichia Coli* (E-coli) and groups of microorganism are classified under biological parameters. Measurements of these indicators can be used to indicate and determine the classification of the river by comparing with the national water quality standards of Malaysia from Water Environment Partnership in Asia (WEPA) and Interim National Water Quality Standards for Malaysia (INWQS). When these conditions are not met, species population in the water become stress and eventually dies. Therefore, a good water quality is important for maintaining a healthy river and ecosystem.

1.1 Study Area

According to New Straits Times, February 2014, a patch of black water the size of a football field has been spotted at Ferringhi beach [6]. The black water stretching for about 100m from the Sungai Batu Ferringhi, which believe is the source of the pollution. A loosen control valve from a nearby sewage treatment plant is the cause of the black effluence that being released to the river then flow out to the sea. The

possibility of black effluence is the bacteria called Escherichia Coli (E-coli) [6]. Both faecal coliform and E.coli reading's in the river were at a staggering 16,000 cfu per 100ml [6].

1.2 Research Scopes

1. What is the current Water Quality Index (WQI) of Sungai Batu Ferringhi?
2. Are the concentration of E.Coli reduces?

1.3 Objectives

Although a massive cleanup was carried out by the Department of Environmental on February 2014, this research is to analyze the latest characteristics of water quality at Sungai Batu Ferringhi. The objectives are the following:

1. To investigate the current water quality indexes through several biological and physio-chemical parameters of Sungai Batu Ferringhi;
2. Classify the Sungai Batu Ferringhi in accordance to the Water Quality Index (WQI) Malaysia.

2.0 Research Methodology

2.1 Overall Methodology Process Flowchart

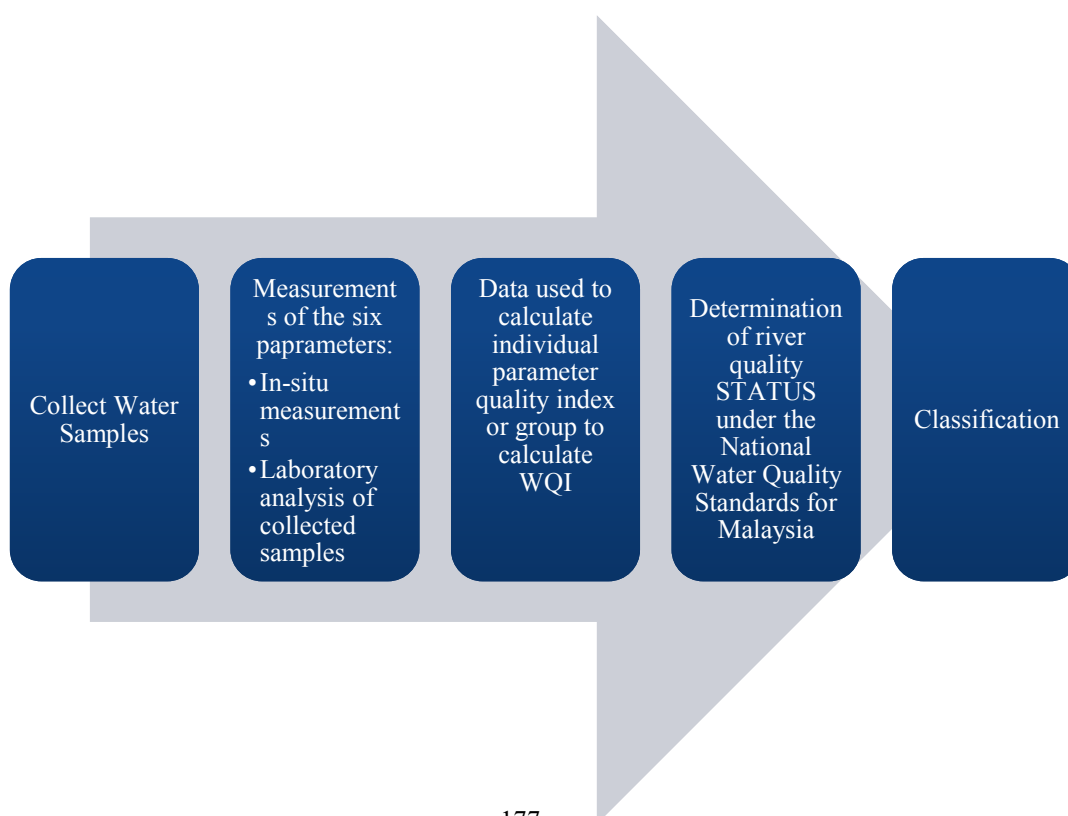


Figure 1. Procedure for Calculating Water Quality Index (WQI) [7].

2.2 Sampling Surface Waters

The sample is taken 10 cm below the surface away from the edge using telescopic sampling system or polyethylene dipper (TW-06282-90) at predetermined locations. The samples were collected from 3 different predetermined locations including upstream, mid-stream and downstream of Sungai Batu Ferringhi. All the sample containers were labeled before site collection. The samples were collected by directly filling the container from the surface body and by decanting the water from a collection device [8]. During transferring the samples using a collective device, the device was avoided by from contacting with the sample containers. Preservations have been done on the site immediately at the time of sample collection. Collected samples were placed into the icebox with temperature approximately 4 °C during transportation to lower or retard the metabolism of the organism on the sample. All the samples were stored in the refrigerator with temperature less than 6 °C with covered layer to maintain dark condition. The overall laboratory analysis was completed within 14 days from the date of sample collection.



Figure 2. Sampling Station include Upstream (Top Tight), Midstream (Bottom Left) and Downstream (Bottom Right)

2.3 In-Situ Measurements

The in-situ parameters include pH, Temperature and Dissolved Oxygen (DO) were conducted on site. Temperature and pH were measured using portable probe meter (Microcomputer pH Meter, TI9000) by WalkLAB that provided by the university laboratory. For DO, a portable Dissolved Oxygen Tester (Extech DO600) was used at the site.

2.4 Ex-Situ Measurements

Table 1. Standard Methods Used In Chemical Analysis for Liquid Samples [8].

Parameters	Analytical Methods
Biological Oxygen Demand (BOD)	APHA 5210B: 5-Day BOD Test
Chemical Oxygen Demand (COD)	APHA 5220C: Closed Reflux, Titrimetric Method
Ammonia Nitrogen (NH ₃ – N)	APHA 4500 - NH ₃ C
Dissolved Oxygen (DO)	APHA 4500 O-C or Portable Meter
E.coli	USEPA 1603

All the sample preparation and preservations conducted were following on the standard procedures provided by American Public Health Association (APHA) and United States Environmental Protection Agency (USEPA) Methods

2.5 Laboratory Analysis

The laboratory analysis results were recorded and Water Quality Index (WQI) equation was applied to determine the water quality index of the samples. Refer to Eq. (1) below:

$$WQI = 0.22SIDO + 0.19SIBOD + 0.161SICOD + 0.15SIAN + 0.16SISS + 0.12SIpH \quad \text{Eq (1)}$$

where;

SIDO = SubIndex DO (% saturation)

SIBOD = SubIndex BOD

SICOD = SubIndex COD

SIAN = SubIndex NH₃-N

SISS = SubIndex SS

SipH = SubIndex pH

$0 \leq WQI \leq 100$

Subindex, SI was calculated using the equation as shown on Table 3. Different parameter has different subindex with different ranges.

Table 2. Best-Fit Equations for the Estimation of Various Subindex Values [9].

Subindex, SI	Equation	Ranges
Dissolved Oxygen, SIDO	= 0	For $x \leq 8\%$
	=100	For $x \geq 92\%$
	$= -0.395 + 0.030x^2 - 0.00020x^3$	For $8\% < x < 92\%$
Biochemical Oxygen Demand, SIBOD	$= 100.4 - 4.23x$	For $x \leq 5$
	$= 108e^{-0.055x} - 0.1$	For $x > 5$
Chemical Oxygen Demand, SICOD	$= -1.33x + 99.1$	For $x \leq 20$

Ammoniacal Nitrogen, SIAN	$= 103e^{-0.0157x} - 0.04x$	For $x > 20$
	$= 100.5 - 105x$	For $x \leq 0.3$
Suspended Solids, SISS	$= 94e^{-0.537x} - 5 \text{ abs}(x - 2)$	For $0.3 < x < 4$
	$= 97.5e^{-0.00676x} = 0.05x$	For $x \leq 100$
pH, SIPH	$= 71e^{-0.0016x} - 0.015x$	For $100 < x < 1000$
	$= 0$	For $x \geq 1000$
	$= 17.2 - 17.2x + 5.02x^2$	For $x < 5.5$
	$= -242 + 95.5x - 6.67 x^2$	For $5.5 \leq x < 7$
	$= -181 + 82.4x - 6.05 x^2$	For $7 \leq x \leq 8.75$
	$= 536 - 77.0x + 2.76 x^2$	For $x \geq 8.75$

The x in Table 2 represents the concentration of each parameter in mg/L except for pH. After each subindex for each parameter has been calculated, the values will be substitute into Equation 3 to calculate Water Quality Index, WQI. The classification of river will be conducted once the value of WQI is confirmed. The classification of river water is based on Table 3 below.

Table 3. Classification of Water Quality Index [9].

Parameter	Unit	Class				
		I	II	III	IV	V
Ammoniacal Nitrogen	mg/l	< 0.1	0.1 - 0.3	0.3 - 0.9	0.9 - 2.7	> 2.7
Biological Oxygen Demand	mg/l	< 1	1 - 3	3 - 6	6 - 12	> 12
Chemical Oxygen Demand	mg/l	< 10	10 - 25	25 - 50	50 - 100	> 100
Dissolved Oxygen	mg/l	> 7	5 - 7	3 - 5	1 - 3	< 1
pH	-	> 7	6 - 7	5 - 6	< 5	> 5
Total Suspended Solid	mg/l	< 25	25 - 50	50 - 150	150 - 300	> 300
Water Quality Index (WQI)	-	< 92.7	76.5 - 92.7	51.9 - 76.5	31.0 - 51.9	> 31.0

2.5.1 Total Suspended Solids

APHA 2540D: Total Suspended Solids Dried at 103-105 °C is the analysis standard for determining the total suspended solids in water. In this final year projects, the analytical procedures from the APHA Standards were followed but not the equipment set-up. For the experiment set-up, the operating principle remained the same but different type of apparatus was used as shown in the following figure.

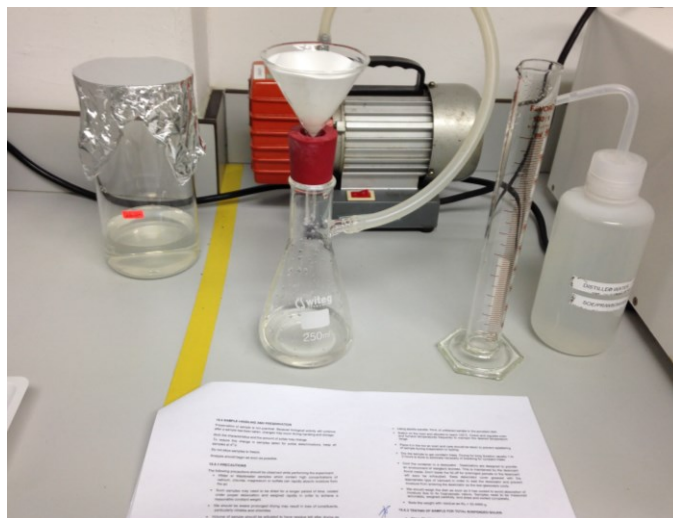


Figure 3: Experimental Set-up for Total Suspended Solids

3.0 Results and Discussion

3.1 Physical Parameters

3.1.1 Total Suspended Solids

Total Suspended Solids (TSS) represents the amount of the particles presence in the water. It consists of inorganic and organic particles. High concentration of TSS is one of the many reasons why the water quality deterioration leading to aesthetic issue [10]. The increase of not only increase the cost of water treatment, it is also caused some impacts of ecological degradation of aquatic environments. The water sample from Sungai Batu Ferringhi only contains organic particles based on the assumption that no any other industrial (Heavy or Light) area is built along the river. There is an existing of a small-scale Tilapia fish farm being built at the side of Location A. The concentration of TSS is the highest at Location A (Up-Stream) of the river with the mean value of 2.49 mg/L. The high mean value of TSS found at Location A is believed cause from the discharge of water from the fish warm when the water of the feedstock is being changed. All the water that contains organic matters is directly discharged into the river. Despite the concentration is at the highest on Location A, the concentration decreases along the river. Location B has the mean value of 1.47 mg/L while Location C has the lowest mean value of 1.38 mg/L. The concentration trend of TSS is decreased from 2.49 to 1.38 mg/L which indicate that the organic matter is being dissolved along the river by the microorganism. Location A, B and C are classified as Class I under the Department of Environmental Water Quality Index Classifications since the concentration of TSS is less than 25 mg/L.

3.1.2 pH

Location A has the value of 7.52, B with the value of 6.97 and lastly Location C with the value of 6.38. The pH value started to decline from 7.52 to 6.38 as it reaches Location C. Location A is more approach to alkaline region while B and C are started to approach to acidic region. In another words, the pH from A to C is declined from alkaline region to acidic region. This indicates that activity of hydrogen ion started to increase right after the water flow out from location A. Despite the activity of hydrogen ion increases, the status of location A and B are close to neutral while the

pH value at Location C is considered slightly acidic. In general, the pH values recorded at Location A, B and C are almost at neutral level. Based on the DOE Water Quality Index Classification, Location A is classified as Class I whereas for Location B and C are classified under Class II. The pH values for all locations are fall within the acceptable limit of 6 to 8 [11].

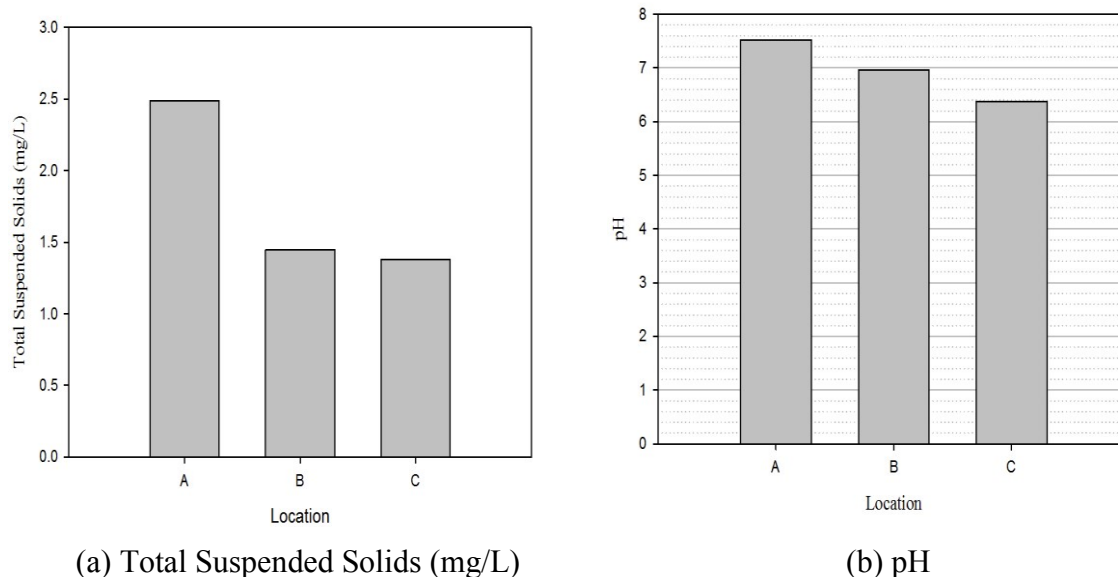


Figure 5: Concentration of physical parameters from sampling locations.

3.2 Chemical Parameters

3.2.1 Dissolved Oxygen

The average concentration of DO obtained from Location A to C is 8.97 mg/L, 8.15 mg/L and 8.01 mg/L as shown in Figure 4.4.1. The concentration of DO has been depleted from 8.97 mg/l to 8.01 mg/L along the river. Location A has the highest concentration of DO since the concentration of COD and BOD is the lowest. This confirmed the sentence saying that the concentration of DO is lower due to high concentration of COD and BOD. This is proven by referring to the concentration of DO, COD and BOD at Location C. The concentration of COD and BOD at Location C is the highest but lowest concentration of DO. The low concentration of DO is due to high COD and BOD concentration which rapidly consumed the oxygen content of the river during the decomposition of organic matters, suspended solids and etc. According to DOE Water Quality Index Classification, Location A, B and C are classified under Class I as the concentration of DO in water is higher than 7 mg/L. Despite with the high concentration of BOD and COD, the concentration of DO is classified under Class I.

3.2.2 Biochemical Oxygen Demand

Location A has the value of 5 mg/L, Location B with 8 mg/L and lastly Location C with the concentration of 10 mg/L. the concentration of BOD at Location B increased from 5 mg/L to 8 mg/L and eventually reached to 10 mg/L at Location C. This increasing trend of BOD level in the river is due to the oxygen demand required for breaking down the organic matters by the microorganism increased. The microorganism at Location B has to dissolve the organic matters from the discharge

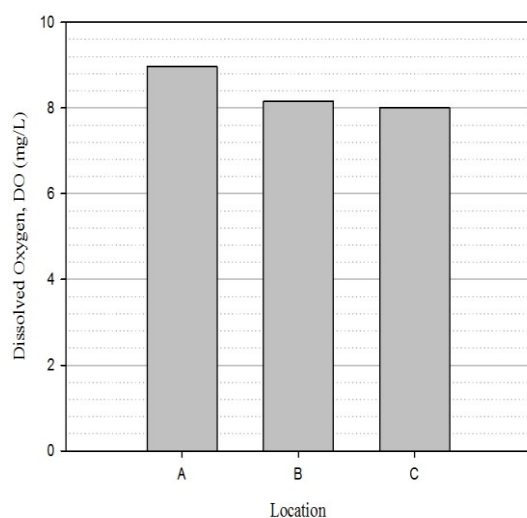
water at Location A as the organic matters flow to B. Therefore, the concentration of BOD is raised from 5 mg/L to 8 mg/L. For Location C, the burden of microorganism to dissolve organic matters increased. At the Location C (downstream), the area is surrounded by residential area, restaurants and a sewage treatment plant is sitting right beside the downstream thus, the source of pollutions determined. Some of the discharge from the residential areas or restaurants might escape and flew into the river. Hence, the oxygen demand of microorganism required to break down the organic matters at Location C is the highest. As stated by the Department of Environmental (DOE) Water Quality Index Classifications Malaysia, Location A is classified as Class III whereas Location B and C are classifies as Class IV. According to Interim National Water Quality Standards (INWQS) for Malaysia, extensive treatment is required at Location A where Location B and C can be only used for irrigation purposes according to INWQS as the concentration falls between 6 to 12 mg/L.

3.2.3 Chemical Oxygen Demand

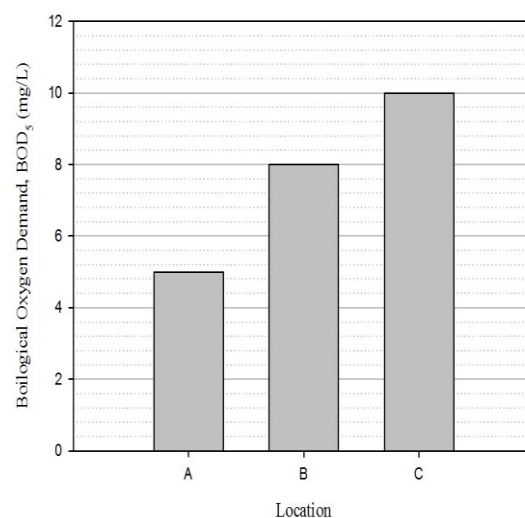
Location A has the lowest value of 32 mg/L, Location B with the concentration of 48 mg/L and maximum value of 64 mg/L at Location C. According to Figure 4.3, the concentration of COD has been increased from Location A to C. For Location A, 30 mg of oxygen is being consumed per litre of solution. The concentration above 25 mg/L is classified as Class III according to DOE Water Quality Index Classification [9]. Both Location A and C are classified as Class III and Location D is classified as Class IV with the concentration of 64 mg/L. Location C has the higher concentration of COD value compared to others is due to high decomposition of organic matters and suspended solids that produced from the activities nearby. Extensive requirement is needed at Location A and C needed extensive treatment if the water is used as water supply according to NWQS for Malaysia while the water at Location C is only for irrigation purposes and not consumable. Location C has the highest concentration of COD compared to other locations due to higher decomposition demand of organic and inorganic contaminants from the surrounding activities as mentioned in section 3.2.2.

3.2.4 Annoniacal Nitrogen

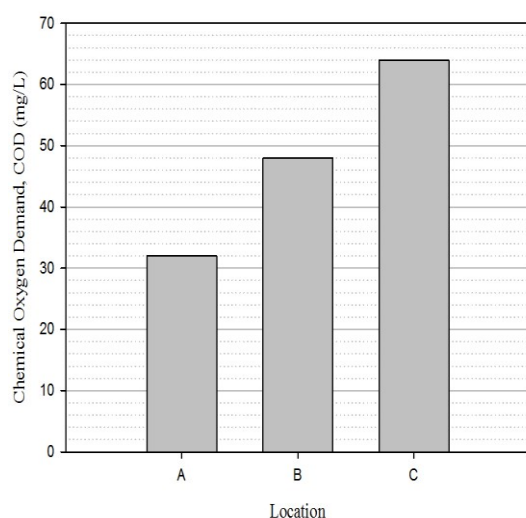
Location A has the value of 0.3 mg/L and Location C with the concentration of 0.1 mg/L. For Location B, the concentration for $\text{NH}_3\text{-N}$ cannot be detected, as the value is not more than 0.1 mg/L. 0.3 mg/L of $\text{NH}_3\text{-N}$ was detected at Location A is believed that caused by the fish farming activity beside the stream. The discharged water from the farm which contains high concentration of excreta that produced by the fish and is directly being discharged into the river. Hence, high level of ammonia was detected at Location A. Excreta contain organic and inorganic substances including nutrients which pose a potential threat to human health and the environment [12]. According to DOE Water Quality Index Classification, Location A and C are classified under Class II and Location B as Class I. Conventional treatment is required Location A and C.



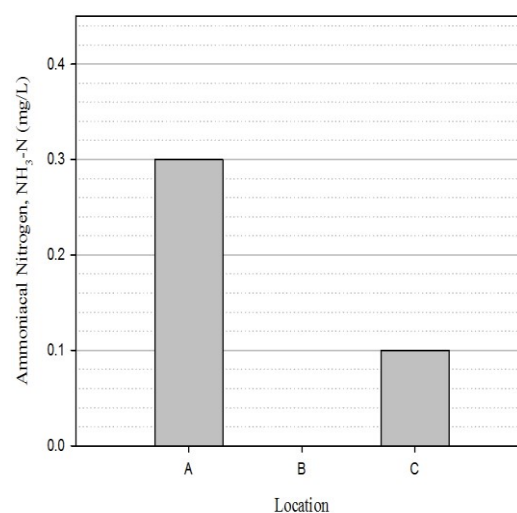
(a) Dissolved Oxygen (mg/L)



(b) Biological Oxygen Demand (mg/L)



(c) Chemical Oxygen Demand (mg/L)



(d) Ammoniacal Nitrogen (mg/L)

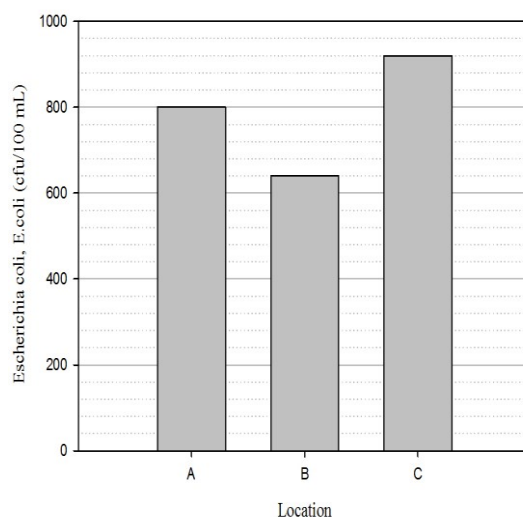
Figure 6: Concentration of chemical parameters from sampling locations.

3.3 Biological Parameter

3.3.1 *Escherichia Coli*

The concentration obtained from Location A, B and C are 800 cfu/100ml, 640 cfu/100ml and 920 cfu/100ml. 800 cfu/100ml of *E.coli* was found at Location A which believe the source of pollution is from the fish farm located at the side of the stream. The discharged water from the farm which contains animal fecal materials are directly being discharged to the river without any treatment. Thus, high colony-forming unit per 100 ml water of *E.coli* was found at Location A. At Location B, moderate amount of *E.coli* was obtained as the bacteria can remain in streambed sediments for long

periods of time [13]. For Location C, 920 cfu/100ml of E.coli was found and this amount is considered high. As mentioned before, Location C is surrounded by hotels, restaurants and a sewage treatment plant. The possible for causing the high concentration of E.coli at the particular area is due to human sources. Human sources include failing septic tanks, leaking sewer lines, combined sewer flows and wastewater treatment plants [13].



(a) Escherichia Coli (mg/L)

Figure 7: Concentration of biological parameter from sampling locations.

3.4 Water Quality Index

Table 4: Water Quality Index of Sungai Batu Ferringhi using WQI Equation.

Location	Subindex, SI						WQI
	DO	BOD	COD	AN	SS	pH	
A	100	79.25	61.0429	69	95.99708	96.51808	84.12
B	100	68.75593	46.55892	100.5	96.62147	99.60040	85.00
C	100	61.31058	35.15014	90	96.66367	95.79165	79.73
Overall WQI							82.95

Based on the WQI calculated from Table 4, all the locations are classified under Class II according to DOE Water Quality Index Classification. The calculation shows that Location A to C has the WQI of 84.12, 85 and 79.73 respectively. Location C is considered slightly polluted while Location A and B are considered clean. The overall WQI obtained by averaging the WQI from all the locations obtained is 82.95. The overall WQI also indicate that Sungai Batu Ferringhi is categorized as Class II. According to DOE Water Quality Index Classification, the overall WQI of Sungai Batu Ferringhi is considered clean. Although the overall WQI falls with the range of 81-100 where is considered clean, 82.95 is falls on the lower region of the clean classification. In another words, the water quality of Sungai Batu Ferringhi is close to the region of slightly pollution with the range of 60 – 80.

4.0 Conclusion

As can be seen from the findings, the water quality from Location A to C has been depleted along the river. This indicated that the level of pollution has been increased despite that the overall WQI of Sungai Batu Ferringhi is considered clean according to DOE Water Quality Index Classification based on water quality index. The overall WQI determined is 82.95 and Sungai Batu Ferringhi is classified as Class II. In term of biological parameter, the concentration of E.coli has been reduced from 16,000 cfu/100ml to 900 cfu/100ml. Conventional treatment is required for Sungai Batu Ferringhi and is only suitable for recreational use only for body contact.

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Electromagnetic Analysis of a Novel Double Rotor Interior Permanent Magnet Motor

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Abstract

Among various types of electric motor, permanent magnet motor is competent for high torque applications. Its torque producing point is resultant of air gap flux linkage between permanent magnet inbuilt in rotor and the stator winding. The reduction in air gap length improves the flux linkage, however it can only be reduced to a certain extend due to torque pulsation occurrence that increases cogging torque due to retention capability of the machine. In this paper, a novel Double Rotor Interior Permanent Magnet (DRIPM) motor is proposed for improved torque performance. The key to this proposed structure is by introducing an additional outer rotor to the conventional Interior Permanent Magnet (IPM) motor structure. Consequently, this double rotor structure provides higher torque generation through an increase in torque producing point by utilising the flux linkage at stator yoke, meanwhile allowing the reduction of air gap length as the attraction of magnetic flux is distributed evenly from the inner and outer rotor. An electromagnetic analysis on the effect of torque producing capability to utilize the stator yoke flux is analysed using finite element method is done. In this research, conventional IPM motor, Double Magnet Permanent Magnet (DMPM) motor, and the proposed double rotor interior permanent magnet motor are evaluated for comparison through the motor constant square density and average torque. The proposed structure provides an improvement of 77% and 6% of the motor constant square density value than that of the conventional motor and DMPM motor respectively, while an increase of 51% and 17% of average torque value compared to the conventional motor and DMPM motor are reported in this paper.

Keywords: Double rotor, air gap flux linkage, interior permanent magnet motor, finite element analysis, motor constant square density.

1. Introduction

Over the last years with technology advancement, electric motors being an important element for electromechanical energy conversion in industry [1, 2]. Electric motors are then continued to research to improve its torque for lower power consumption especially for applications like Electric Vehicle (EV) [3, 4]. As a result, motor with higher torque generation draws lesser current from EV during transient state of acceleration and braking, allowing EV to travel for a further distance. In addition, with the recent development of permanent magnet, high air gap flux density can be obtained with the significant improved residual flux properties, thus permanent magnet motors have been a popular research topic nowadays to suit the modern technology needs. Double rotor permanent magnet motors however becoming a research topic for such applications and is expected to provide higher torque generation in comparison to the conventional Interior Permanent Magnet (IPM) motors.

With the structure of double rotor motor to a vehicle, each rotor can operate individually to perform electronic differential to provide the required torque for each driving wheel and at different wheel speed [5]. The function of continuous variable transmission to power split can also be done with double rotor motors so that the internal combustion engine in hybrid electric vehicle can perform at narrow speed region to maximize the fuel efficiency [6]. Likewise double rotor motor is used for wind turbine to split the output power to obtain the optimal efficiency for wind energy harvesting [7]. In this paper, a novel Double Rotor Interior Permanent Magnet (DRIPM) motor is proposed for improve torque performance in comparison to the conventional IPM motor. As air gap flux linkage between the stator and rotor is the factor for torque production, maximizing the air gap flux linkage in directly improves the motor torque performance [8, 9]. Thus the main objective is to improve the motor constant square density through an increase in torque producing capability of the proposed structure by maximizing the air gap flux linkage around the stator core of an IPM motor. The mechanical and magnetic evaluation of the proposed DRIPM motor is compared to the conventional motor for the same sizing and volume.

2. Machine Design

Fig. 1 is the proposed DRIPM motor exploded view with the stator is made up with double header stator core of 24 poles with coil winding of star connection, while the stator core is a T and I structure of stator laminations. The inner and outer rotor are made up with laminated rotor cores of 4 poles with each facing at the mutual axis.

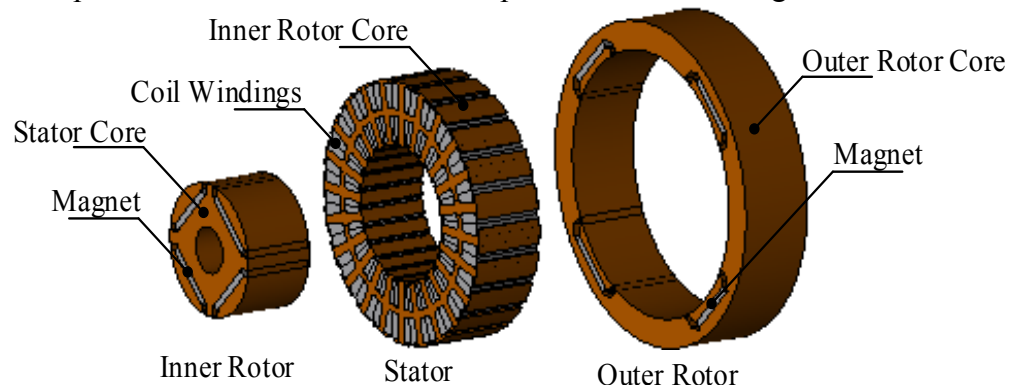


Figure 1. Double Rotor Interior Permanent Magnet Motor (Exploded View).

Each pole of the inner and outer rotors are inbuilt with permanent magnet of the same size and properties. The double rotor structure gives an advantage to overcome the limitation of torque pulsation occurrence in conventional single rotor motor which constrains the minimum size of air gap length. Table 1 shows the structural dimensions of DRIPM motor. The theory of increasing the torque characteristic for motor reluctance through maximizing the flux by double the rotor is presented in [10]. The design for both conventional and proposed motor are using the design guidelines presented in [11].

Table 1. DRIPM Motor Design Parameters.

Parameter	Unit (<i>mm</i>)
Outer diameter	112
Outer rotor inner diameter	95
Air gap length	0.5
Inner rotor outer diameter	41
Shaft diameter	16
Permanent magnet length	22
Permanent magnet height	2.5
Stack length	65
Turns per pole	70
Rated current	5 A
Outer rotor pole arc	36 <i>deg</i>
Inner rotor pole arc	90 <i>deg</i>
Stator inner surface pole arc	11 <i>deg</i>
Stator outer surface pole arc	11 <i>deg</i>

3. Motor Operating Principles

Permanent magnet motors operating principles is based on the power effects of magnetic circuit that tend to minimize the opposing magnetic flux lines of magnetic circuit [12]. It operates based on the interaction of magnetic field established by electromagnet of armature winding with that of the permanent magnet inbuilt at rotor [12]. For a three phase motor, when current injection to the motor in phase A, air gap flux linkage between stator and rotor is then generated to produce the torque. As torque is produced, the rotor starts to rotate to minimize the opposing magnetic flux lines of the magnetic circuit governed by Fleming's left hand rule [12]. Meanwhile when the opposing magnetic flux for phase A is at minimum, current is then injected to next phase for continuous rotation of the rotor. Saying so, the torque produced by a motor depends on the air gap flux linkage as shown in Fig. 2.

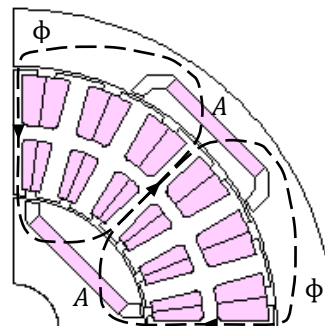


Figure 2. Operating Principles of DRIPM Motor.

4. Electromagnetic Torque Production Theory

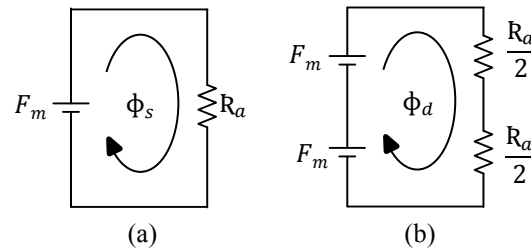


Figure 3. Magnetic Circuit (a) Single Rotor (b) Double Rotor.

Fig. 3 (a) shows the equivalent magnetic circuit of the conventional permanent magnet motor while Fig. 3 (b) illustrates the circuit of the motor with double rotor. The selection design of the pole-arc is important since it is significant in influencing the torque producing capability by the motor. Reducing the air gap length between stator and rotor increase the magnetic flux linkage [8, 9]. On the contrary the properties of permanent magnet with strong attraction of flux results in cogging torque especially when the motor is moving at a lower speed, thus there is a limit to the air gap length [12, 13]. Eq. (1) shows the basic equation for magneto motive force (F_m). The relation of flux linkage (Φ_s) of single rotor to air gap reluctance is presented in Eq. (2) below.

$$F_m = \Phi_s R_a \quad (1)$$

$$\Phi_s \propto \frac{1}{R_a} \quad (2)$$

where R_a is the air gap reluctance [A/Wb]. To improve the torque performance of the motor, it can be done by either by optimising control circuit or to optimise the parameters of the motor especially the pole arcs. The motor is then introduced an outer rotor to overcome the torque pulsation factor which allow to reduce the air gap length of the motor [14]. The reduced air gap length not only minimizes the reluctance contact flux linkage area, but the structure through dual air gap also double the torque producing point. The introduction of the dual air gap increases the magneto motive force around twice that of the conventional motor is shown in Eq. (3). The flux linkage (Φ_d) over the double rotor air gap reluctance is expressed as in Eq. (4).

$$F_m + F_m = \Phi_d \left(\frac{R_a}{2} + \frac{R_a}{2} \right) \quad (3)$$

$$\Phi_d = \frac{2F_m}{R_a} \quad (4)$$

The improvement in magnetic flux however will increase the torque of the motor is be proven by Eq. (5) where torque is directly proportional to the square of magnetic flux.

$$T = \frac{1}{2} L \Phi_d^2 \quad (5)$$

where T is torque $[Nm]$ and L is the inductance $[H]$. Given from Eq. (5), when the flux of a motor increases it also affects in increasing the torque. Thus it shows that the double rotor motor have better magnetic flux and torque producing capability.

5. Finite Element Analysis Method

Finite Element Analysis (FEA) tool is used to design and analysis of the motor constant square density as well to find the equivalent nodal force from distributed load force in stress analysis based on the numerical method [10]. The performance of a motor is greatly dependent on its geometry, hence studies using magnetic circuit are difficult. To provide an accurate analysis for the motor design, an electromagnetic field analysis using finite element method is necessary. The conventional IPM motor, DMPM motor, and proposed DRIPM motor are designed and simulated using the same method of FEA. From the simulation, the direction of flux flow, magnetic flux density, and the torque performance of the motor are evaluated. As shown in Fig. 4 is the flux density of the proposed motor at different rotational angle position so that to maximize the air gap flux linkages by observing the flux flow. The motor is position at rotational angle of 0° , 7.5° , 15° , 22.5° , 30° , 37.5° respectively as shown from Fig. 4 (a) to (f).

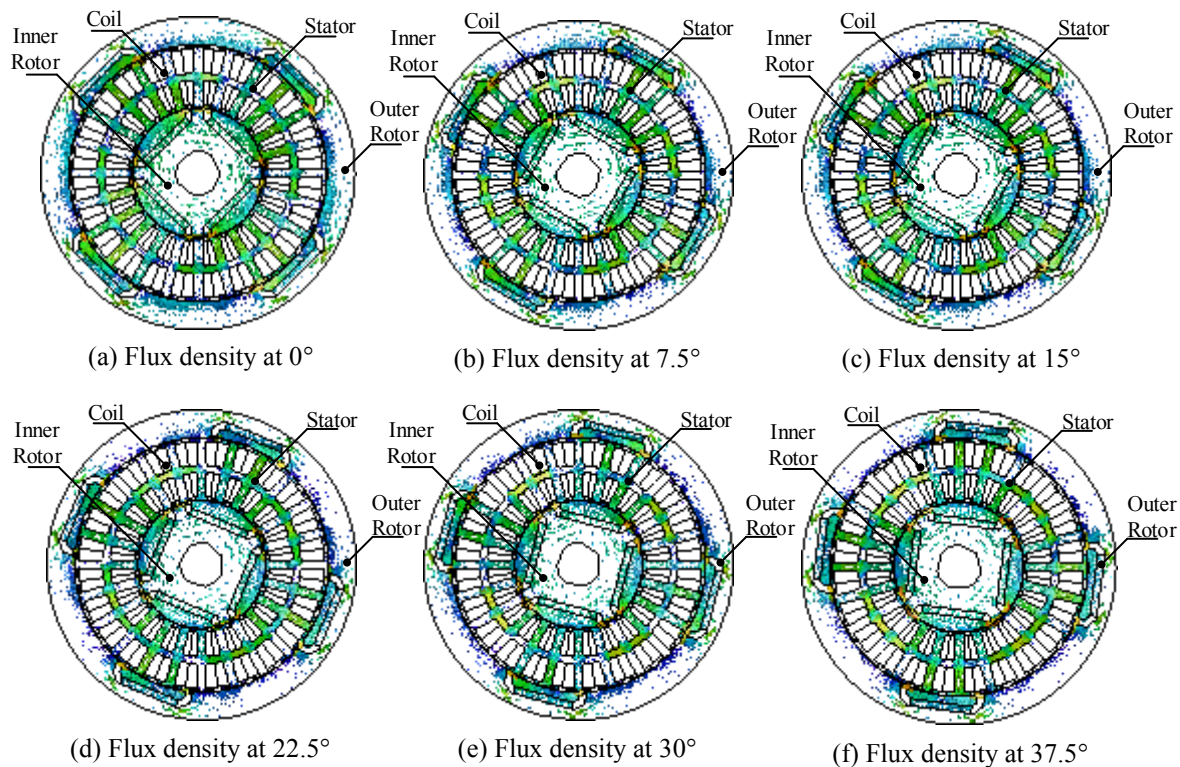


Figure 4. Flux Flow for Various Rotational Angle.

The lines around the motor indicate the flux saturation point and are evenly distributed among each quarter segment, thus allowing the motor to rotate freely at a slower rotational speed. As shown in Fig. 4 (a), the flux saturated around stator of 45° , 135° , 225° and 315° as the position of permanent magnets. Likewise the saturated flux is aligned between the permanent magnets and the stator pole for Fig. 4 (b) to (f) due to the attraction of magnetic flux, thus allowing the rotation of the rotors.

6. Results and Discussion

6.1 Evaluation Parameters

For comparison on the level of performance for conventional and proposed structure, the methods of calculation motor constant square density (G) is used. This evaluation is very useful as it includes the torque, power, and volume of the machine designs. The motor constant square density (G) is given as in Eq. (6).

$$G = \frac{(K_m)^2}{V} \quad (6)$$

where K_m is the machine constant in $[Nm/A/W^{-(1/2)}]$, V is the volume of the machine $[m^3]$. The machine constant can be further expressed as in Eq. (7).

$$K_m = \frac{K_T}{\sqrt{P}} \quad (7)$$

where K_T is the torque constant $[Nm/A]$ and P is the input power to the coil winding $[W]$. Meanwhile the torque constant is given as in Eq. (8).

$$K_T = \frac{T_{avg}}{I} \quad (8)$$

where T_{avg} is the fundamental torque $[Nm]$ and I is the maximum current input to the machine $[A]$.

6.2 Static Torque Characteristics

Fig. 5 shows the average torque of DRIPM motor produced at no load when single phase current is injected at different phase angle from 0° to 90° with an interval of 10° in between. It can be observed that the torque is highest at the 10° where rotor starts to rotate from the original position with excitation from the single phase current magnetic flux. However as the rotor becomes unaligned with the excited stator the torque generated is reduced gradually. At phase angle 0° is considered as happy state as the air gap flux is not contributed to the torque due to excited stator is aligned with the position of permanent magnet.

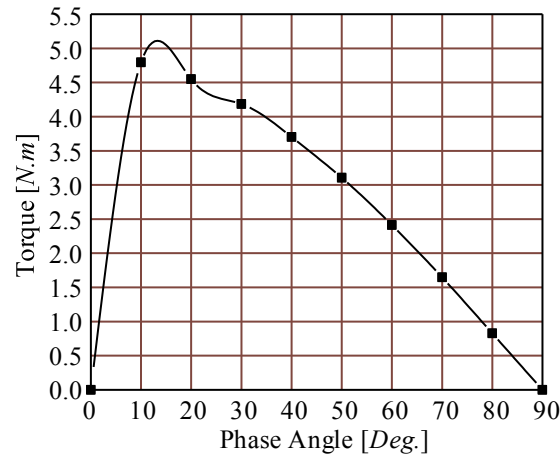


Figure 5. Static Torque Characteristics.

6.3 Torque Current Characteristics

As shown in Fig. 6 is the torque-current characteristics of DRIPM motor with different input current of 2A, 3A, 4A, and 5A respectively to determine the relation between input current and torque. The torque characteristics at each input current shows the same behaviour. From the graph, the increase of excitation current increases torque producing capability of the motor. However there is a rated current for every motor depending on the thickness of coil winding that can withstand the amount of heat.

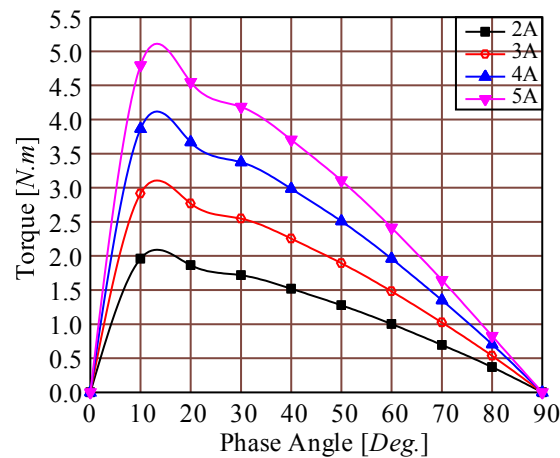


Figure 6. Torque-Current Characteristics.

6.4 Three Phase Torque Characteristics

Fig. 7 (a) shows the torque generated when individual phase is excited sequentially. Each phase current is given an input of 5A but excited with phase angle difference of 10° intervals. As shown in the graph, phase A is excited at 0° until when it reaches phase angle of 10° , phase current B is excited, and phase current C at 20° . The sequential excitation loop is repeated using appropriate control system method, thus generating complete excitation phase as shown in Fig. 7 (b). With this sequential excitation method purpose to minimize the torque ripple while maintaining the average torque. The proposed DRIPM motor provides 51% and 17% more average torque in comparison to that of the IPM motor and DMPM motor respectively.

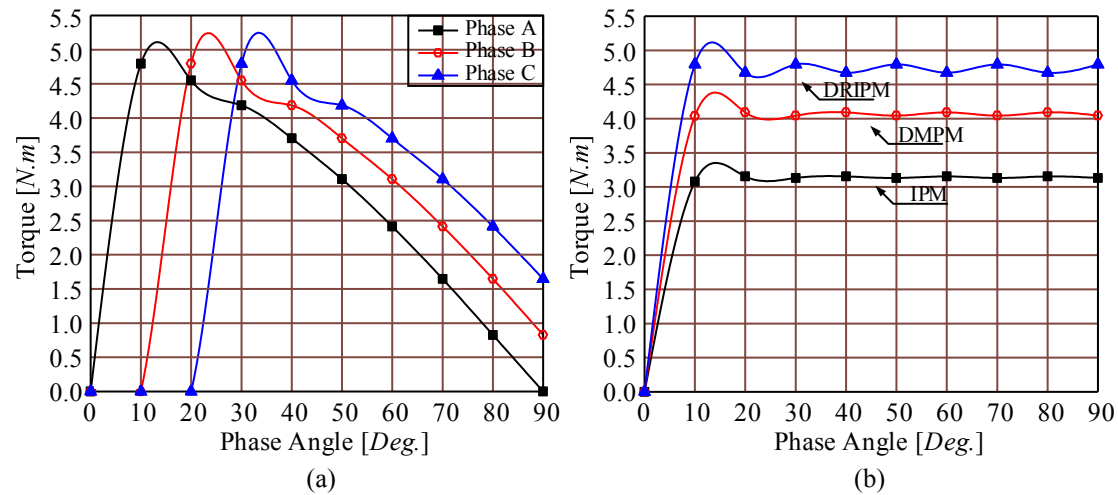


Figure 7. Dynamic Torque Characteristics
(a) Three Phase Static Torque (b) Dynamic Torque.

6.5 Efficiency Characteristics

Fig. 8 shows the efficiency characteristics of DRIPM motor. Under the conditions of 4A current amplitude at rotational speed 1,800 rpm, the results indicate that DRIPM motor obtains a maximum efficiency of 81% at phase current of 0°. As the phase angle increases, the efficiency reduces with generated output torque as mentioned in results from Fig. 5 earlier. The efficiency of the motor however can be improved by reducing the losses, especially the main contribution from iron loss around the stator and joule loss from the coil winding.

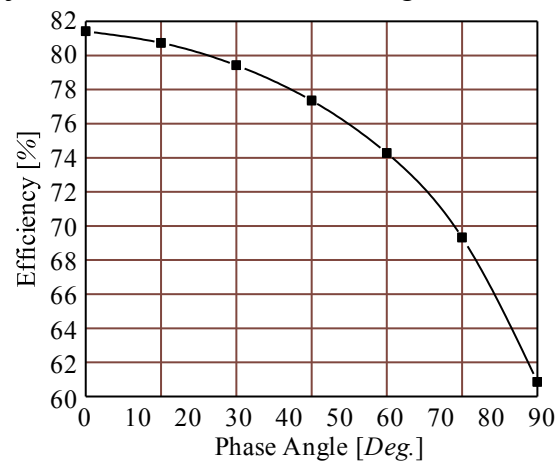


Figure 8. Efficiency Characteristics.

6.6 Comparative Evaluations for Improvement in Torque Density

Fig. 9 is the comparison for IPM, DMPM, and DRIPM motors for static and dynamic characteristics. All three motors are evaluated under the same sizing and parameters. Fig. 9 (a) shows that the static torque at maximum when injected current at optimal phase current. The result shows that IPM, DMPM, and DRIPM motors provides highest torque of 3.14 Nm, 4.09 Nm, and 4.80 Nm at 20°, 20°, and 10° respectively. For Fig. 9 (b) is the load torque characteristics comparison. The proposed DRIPM motor provides an improvement of 54% and 25% of dynamic torque compared to the IPM and DMPM motors respectively. From these two graphs,

it is observed that the improved torque of DRIPM motor is not completely due to the fact of double magnet as DRIPM motor has higher average torque than DMPM motor.

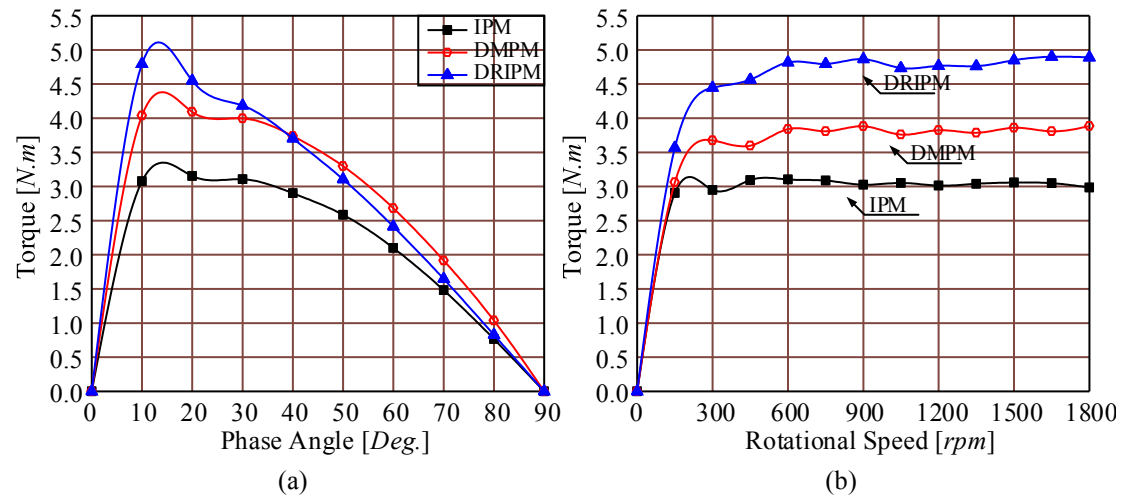


Figure 9. (a) Static Characteristics (b) Dynamic Characteristics.

Table 2 shows the evaluation on IPM motor and DRIPM motor torque characteristics. It demonstrates the static characteristics value derived from the different current phase considering the motor constant square density.

Table 2. Comparison of Motor Constant Square Density.

Parameter		IPM	DMPM	DRIPM
I	[A]	5	5	5
V	[m ³]	$5.99e^{-4}$	$5.99e^{-4}$	$5.97e^{-4}$
T_{avg}	[Nm]	2.821	3.658	4.267
K_t	[Nm/A]	0.420	0.543	0.558
K_m	[Nm/A/W ^{-(1/2)}]	0.042	0.054	0.056
G	[Nm ² /A ² /W/m ³]	2.944	4.927	5.219

7. Conclusion

Static measurement characteristics of the double rotor interior permanent magnet motor developed on the basis of increasing the air gap by proposing an outer rotor. The proposed DRIPM motor provides an improvement of 77% and 6% for motor constant square density compared to the conventional IPM motor and DMPM motor respectively. The proposed DRIPM has 51% and 16% increment of average torque than that of the conventional IPM motor and DMPM motor respectively. However the drawback of this motor is that it produces high iron and joule loss due to the design structure of stator and coil winding located in the middle of the motor. For future work, it is recommend to use higher grade silicon steel with lower core loss characteristics for the laminated core.

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Improvement in the Performance of the Double Rotor Switched Reluctance Machine Using Magnetic Circuit Design

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Abstract

The need of magnet-less machine for industrial applications are increasing, and one of the most common magnet-less machine is switched reluctance machine. Switched reluctance machine utilises the basic concept of attraction and repulsion principle, and together with the air-gap reduction an improvement in the production of the torque generation is separated earlier. The concept of dual air-gap to improve the torque density of the switched reluctance machine is attempted by researchers in recent times. The concept of dual air-gap shows a high starting torque density in the machine which allows an early steady state in the machine performance compared to the conventional machine. As the drawback, the dual air-gap machine is not able to produce higher torque average and drags is presence for industrial application. Therefore, a novel through modification of magnetic circuit of the dual air-gap in double rotor switched reluctance machine is proposed. In this paper, a comparison in terms of motor torque constant square density between three machines of conventional switched reluctance machine (SRM), double rotor switched reluctance machine (DRSRM), and the proposed dual air-gap machine is presented. The results shows that there is an improvement in the average torque by 13% compare to the SRM and 39% compare to the DRSRM. The proposed dual air-gap machine, it is also showing an improvement in motor constant square density by 37% and 114% of SRM and DRSRM, respectively.

Keywords: dual air-gap, double rotor, switched reluctance, motor constant square density, torque generation.

1. Introduction

The first machine around 1830s with the based concept of electromagnet was reluctance machine. The reluctance machine has certain novel features and its reinvention has brought new possibility due to the inexpensive and high power switching devices [1]. It has a simple structure in comparison to the induction or synchronous machine. There are many application which has been developed through the basic understanding of switched reluctance machine such as, for elevator application [2], washing machine [3], and wind application [4].

In this present day, the need for switched reluctance machine is increasing, because of the skyrocketing price for rare earth magnets. Most researchers nowadays are trying to improve torque output capability in a wide range of speed operating system in which has the high fault tolerance capabilities [5-6]. The optimization of the reluctance machine design for industrial applications are important. There are many different approached for the improvement of reluctance machine attempted by various researchers such as, it can be done by torque ripple minimization [7-8], current control [9], or structural and mechanical parameter optimization [10].

In order to produce an improvised switched reluctance machine design, using dual air-gap the guideline and presented in [11-16] is utilized. The switched reluctance machine which previously developed in [11-12] is evaluated. Also the previous SRM and DRSRM are designed and analyzed through numerical tool. It has been identified that the torque generation in conventional switched reluctance machine is depends on the air-gap distance between rotor and stator; and from the basic concept of reduction in the air-gap area, a double rotor switched reluctance machine [13-14] which has the dual air-gap magnetic circuit with modified magnetic circuit is introduced. The previous dual air-gap magnetic circuit shows that the torque generation characteristics in the machine performance has a high starting torque and it reaches its steady state much faster compare to the conventional switched reluctance machine. However, there is drawback in the previous double rotor switched reluctance machine designed, where the machine volume is much higher compare to the conventional machine and the torque produces is lower. Although there are some drawbacks, the dual air-gap magnetic circuit has open the possibility for switched reluctance machine to advance in the used of industrial applications. In this paper, a dual air-gap through a new magnetic circuit is proposed [13-16], a novel design of double rotor switched reluctance machine with a higher torque generating capability is introduced. In order to identify the performance of the proposed machine, finite element analysis is presented and motor constant square density is used as an evaluation parameters of all the machines with same volume and size are being compared. From this analysis, it is shows significant changes the percentage improvement of the proposed machine compared to the previous machine designs.

2. Design Concept

As the operation of reluctance machine lies in the basic principle of attraction and repulsion. The torque generation capabilities of the reluctance machine is produce in the air-gap of the electromagnetic force. The generation of magnetic flux in Double Rotor Switched Reluctance Machine is given in the Equation (1) as,

$$NI = \phi(\mathfrak{R}_{g1} + \mathfrak{R}_{g2}) \quad (1)$$

where ϕ is the magnetic flux, N is number of turns, I is current, $\mathfrak{R}_{g1}$ and, $\mathfrak{R}_{g2}$ are air-gap magnetic reluctance. The $\mathfrak{R}_{g1}$ of the dual air-gap magnetic design $\mathfrak{R}_{g1}$ is given in Equation (2),

$$\mathfrak{R}_{g1} = \frac{\ell_{g1}}{\pi\mu_o r_{g1}^2} \quad (2)$$

where ℓ_{g1} is the length of the first air-gap, μ_o is the material permeability, and r_{g1} is the first air-gap radius. The $\mathfrak{R}_{g2}$ of the dual air-gap magnetic design $\mathfrak{R}_{g2}$ is given in Equation (3),

$$\mathfrak{R}_{g2} = \frac{\ell_{g2}}{\pi\mu_o r_{g2}^2} \quad (3)$$

where ℓ_{g2} is the length of the second air-gap, and r_{g2} is the second air-gap radius. The magnetic circuit used in the dual air-gap of the double rotor switched reluctance machine is designed from the Eq. (1-3) are presented in Fig. 1,

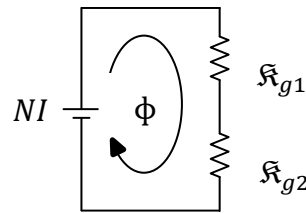


Figure 1. Equivalent Machine Magnetic Circuit

The structural dimension of the proposed dual air-gap switched reluctance machine for dual air-gap machine based on the guideline [14] is presented in Table 1 and the 3D model machine design of the proposed double rotor switched reluctance machine is presented in Fig 2.

Table 1. Proposed Structure Specification

Parameter	Value
Diameter	80 mm
Outer air-gap length ℓ_{g1}	0.1 mm
Outer air-gap length ℓ_{g2}	0.1 mm
Outer rotor pole arc	40°
Inner rotor pole arc	50°
Stator outer teeth pole arc	14.25°
Stator inner teeth pole arc	40°
Number of turns per phase	346 turns

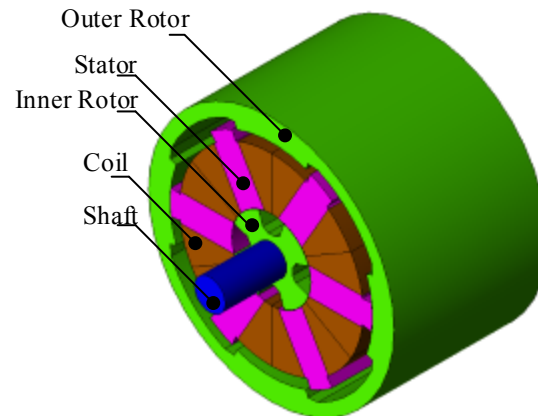


Figure 2. Proposed Double Rotor Switched Reluctance Machine

3. Finite Element Analysis (FEA)

Finite Element Analysis (FEA) tool is used as an identifier of the torque density in the machine design. In this machine design experiment the finite element analysis of the proposed machine uses industrial standard FEA tools based on the JMAG [15-16] software. The proposed machine magnetic flux characteristics is presented in Fig. 3,

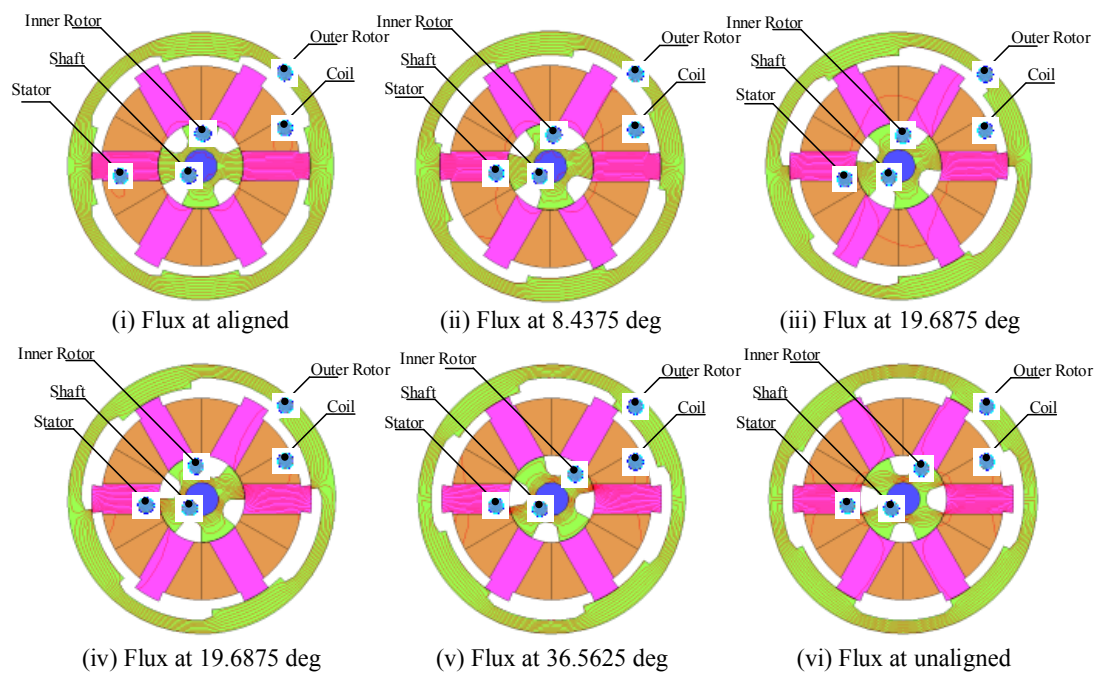


Figure 3. Proposed Double Rotor Switched Reluctance Machine Circuit

The magnetic flux at different positions between the stator core and double rotor core are presented. In this condition, when the machine at aligned position, the magnetic flux produces at its maximum. As the rotor starts to move further away from the initial position at 0° , the magnetic flux is gradually decrease and at the same time the torque is starts to generate, and then when the rotors reaches its complete unaligned position the flux linkage is reached its minimum constant value.

4. Results and Discussion

4.1 Evaluation Parameters

For comparison on the level of performance for conventional and proposed structure, the methods of calculation Motor Constant Square Density G is used. This evaluation is very useful as it includes the torque, power, and volume of the machine designs. The Motor Constant Square Density G is given as in Equation (4).

$$G = \frac{(K_m)^2}{V} \quad (4)$$

where K_m is the machine constant in $[Nm/A/W^{-(1/2)}]$, V is the volume of the machine $[m^3]$. The machine constant can be further expressed as in Equation (5).

$$K_m = \frac{K_T}{\sqrt{P}} \quad (5)$$

where K_T is the torque constant $[Nm/A]$ and P is the input power to the coil winding $[W]$. The torque constant is given as in Equation (6).

$$K_T = \frac{T_{avg}}{I} \quad (6)$$

where T_{avg} is the fundamental torque $[Nm]$ and I is the maximum current input to the machine $[A]$.

4.2 Dynamic Characteristics

Dynamic characteristics are important for studying the state of the machine under the normal operating condition with load. In the dynamic characteristics experiment the excitation state is created based on the alternating conditions between opening and closing switches in accordance with the position of the rotor's rotation. It can be predicted that the timing setting of an alternating conditions is able to causes a major changes in the torque properties. In the analysis results of the dynamic characteristics experiment in torque waveform is presented in Fig 4., The graph in Fig. 4 shows that the torque waveform of dynamic characteristics is presented when the voltage application width θ_w is 30 deg with the changing voltage application θ_s starts $-5\ deg$, $0\ deg$, and $5\ deg$. The results shows that the changing application at $-5\ deg$ in application width of 30 deg, gives high torque generations compare to other changing voltage applications. From this experimental results it can be explained that the best voltage time changes for the circuit controller is 5 degree early within the 30 degree application ranges.

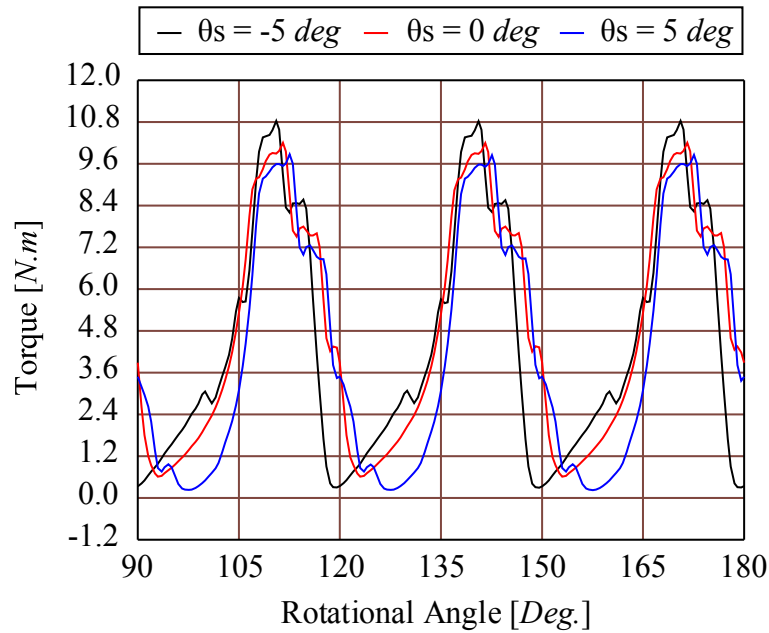


Figure 4. Torque Characteristics (θ_w : 30 deg)

4.3 Drive Characteristics

These type of machines require electronic control drive in order to operate at the operational condition. In the drive characteristics experiment the physical phenomena analysis of the magnetic circuit and drive circuit is created, where both is use to create a torque analysis model. The circuit diagram which designed for this experiment contains a voltage source and an ON/OFF square wave voltage of three-phase switching are controlled depending on the timing settings Fig. 5 shows that whether the iron loss is taken into account or not, it shows no effect on the torque production because of the iron loss ratio to output is small. Fig. 6 shows the efficiency of the machine when it moves at different rotational speed, and when the rotation speed at 1200 rpm shows that efficiency and the peaks efficiency of the proposed machine is about 89%.

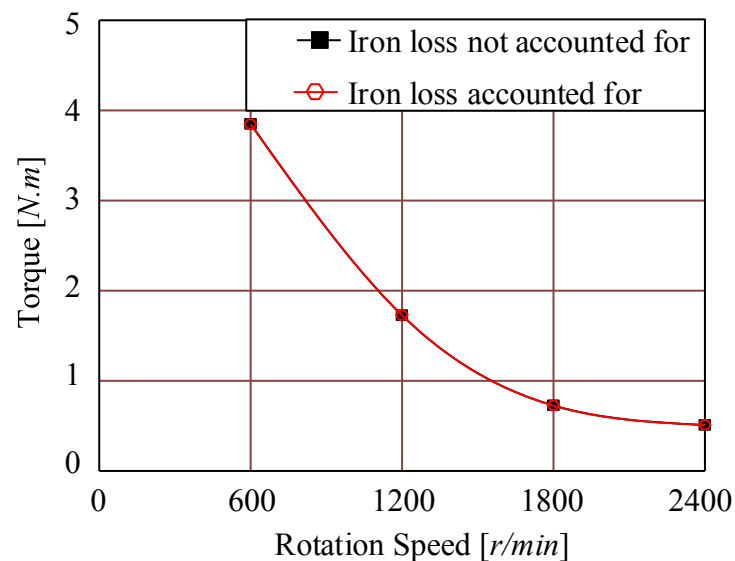


Figure 5. Speed Torque Characteristics

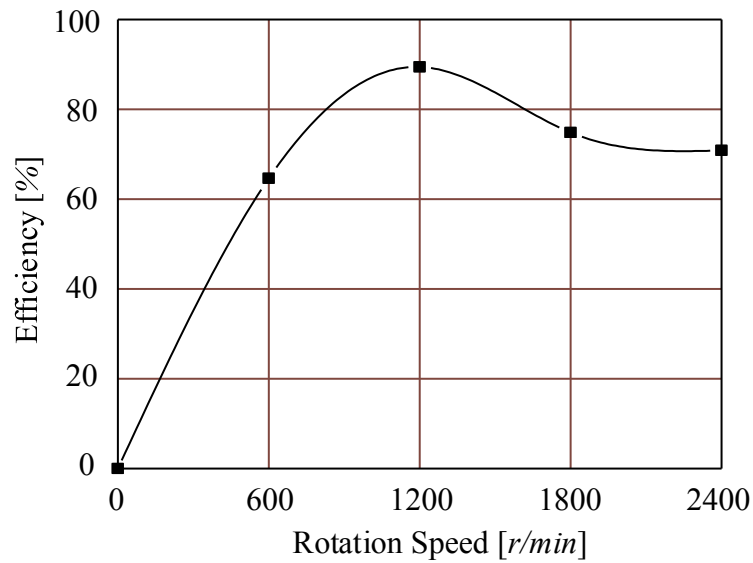


Figure 6. Efficiency Characteristics

4.4 Current Characteristics

In the I-Ps characteristics experiment the physical phenomena analysis of the magnetic circuit is created using torque analysis model for the simulation of the circuit model from the coil drive circuit are presented in Fig. 7. The analysis experiment results from the current characteristics are the magnetic flux for the current value of 3A at unaligned and aligned position is presented.

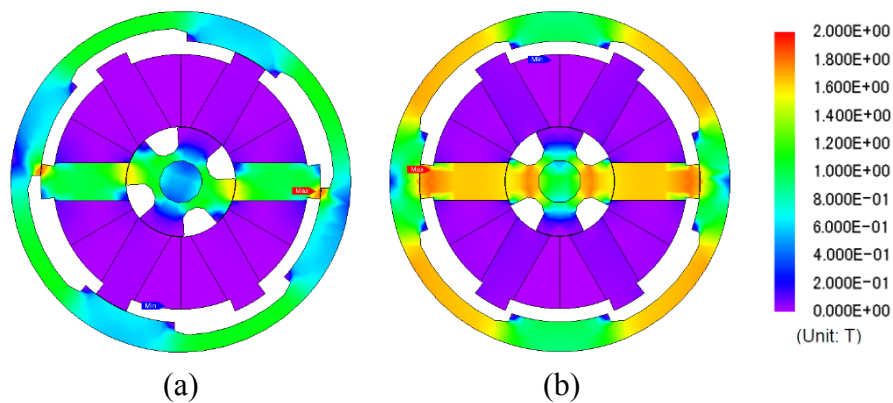


Figure 7. Magnetic Flux Intensity (a) unaligned (b) aligned

Fig. 7 shows the machine magnetic flux linkage conditions at two different positions. It can be seen when the machine at unaligned position (a) the flux linkage around the machine is produces $0.6 - 0.8T$ and when the machine is at aligned position (b) the flux linkage around the stator is produces $1.2 - 1.6T$. It can be explain that when the machine is at aligned position the magnetic resistance is dominant; as the machine is at unaligned positions the current is gradually increases and the magnetic flux gradually decreases.

4.5 Comparative Evaluations

Fig. 8 shows the machine static characteristics of the proposed Improved Double Rotor Switched Reluctance Machine (IDRSRM). It has higher torque generation compare to Switched Reluctance Machine (SRM) and Double Rotor Switched Reluctance Machine (DRSRM).

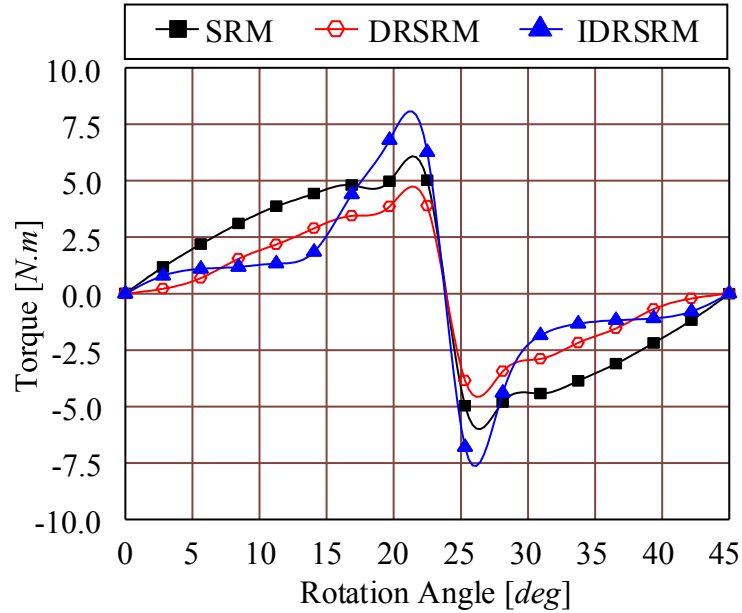


Figure 8. Static Torque Characteristics

Fig. 9, the DRSRM shows that the machine design has the capabilities to reach steady state faster than the other two machines, moreover it has highest starting torque compare to the SRM and proposed machine.

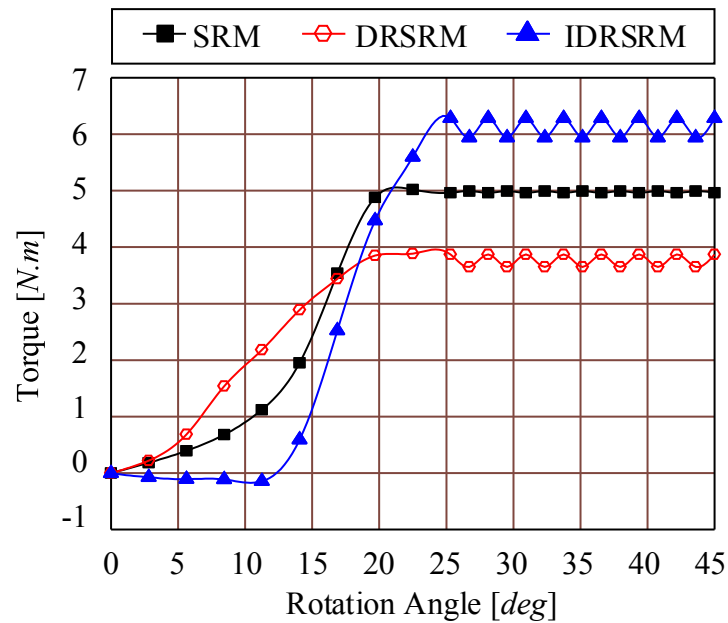


Figure 9. Machine Operational Static Characteristics

In Table 2, the comparative evaluation of motor torque constant square density between the proposed machine, double rotor switched reluctance machine and conventional switched reluctance machine with the same diameter is presented.

Table 2. Comparison on Figure of Merit

Figure of Merit	SRM	DRSRM	IDRSRM
$I [A]$	5	5	5
$V [m^3]$	$2.13e^{-3}$	$2.20e^{-3}$	$1.99e^{-3}$
$T_{avg} [Nm]$	3.85	3.13	4.36
$K_t [Nm/A]$	0.77	0.63	0.87
$K_m [Nm/A/W^{-\frac{1}{2}}]$	0.077	0.063	0.087
$G [Nm^2/A^2/W/m^3]$	27.87	17.84	38.20

As it can be seen in Table 2, the average torque of the proposed machine structure is gradually increase over the conventional switched reluctance machine and double rotor switched reluctance machine. In addition, the motor torque constant square density value of the proposed machine showing an increase by twice of the conventional Switched Reluctance Machine.

5. Conclusion

The proposed machine is developed based on the basic of double salient dual air-gap structure. The proposed design is structured, simulated, and evaluated using the standard finite element analysis. The results of the conventional switched reluctance machine (SRM), double rotor switched reluctance machine (DRSRM), and novel double rotor switched reluctance machine (IDRSRM) are compared as for performance evaluation. The initial investigation shows that a percentage improvement in the motor constant square density by 37% in the comparison of SRM and 114% in the comparison of DRSRM and the improvement of the proposed IDRSRM. The average torque which improved by 13% in comparison to the conventional SRM and 39% compare to the DRSRM, all the machine which were compared are for the same size and volume of the machine design.

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Development of a Design Optimization Methodology for a Home Appliance Product Part Design

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Abstract

The motivation behind this research study is the idea of optimization which can be very beneficial as it can help future production in terms of costing, research and development of better designs to improve older counterparts. The main objectives of this research project are to utilize the Altair HyperWorks software to perform optimization on a fan motor bracket top plate to craft a Standard Operating Procedure (SOP), implement optimization technology to create a SOP for the optimization process of a home appliance product part design and to perform experimental modal analysis on the product part. Modal analysis and experimental modal analysis will be performed on the product part design using NX Nastran, *Brüel & Kjær* MTC Hammer and Pulse Reflex where the natural frequencies and mode shapes can be obtained from the software for validation. In accordance with that, the optimization results obtained will be used to compare the effects of optimization on the dynamic properties of the model. The equipment used in this research study are mostly industrial based CAE software comprising of Altair HyperWorks and NX Nastran. At the end of this research project, the results to be accomplished would be the familiarization of the standard operating procedure to perform an optimization process using Altair HyperWorks and NX Nastran, the ability to perform an experimental modal analysis on a product part design, the maximization of the natural frequency and stiffness of the home appliance product part design and to avoid resonance in the product part design. By utilizing topography optimization, parametric beads were inserted into the model part, increasing the stiffness of the design. In addition to that, the stiffness of the part design is found to have increased after performing an optimization procedure. Thus, the fan motor bracket top plate is less prone to experience resonance at a lower frequency.

Keywords: Optimization, Home Appliances, Vibration Attenuation, Modal Analysis.

1. Introduction

1.1 Research Background

In the manufacturing industry today, the reliability of the 3D mechanical design of a product part is very crucial as it saves an abundance of time and resources by first performing computational analysis on the 3D model in computer software. Along the years, engineers have learned to trust Computer-Aided Engineering (CAE) tools such as Finite Element Analysis (FEA), Computational Fluid Dynamics (CFD) and motion simulation [1]. However, when transitioning into the manufacturing stage, material wastage becomes a major factor in company losses. Thus, all the modern manufacturing enterprises today are determined to develop the best optimized reduced weight and cost effective products that meet the intended design functionality and reliability. In addition to that, optimization of a part design can also increase the value of the product by means of cost reduction through efficient material usage. Besides that, an optimization process will also help increase the designer's knowledge of their product behaviour and improve their design while obeying the data obtained from the previous analysis. This structural optimization tool helps in reducing production time as well. In the last few years, structural optimization has emerged as the valuable tool to develop new design proposals especially in automobile and aircraft industries [2].

Nowadays, computer software such as ANSYS and SolidWorks already have the optimization module integrated into the software [2]. For an optimization process to be performed, three criteria are required by the designer which are the design parameters, constraints of the part design and the objectives of the optimization process. The design parameter simply means the design variables which the designer wants to adjust to save material usage during manufacturing. As for the constraint, the designer or user can define the allowable ranges to be obtained in the simulation result. The objectives or goals of the product is to determine the optimization output in terms of reducing material wastage or minimizing model size and others.

The purpose of this project is to produce a standard operating procedure (SOP) to undergo an optimization process on a simple home appliance part design. In this case, an internal component of an air-conditioner manufactured by Panasonic **HA Air-Conditioning** Malaysia Sdn. Bhd. will be used as the project material. By performing an optimization on a simple structure, the manufacturing process of the product part design will take less time as numerical analysis will aid in determining the best design for manufacturing to obtain the optimal design. Besides that, the main function of an optimization procedure is to identify the most optimum design for the component whereby the strength of the part design is the most efficient and can withstand high force and pressure. The idea of optimization is very beneficial as it can help future production in terms of costing, research and development of better designs to improve older counterparts. In the near future, the sustainability of the products manufactured by Panasonic will be able to surpass other competitor's products by a wide margin based on the application of optimization whereby the strength and stiffness of the product can withstand high workloads and long durations of time. Thus, creating a SOP for optimization is crucial to challenge new competitors and lead the pack in the air-conditioning industry.

In addition to that, this project also studies the benefits of an optimization procedure on a modal analysis of a structure. The purpose of a modal analysis is to identify the mode shapes produced by a design structure whereby the model reacts to the various natural frequencies when resonance is achieved. Thus, the stiffness of the

model can be found by using the natural frequency equation which will be explained more in the literature review section of this report. This is where optimization plays an important role in determining the most optimum design to attain a stiffer model structure. From this, the optimized model will only reach resonance at a higher natural frequency ensuring the longer lifespan of the product part when external forces are present in the working system.

1.2 Project Scope

In the industry today, there are four types of structural optimization techniques. The first being size optimization, shape optimization, topography and lastly topology optimization. The project covers topography optimization as topology optimization utilizes the density and homogenization method [3]. The assembly of the part design also hinders the ability to carry out topology optimization as material reduction will not enable proper installation of the fan motor bracket top plate as well as manufacturing feasibility. Besides that, the response surface method is also covered in this project. Thus, the boundary of the project includes the design parameters, constraints of the part design and objectives of the optimization process. In accordance to the scope, experimental modal analysis will also be carried out on the product part design where the purpose of the optimization process is to increase the stiffness and robustness of the design where validation is required by comparing the results to the numerical modal analysis. In accordance to that, the range of random vibration frequencies that the structure is being subjected to is only for filled transport packages and unit loads. In addition to that, the scope for this project is only limited to an investigation of an air-conditioning component.

1.3 Project Objectives

For this research project, the objectives are to utilize the ANSYS software to perform optimization on a simple steel plate to craft a Standard Operating Procedure (SOP), perform numerical modal analysis to obtain mode shapes of a fan motor bracket top plate, perform experimental modal analysis to validate numerical modal analysis results with physical testing and to implement optimization technology to create SOP for the optimization process of a fan motor bracket top plate to increase material stiffness using Altair HyperWorks.

2. Research Methodology

2.1 Finite Element Modal Analysis

The research paper also consists of a computational analysis which utilizes the capabilities of numerical modal analysis to simulate the dynamic properties of the fan motor bracket top plate in a free-free condition using NX Nastran. Following the procedure to undergo the analysis, some minor adjustments must be made beforehand to increase accuracy in the mode shapes obtained. Computer modelling alone cannot determine the dynamic behaviour of a structure completely. Therefore, modal analysis was formulated to determine the dynamic characteristics of a system in forms of natural frequencies and mode shapes [4]. In the research study, the free-free condition will be used as the basis of the project where no external forces will be acted on the product part. In a free-free condition, the dynamic characteristics of the simulation

model is determined by observing the mode shapes of the model. From this, the natural frequencies of the model at which mode shapes are formed can be obtained. However, the failure of determining the most optimum design for a model will hamper the capabilities of modal analysis. Therefore, a new method must be researched to fuse optimization and modal analysis together to form a robust design simulation. The mode shapes and regular frequencies of a structure are its fundamental dynamic properties. Modal analysis is utilized to differentiate these mode shapes and their eigenvalues. Thus, the basic structural dynamic information obtained from the modal analysis gives an accurate identification of the structural properties of the mode shapes. In addition, modern modal analysis test methods have been created to enhance testing and reduce information requirement for analysis to give the dynamic properties of the structure. To carry out a modal analysis procedure through NX Nastran, the solver normally utilized is the Lanczos algorithm [4]. However, in modal analysis, there are certain limitations which have yet to be solved by researchers in today's generation. For instance, non-linear structures tend to affect the analysis and introduce problems in the information attainment as well as disrupt the evaluations of natural frequencies from the mode shapes. As the volume of the model increases, the properties of the structure also changes which is generally insufficient to perform a direct model analysis [5]. The range of frequencies must be increased to enable the software to compute the mode shapes where resonance occurs. Besides that, another limitation in modal analysis is the inability to specifically analyze the forced response problems, transient response problems and random response of the model structure. In accordance to that, the mode shapes produced from the modal analysis might not have significant differences when the material assignment to the model in the pre-processing is changed. This problem proceeds as an issue when various materials are analyzed which makes it more difficult for the designer to evaluate the relationship of different materials on mode shape attainment.

2.1.1 Geometry and Mesh Checking

Before numerical analysis can be done, the part geometry as shown in Fig. 1.0 must first be checked and cleaned using the NX Nastran modelling tools. The idea behind this procedure is to remove any holes found in the model part, remove unnecessary convex and concave fillets, maintaining an overall constant thickness throughout the model and checking other part features which has no discernable effect on the results. This procedure is important as structure features can cause low quality mesh.

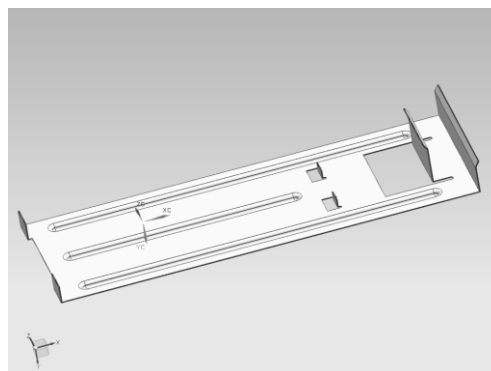


Figure 1.0 Geometry of the Fan Motor Bracket Top Plate

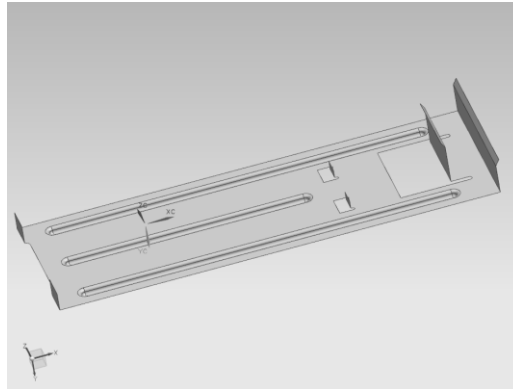


Figure 1.1 Midsurface Offset of Part

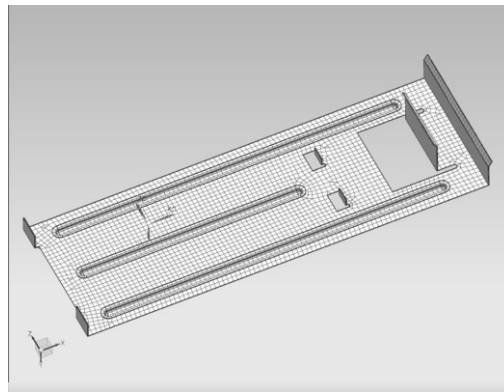


Figure 1.2 Mesh of the Fan Motor Bracket Top Plate

The idea behind this current step is to allow easier shell meshing whereby the part is offset to half of its initial thickness where the overall thickness of the structure is 0.7mm. Shell meshing was utilized in this study instead of volumetric meshing as it saves computational time due to the lower number of elements used and the quality of the mesh can be monitored easily [6]. In accordance with that, a low number of triangular elements and an abundance of quadratic elements were used in the meshing procedure which indicates a high quality mesh as shown in Fig. 1.2. The element size set for the meshing was 3.0mm in order to save computational time as well. Besides that, the material properties are also inserted into the mesh input whereby the material tested is rolled steel. The properties of steel are shown in Table 1.0 below:-

Table 1.0 Rolled Steel Properties

Mass Density (kg/mm ³)	Young's Modulus (kPa)	Poisson Ratio
8.75x10 ⁶	213x10 ⁶	0.29

2.1.2 Normal Mode Analysis

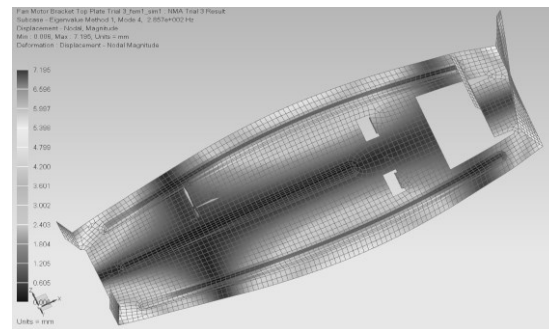


Figure 1.3 Mode Shape of Model at 285.7 Hz

For the finite element modal analysis of this study, the SOL 103 Real Eigenvalues is used. The Lanczos method was utilized in this study to extract the real eigenvalues as it is efficient in extracting eigenvalues and eigenvectors. The square root of the eigenvalues give the natural frequencies of the model whereas the eigenvectors give the normal modes of the structure. Fig. 1.3 depicts the mode shape of the structure at 285.7 Hz where the part experiences resonance. In addition to that, the range of the natural frequency tested was set to be from 1 Hz to 300 Hz for normal modes extraction following the ISO 13355:2001 which states that the natural frequency of the structure being studied is for filled transport package and unit loads and not subjected to higher random vibrations due to it being an internal component of an outdoor air-conditioning unit [7].

2.2 Experimental Modal Analysis

In this study, the roving hammer test was carried out on the structure. For this study, the Multiple Input Multiple Output (MIMO) was used where the multiple inputs refer to multiple excitation points where a hammer is used to knock the points and the multiple output points refers to the usage of accelerometers to measure the dynamic response of the structure. By incorporating multiple hitting points and accelerometer points, the response of the structure is easier to be monitored and measured. In the case of a MIMO testing procedure, it is easier to perform the experiment as some reference points might not be able to measure a mode accurately where other reference points are able to capture the mode thus obtaining good quality results [8].

2.2.1 Pre-Test Planning

In Fig. 2.0, it shows the modal assurance criterion (MAC) plot for the test analysis model (TAM) and the finite element model. The purpose of doing this procedure is to ensure that the accelerometer points and knocking points selected are well correlated with the finite element model to ensure the TAM's effectiveness and reliability. TAM is important to set-up the geometry for modal testing. It represents the characteristics of the model but comprising of limited degree of freedoms. By exciting critical degree of freedom points, it simplifies the test structure and in turn saves time for testing. The TAM can be produced by manually selecting the points on the structure based on elements comprising of nodes.

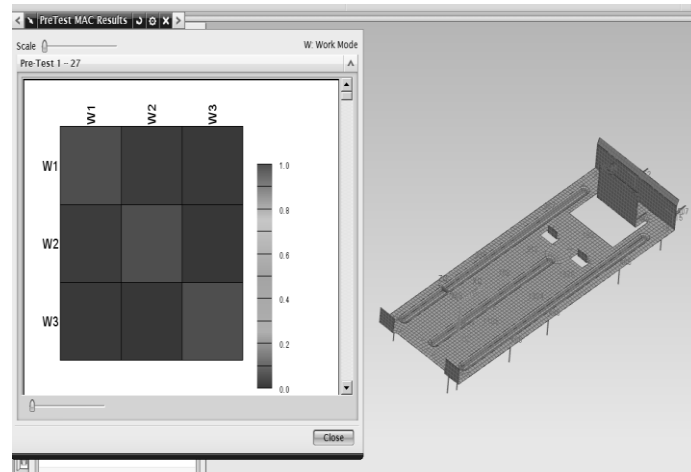


Figure 2.0 Correlation of Numerical Modal Analysis and Test Analysis Model

2.2.2 Experimental Set-Up

For the experimental set-up, the Pulse Reflex software was used to obtain the structures wireframe to depict the basic shape of the model geometry. In Fig. 2.1, the points shown are extracted from the test analysis model. Lines are drawn from point to point to create the shape of the structure. These points consisting of 4 uniaxial accelerometers and knocking points are then inserted into *Brüel & Kjær* MTC Hammer for accelerometer placement and knocking procedures. Then, data is measured and collected in the form of frequency response function (FRF) graphs when the structure is excited at the corresponding knocking and accelerometer points using the roving hammer. These FRF graphs as shown in Fig. 2.2 contain the mode shapes of the structure at certain natural frequencies. Each peak shows the mode shapes of the structure [9].

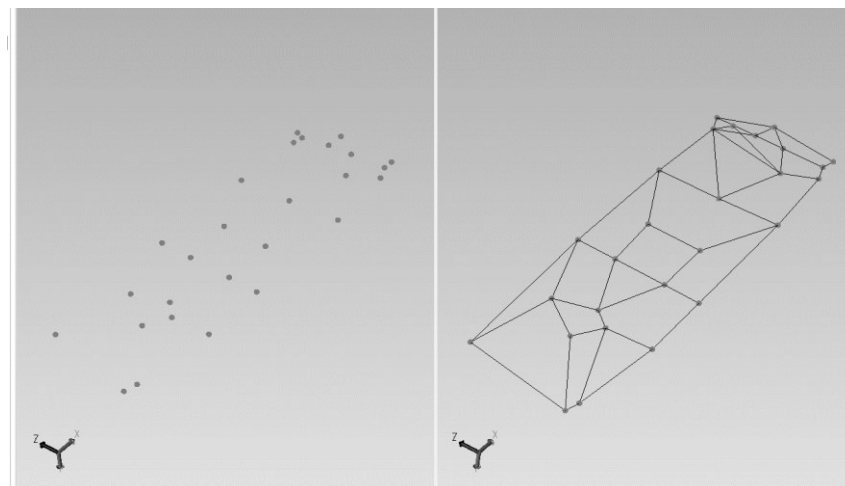


Figure 2.1 Geometry Decimation of Structure

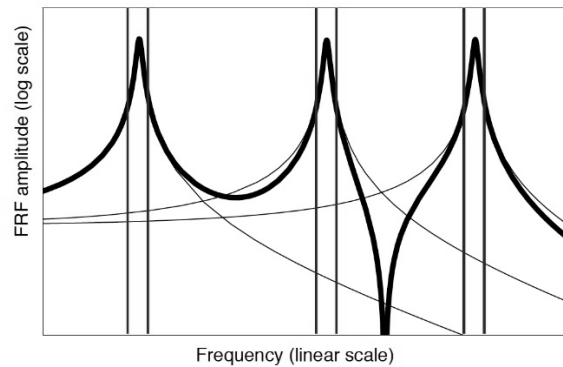


Figure 2.2 Example of an FRF graph



Figure 2.3 Sensor Placement and Hanging Method



Figure 2.4 Insulation of Test Rig

The scope of this research only covers the replication of a free-free boundary condition where the structure is hung by using elastic chords to simulate a free moving body without constraints as seen in Fig. 2.3. By constraining the movement of the structure, the results obtained from performing the experimental modal analysis (EMA) will be inaccurate causing undetermined dynamic properties. Besides that, the accelerometer wires can also act as constraints to the structure. Therefore, the wires are placed far apart from each other to prevent tangling and interference with one another during testing.

In addition to that, the test rig utilized is also insulated with foam padding to reduce any random vibrations from the ground from affecting the results of the EMA. Thus, the structure will be able to vibrate freely without environmental errors.

2.3 Altair HyperWorks Optimization Process

2.3.1 Optimization Procedure of Numerical Model

In HyperWorks, there are three sub-applications which are used for an optimization process. These applications are HyperMesh, Optistruct and HyperView. This section lays out the overall optimization process carried out in Altair HyperWorks. The Standard Operating Procedure is shown in Fig. 2.5 below:-

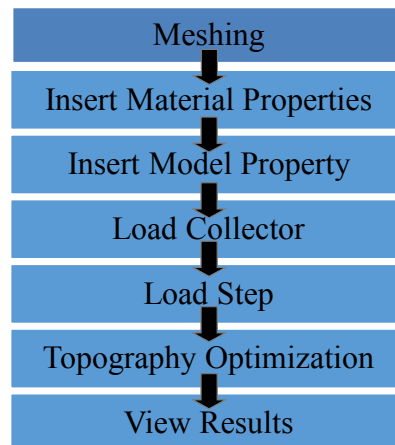


Figure 2.5 Flow Chart of Optimization Process in HyperWorks

All the steps in the Figure above are carried out in HyperMesh where boundary conditions are inserted and design variables are set. For the meshing procedure, the element size is set as 3mm and the mesh type is set to mixed where tetrahedron and hexadecimal mesh types are used.

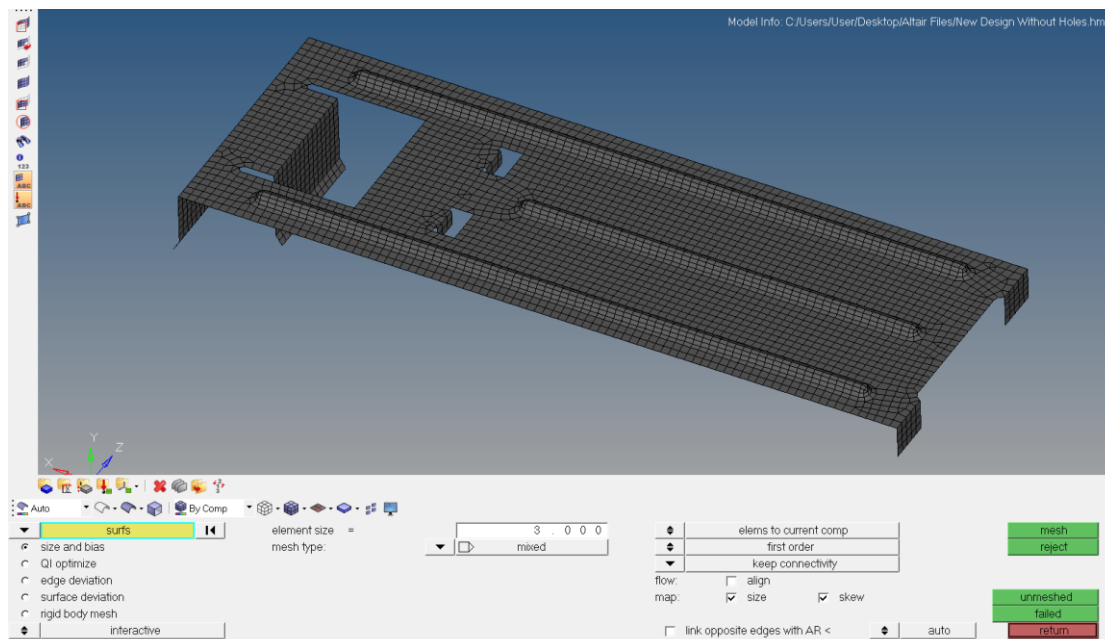


Figure 2.6 Meshing Setting

The first step of the optimization process is to insert the material properties into the model part. In HyperMesh, the mass density, young's modulus and poisson ratio are only required for the material properties. The input data is similar as stated in Section 3.1.1.

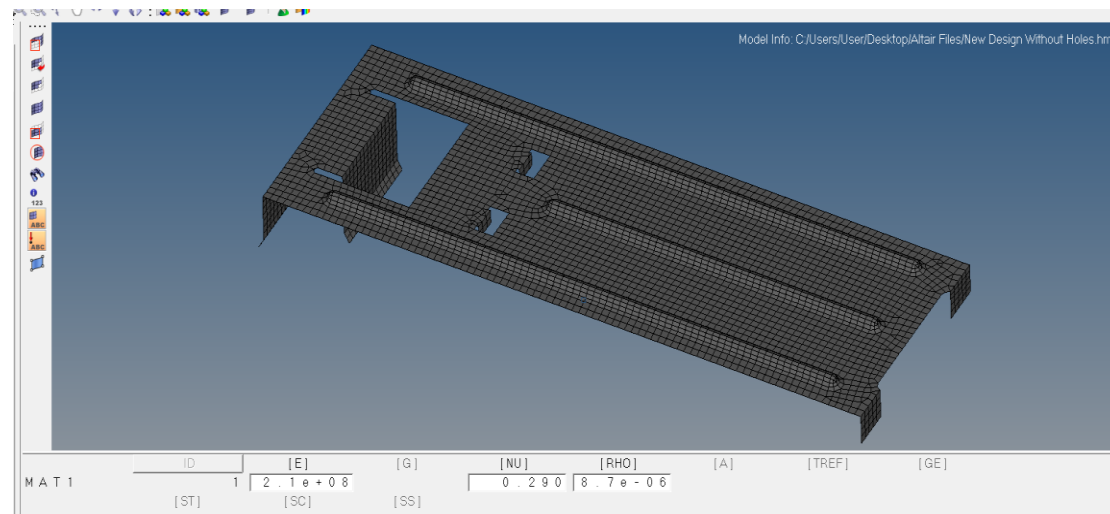


Figure 2.7 Material Properties Setting

As for the model property, the thickness of the model is input value. For this model part, the plate thickness is 0.7mm. The PSHELL card image is selected as the model part inserted into the software is a shell and not a solid. A shell design part has a lower computational processing time as compared to a solid design part. Thus, making the optimization process more efficient.

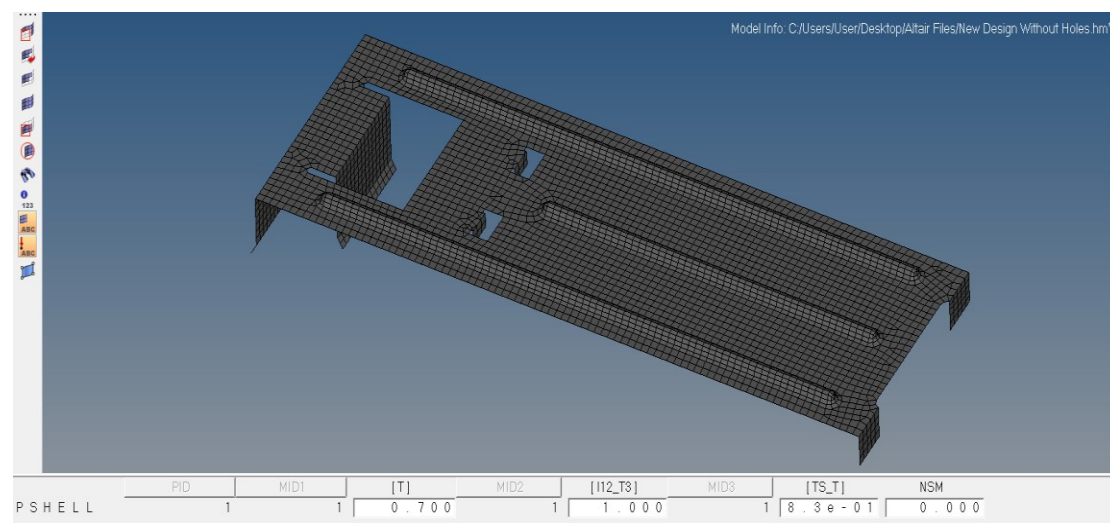


Figure 2.8 Model Property Setting.

As for the load collector, the input data is the range of frequency whereby the model experiences. For the research paper, the range covered is between 1 Hz and 300 Hz. The number of modes to extract is not set here as the range is already inserted into the software.

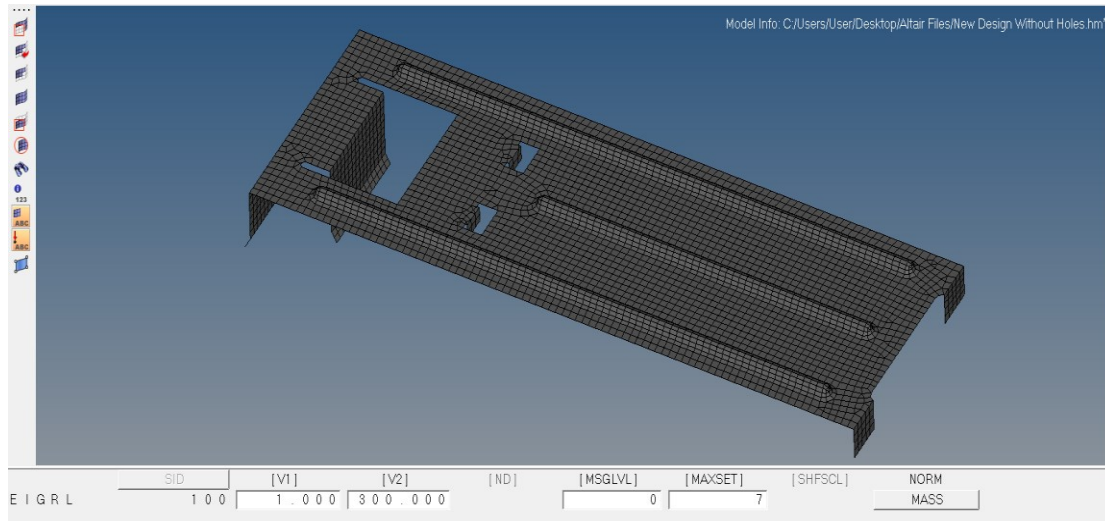


Figure 2.9 Load Collector Setting

In load step, the type of analysis is set as normal modes to obtain the mode shapes of the design part. This is done to ensure that the software produces the required data only.

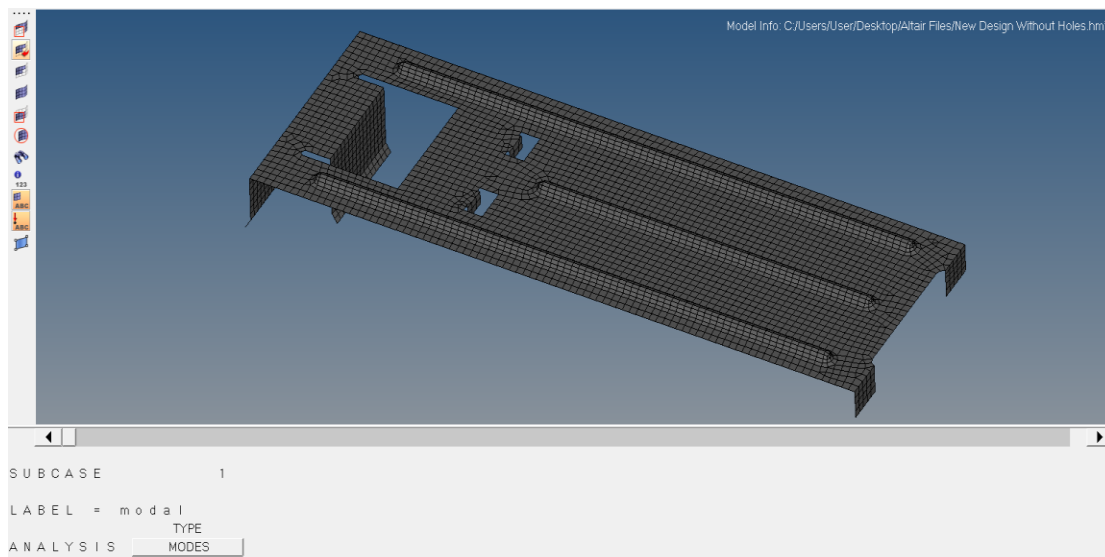


Figure 2.9.1 Load Step Setting.

2.3.2 Topography Optimization

To carry out this procedure, the design space is first selected based on the limitations of the model part. For the fan motor bracket top plate, only a small area is allowed to be altered utilizing the optimization technique. The required input data for a topography optimization are bead width, draw angle and draw height. Selection of the design space is in the form of node selection. Thus, the start and end location of bead creation is set by selecting the nodes on the model part. By inserting these parameters, the software is able to compute the necessary data to produce a new design. The bead height is set as 7mm, draw angle to be 60° and draw height to be 3.5mm. Then, by running Optistruct, optimal results are obtained which are then displayed in HyperView.

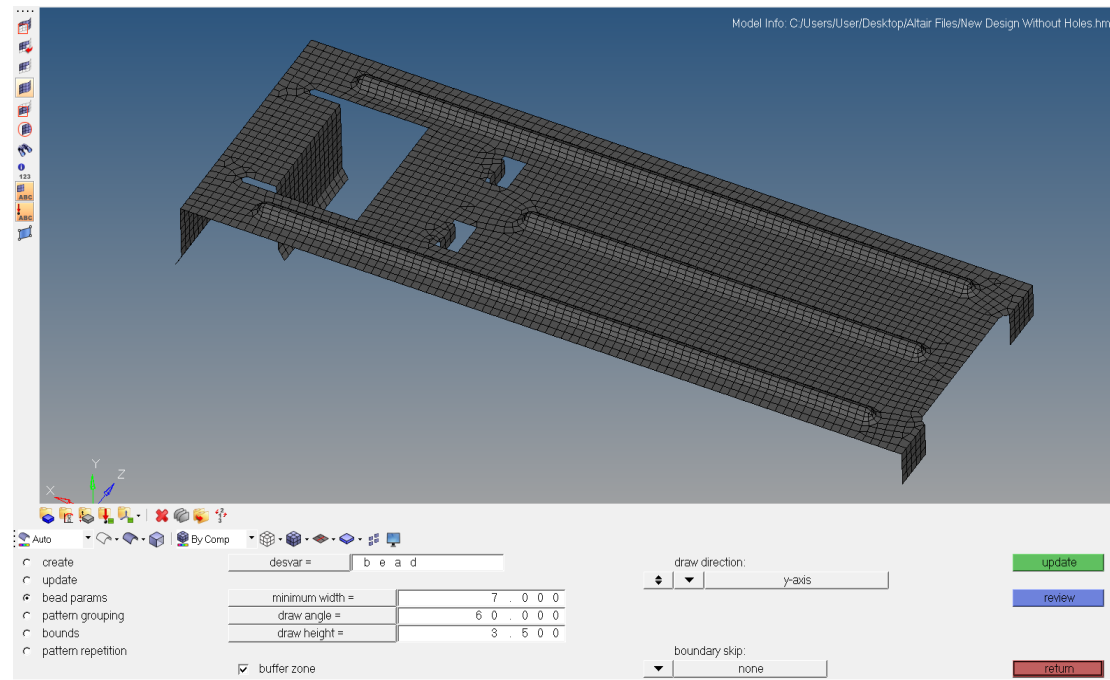
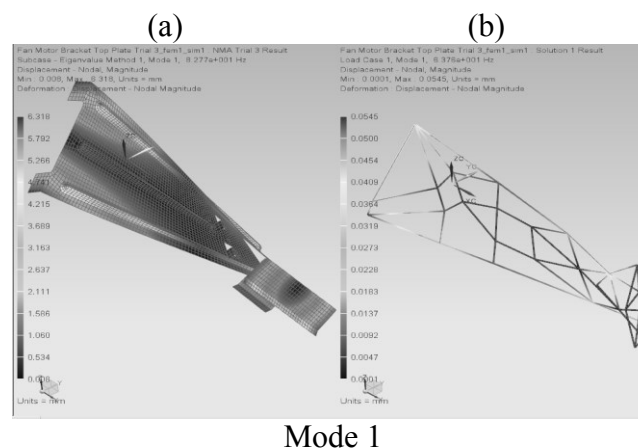


Figure 2.9.2 Topography Setting

3. Results & Discussion

3.1 Correlation of Experimental Modal Analysis and Experimental Modal Analysis



As seen in Fig. 3.0, the mode shapes of the EMA and Finite Element (FE) modal analysis are almost similar to each other. This shows that the experiment was conducted smoothly and accurately. This comparison is made to show validation of EMA with FE modal analysis which applies for real world application. By performing the test, only 4 mode shapes can be extracted. Thus, assuring that computational analysis can also be used to produce results similar to that of experimental results. In addition to that, time can also be saved by performing FEA whereby experimental procedures and set-up take an absurd amount of time before any results can be obtained. However, this validation process is important to justify the precision and accuracy of real testing results in the industry.

(a) (b)

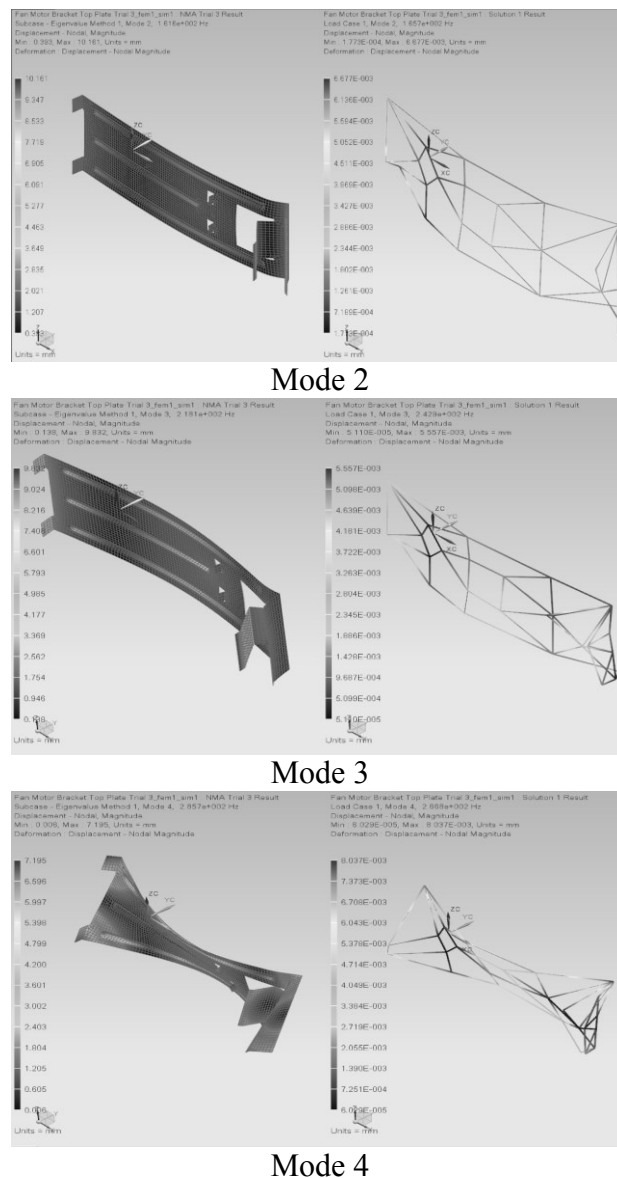


Figure 3.0 The Comparison of the Numerical Modal Analysis Mode Shapes (a) and Experimental Modal Analysis Mode Shapes (b) for Mode 1, 2, 3 and 4 of the Fan Motor Bracket Top Plate

Table 2.0 Correlation of Mode-Pairs

FE Modal Mode	Finite Element Modal Analysis Frequency	EMA Mode	Experimental Modal Analysis Frequency	MAC	Frequency, % Error
1	82.7686	1	63.7643	0.943	29.8041
2	161.581	2	165.651	0.750	-2.4572
3	218.087	3	242.862	0.863	-10.2012
4	285.678	4	266.812	0.920	7.07081

The table above shows the error between the work frequency and the reference frequency. The work frequency shows the mode shapes of the FE modal analysis while the reference frequency shows the mode shapes produced from the EMA. Major errors can be seen in the first, third and fourth mode where the percentage error exceeds 5% as shown in the frequency error data in Table 2.0. These errors arise from the EMA test. External factors such as ground vibration and irregular knocking force are the main contributors for such huge errors. Other errors such as the interference of the accelerometer wires can also lead to inaccurate data collection during knocking. Thus, to perform an error free EMA test, the structure tested has to be placed in a still environment without any presence of wind as well as experience zero random vibrations from the surroundings which can only be replicated in a virtual domain. It can be said that EMA can never be 100% accurate as errors are always present in many forms.

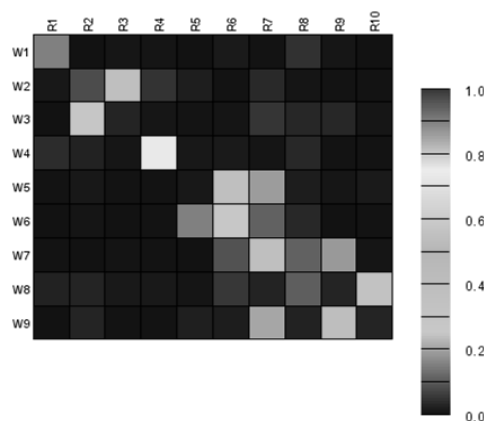


Figure 3.1 Correlation of Numerical Modal Analysis and Experimental Modal Analysis of First Test

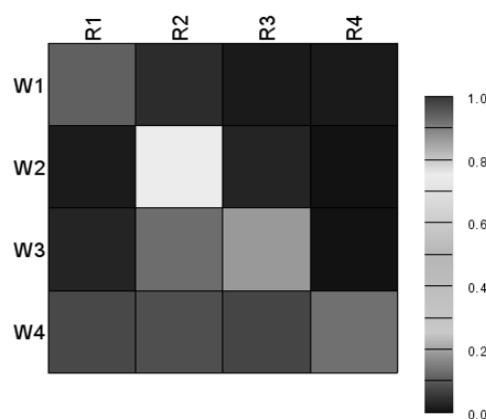


Figure 3.2 Correlation of Numerical Modal Analysis and Experimental Modal Analysis of Second Test.

The MAC plot for the first test as seen in Fig. 3.1, shows bad correlation due to the input of too many accelerometers which constricted the mobility of the structure preventing a free-free boundary condition environment. The number of knocking points set was also found to be a major problem as an abundance of knocking points can lead to high inaccuracy of results arising from human errors. Besides that, the geometry decimation of the first structure was unreliable as the

points selected were not connected to the main body of the structure where the isolated points are moving independently. Thus, for the second test results as seen in Fig. 3.2, the MAC plot was improved by reducing the number of accelerometers utilized, reducing the number of knocking points on the structure and fixing the geometry decimation to allow each point to act dependently on one another to show a better mode representation of the EMA test. In addition to that, a good MAC plot will show a diagonal of 1 and an off-diagonal of less than 0.1 [9].

Table 3.0 Correlation Results of Second Test

		Reference Modes (Hz)			
		R1	R2	R3	R4
Work Modes (Hz)		63.764	165.651	242.862	266.812
W1	82.574	0.943	0.036	0.011	0.011
W2	161.201	0.013	0.750	0.025	0.000
W3	217.575	0.024	0.124	0.863	0.000
W4	285.006	0.074	0.083	0.070	0.920

3.2 Optimization Results

Based on the utilization of Altair HyperWorks software, an optimized design can be obtained which outputs the best feasible design suitable for manufacturing and assembly in an air-conditioning outdoor unit. However, given the limited design space of the fan motor bracket top plate, there is only so much that optimization can do to change the design of the part to increase the stiffness without affecting the assembly configuration. The mass of the actual part was measured to be 179 grams using an electronic mass balance.

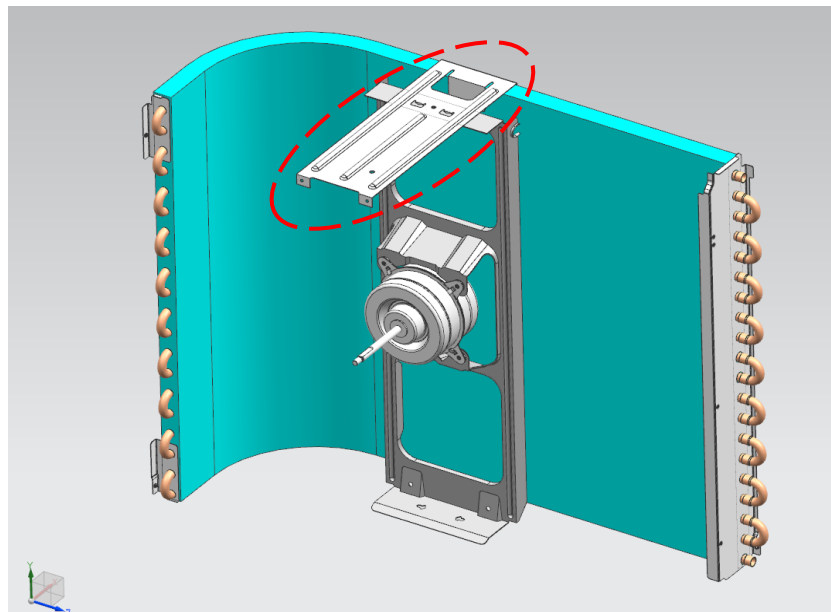


Figure 3.3 Assembly of Fan Motor Bracket Top Plate in an Outdoor Air-Conditioning Unit

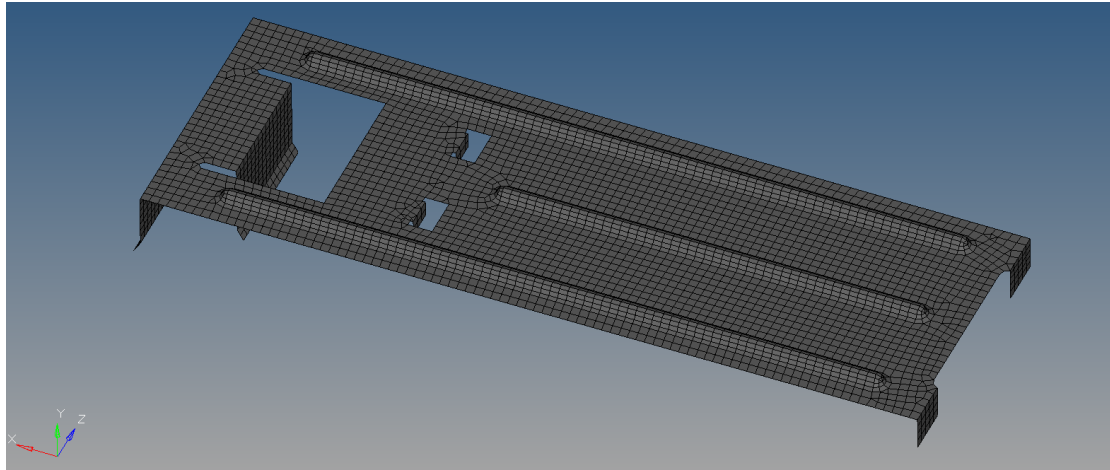


Figure 3.4 Original Design

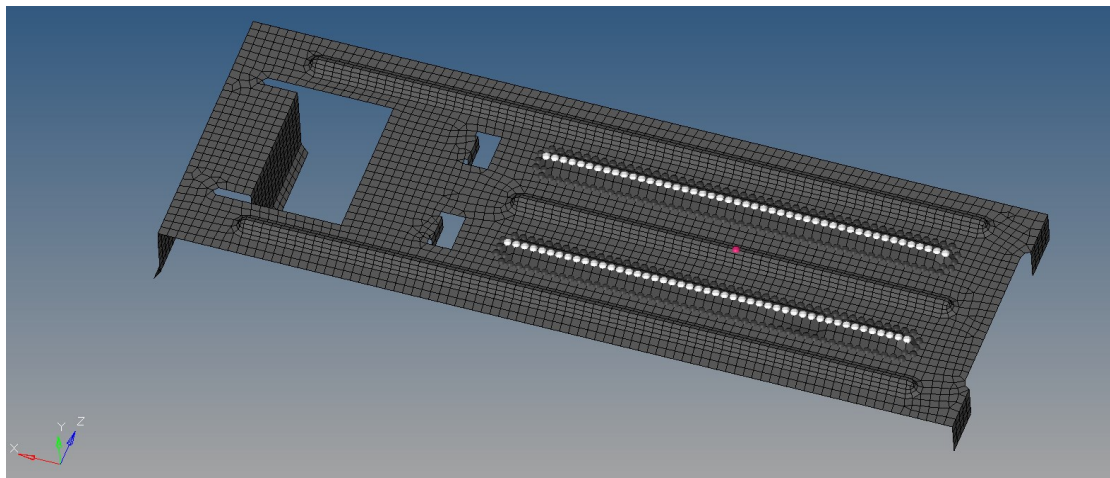


Figure 3.5 Optimal Design

As can be seen from the optimization result above, topography optimization was carried out where parametric bead variables require user input. The criteria required for the optimization procedure are the bead width, draw angle and draw height [16].

Table 4.0 Topography Bead Variables

Bead Width	Draw Angle	Draw Height
7mm	60°	3.5mm

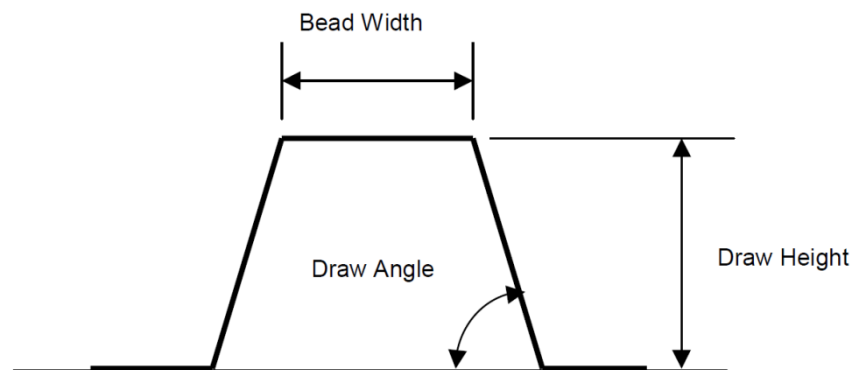


Figure 3.6 Parametric Bead Parameters

Table 5.0 Comparison of Stiffness between Original and Optimal Design

Mode	Original Design		Optimal Design	
	Frequency, (Hz)	Generalized Stiffness, (N/m)	Frequency, (Hz)	Generalized Stiffness, (N/m)
1	86.1	2.93E+05	95.7	3.62E+05
2	167	1.10E+06	169	1.13E+06
3	223	1.96E+06	229	2.06E+06
4	286	3.23E+06	295	3.43E+06

As seen from the table above, there is an increase of stiffness for each mode of the optimal design. The resonating frequency of the modes also increases proportionally with the stiffness. However, the results could only show a single optimal design given the constraints of the design space of the model part. The limited amount of design space is constricted based on the feasibility of manufacturing and company restrictions. Thus, topography optimization can only be carried out on a small portion of the plate. Besides that, the original design already contained bead stiffeners at the sides leaving a small amount of area to change the design of the plate. Hence, by utilizing the optimization module in Altair HyperWorks, the stiffness of the part model could be increased which in turn lowers the possibility of the part to resonate at lower frequencies. By doing so, experiencing vibration during transportation would not pose as a major issue for consumers anymore. Thus, topography optimization has proven its value by increasing product robustness. However, in the Altair HyperWorks software, there is no module to carry out the Design of Experiments procedure as compared to ANSYS. On the other hand, the validation of EMA and NMA using correlation tools has ensured that the actual model part being tested has similar material properties with the numerical model. Therefore, there is no need for an optimization validation in Altair HyperWorks.

4. Conclusions & Future Work

A complete EMA procedure was successfully performed on a fan motor bracket top plate with comparison to the prior study using FE modal analysis. The EMA procedure was performed on a fan motor bracket top plate within a frequency span of 1 Hz – 300 Hz following the ISO 13355:2001 for a random vibration test. As it can be seen, the results obtained from the experimental modal analysis shows a maximum of 30% frequency error when correlated with the numerical modal analysis data. However, in a real world application, the results of FEA can never be applied to consumer products as it is the simulation of a perfect world. Thus, errors are always present in physical testing. The correlation of both EMA and FE modal analysis shows a decent MAC plot but still lacking of accuracy and precision. The mode shapes produced from the EMA tests show close resemblance to the FE modal analysis results where the deformation of the structure is almost identical. The errors arising from EMA testing can be minimized by reducing the number of accelerometers used as well as the reduction of knocking points during testing. Besides that, preparation of a good TAM will also ensure a more accurate EMA test where accelerometer and knocking points are determined. In the near future, an optimization procedure will be carried out on the fan motor bracket top plate to

increase the stiffness of the structure to prevent cracking or yielding at lower frequencies. In other words, increasing the natural frequency of the model part where resonance occurs. By utilizing the Response Surface Methodology (RSM) and Design of Experiments (DOE), design parameters of the structure can be varied to determine the best parameter to increase the lifespan of the home appliance product [10]. On a side note, Altair HyperWorks will be utilized to perform the optimization procedure on the structure.

Acknowledgment

In the whole process of this research, the author would like to extend his gratitude to the General Manager of the Cost Management Department (CMD) in PAPARADMY1, Mr. Cheng Chee Mun for giving me the approval and opportunity to utilize the NX Nastran software and *Brüel & Kjær* equipment available at PAPARADMY1 and to the Deputy Director of PAPARADMY1, Mr. Low Seng Chok for the approval and distribution of the fan motor bracket top plate for testing.

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Optimization of Temperature and Velocity on Heat Transfer Enhancement of Non-Aqueous Alumina Nanofluid

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Abstract

Nanofluids have been a subject of intensive study since pioneering researchers have recently acknowledged its distinctive heat transfer properties which offer unprecedented potential for many future engineering applications. Although numerous researches have been performed in evaluation of the convective heat transfer enhancement of nanofluids, interaction between factors were neglected and optimization of factors affecting the convective heat transfer was never performed. Therefore in this investigation, a multifactorial design method, Design of Experiments (DOE) which takes into account of interaction between factors was adapted in evaluating the effects of temperature and velocity on heat transfer of 1% volume concentration EG-water (mass ratio 60:40) based alumina nanofluid. Besides, optimization of factors, temperature and velocity on the heat transfer enhancement was also performed using both experimental and analytical analysis. The experimental study was executed using a straight circular tube with a constant heat flux condition under laminar flow regime. The ranges of factors were determined at a temperature and velocity ranges of 15 °C to 35 °C and of 0.35 m/s to 0.75 m/s, with Nusselt number and Reynolds number as the corresponding responses. On the other hand, the analytical study was performed using Design Expert (version 7.0) on the basis of Central Composite Design (CCD) and Response Surface Methodology (RSM). Statistical analysis of variance (ANOVA) was also carried out to evaluate the significance of the obtained models. From experimental study and analytical analysis, the maximum heat transfer enhancement was recorded at values of 115.5% and 108.8% for heat transfer coefficient and Nusselt number, respectively. Consecutively, the optimum operating conditions to achieve the highest Nusselt and Reynolds number in the range of this study was determined at temperature of 35 °C and velocity of 0.6 m/s.

Keywords: Nanofluids, Forced convection, Heat transfer, Laminar flow, Optimization

1. Introduction

The unprecedented expansion of power consumption due to the exponential growth of technologies and industries in the recent years has made optimizing efficiency essential in many engineering design processes. Throughout the years, engineers and scientists have invested much effort in improving the productivity and efficiency of various engineering design processes such as the heat transfer process. Heat transfer process portrays a vital role in various fields of applications such as micro-electronics, refrigeration, cooling systems of nuclear power plants, biomedical applications and transportation [1]. However, the performance of heat transfer fluids such as water, ethylene glycol and mineral oils are often limited by their low thermal conductivities. Driven by the industrial needs of device miniaturization and process intensification, numerous methods have been attempted in the past few decades to improve the heat transfer characteristics of existing heat transfer fluids. One of the techniques in augmentation of the heat transfer characteristics is by introducing additives, particularly materials which possess high capabilities of heat transfer.

Initially, pioneering researchers such as Ahuja [2] and Hetsroni *et al.* [3] have performed the addition of micro and milli sized particles into existing heat transfer fluids and observed an improvement in heat transfer. However, these micro and milli sized particles bring major disadvantages. The suspended particles settles rapidly, forms a layer due to aggregation and after a certain period of time, rapidly cause a reduction in heat transfer capacity. Although this challenge can be resolved by increasing the circulation rate, the infliction of friction and erosion will then augment exponentially, causing irreversible damages to the heat exchange system. Moreover, these particles also have the tendency to clog flow channels and cause undesirable pressure drop in fluids [4]. Hence, further researches were performed to resolve the mentioned challenges and along with the advances in nanotechnology, the development of nanofluids was instigated.

Nanofluids are fluid suspensions consisting of the dispersion of nanometer-sized particles that possess attractive features such as a high surface to volume ratio, high mobility and lesser particle momentum as compared to micro and milli- fluids. When nanoparticles are adequately dispersed into a homogenized state, nanofluids contribute various advantageous characteristics such as a significant increase in heat transfer and stability, reduced risks of erosion and clogging and a reduction in pumping power [5]. The pathway of research and innovation in the field of nanofluids was initiated by Masuda *et al.* [6], which performed research of thermal conductivity and viscosity influence of various ultra-fine materials such as titanium dioxide, silicon dioxide and aluminum oxide in Japan. However, it was not until in 1995, where Choi [7] from the Argon National Laboratory (ANL) has conducted similar research in these ultra-fine particles and reported significant enhancement in thermal conductivity and heat transfer of the colloidal suspension. Choi and his colleagues have hence officially introduced and coined the term “nanofluids” for these suspensions.

As a consequence, the significant findings reported by Choi have sparked interests of numerous researchers in investigating the thermal conductivity and heat transfer characteristics of various types of nanofluids. In terms of the investigation of thermal conductivity, researchers such as Xuan and Li [8] have reported a significant enhancement of 55% with only 5% vol. fraction of copper based nanofluids in

transformer oil. Keblinski *et al.* [9] on the other hand has also observed an augmentation in thermal conductivity at a rate of 40% and 150% with a dispersion of only less than 1% vol. fraction of copper nanoparticles and carbon nanotubes (CNT) in ethylene glycol and oil respectively. Besides that, other researchers such as Lee *et al.* [10], Chandrasekar *et al.* [11], Das *et al.* [12], Li and Peterson [13], and Dehkordi *et al.* [14] have all reported similar agreement in the enhancement of thermal conductivity in nanofluids, hence validating the significant effects of nanoparticles in augmenting thermal conductivity.

On the other hand, in terms of heat transfer enhancement, Wen and Ding [15] studied the influence of the addition of alumina nanoparticles in deionized water flowing in a copper tube under laminar flow regime. The results indicated that the Nusselt number was enhanced up to 47% with 1.6% vol. fraction of nanoparticles. Lai *et al.* [16] also performed research on 1% vol. concentration of alumina nanofluids subjected to a constant wall heat flux at a Reynolds number of less than 270 and has reported a maximum enhancement of 8% in the Nusselt number. Besides that, Ding *et al.* [17] also reported notable convective heat transfer enhancement of multi-walled carbon nanotubes (MWCNT) with water as base fluid and have highlighted that the heat transfer enhancement depended on Reynolds number, nanoparticle concentration and pH. Similar agreement was also reported by Heyhat *et al.* [18] using water-based alumina nanofluid as the subject of study. Temperature dependence of convective heat transfer with alumina nanofluids in turbulent flow region under constant heat flux were also investigated by Kwon *et al.* [19] and have reported results of an increase in convective heat transfer coefficient from 14% to 30% as the temperature increased from 22 °C to 75 °C.

From these researches, it can be concluded that temperature and velocity are both significant parameters in influencing the heat transfer of nanofluids. Although numerous investigations were performed in evaluating the heat transfer performance, these studies were performed with the concept of “changing one factor at a time”. This technique is tedious and incapable of reaching the true optimum as interaction is not taken into account. Therefore in this present investigation, the interaction between factors and the optimization of heat transfer in terms of Nusselt and Reynolds number and the interaction between temperature and velocity on the enhancement of convective heat transfer of non-aqueous alumina nanofluids will be investigated and performed. The experimental analysis will be performed under a laminar flow regime inside a straight circular tube and under a constant heat flux boundary condition. On the other hand, the analytical analysis will be performed using Design of Experiments (DOE), which incorporates techniques of Central Composite Design (CCD) and Response Surface Methodology (RSM). By performing optimization, a maximum performance of heat transfer can be obtained. This is especially important when nanofluids are adapted in various fields of applications in the future such as heating, ventilation and air-conditioning (HVAC) systems and pressurized water reactor in nuclear reactors which are all operating in enormous scales. Therefore, a maximized performance of heat transfer will be desired in these systems to attain the highest effectiveness and ultimately resulting in a significant improvement in both cost efficiency and productivity.

2. Methodology

2.1 Preparation of Nanofluids

The nanoparticles chosen for this study were the commercially available γ -aluminum oxide (Al_2O_3) nanoparticles with an average size of 13 nm and a purity of 99.8% purchased from Sigma Aldrich. On the other hand, the base fluid selected was a mixture of ethylene glycol (EG) and distilled water with a mass ratio of 60:40, as this mixture is commonly used as the heat transfer fluid for heat exchangers, automobiles and building heating systems in cold regions (Alaska, Canada, Russia, etc.). Apart from base fluid and nanoparticles, an anionic surfactant, sodium dodecylbenzene sulfonate (SDBS) in technical grade was also purchased from Sigma Aldrich to enhance dispersion.

To prepare a stable and homogenous suspension of alumina nanofluids, the two-step method was adapted. The two-step method is a more affordable technique compared to one-step method and comprises of producing nanoparticles first before dispersing them into a suitable liquid host [20]. To begin, ethylene glycol and water was initially added with a mass ratio of 60:40 and stirred via a magnetic stirrer for an approximate period of 10 minutes. Next, SDBS was added into the mixture with an equal amount of mass used for nanoparticles. Again, the suspension was stirred with a magnetic stirrer for about 15 minutes to ensure homogeneity. According to Dehkordi *et al.* [14], SDBS has shown fair results in dispersing alumina nanoparticles without influencing the thermal conductivity and viscosity of the suspension. Upon achieving a homogenous mixture, alumina nanoparticles of 1% vol. concentration was added to the suspension. The colloidal suspension of inhomogeneous nanofluids was then ultrasonicated for exactly 90 minutes with an ultrasonic bath by Branson (Model 3210 R-MT) with a 40 kHz ultrasonic frequency and power of 350 W. Ultrasonication has the ability of enhancing the dispersion of agglomerated nanoparticles, hence significantly increasing the stability of the suspension. In accordance to Dehkordi [4], 90 minutes of ultrasonication is determined as the optimum ultrasonication time. Alumina nanofluids prepared were found to be stable over a period of more than one week without any observable sedimentation.

2.2 Measurement of Thermal Conductivity and Viscosity of Nanofluids

2.2.1 Thermal Conductivity of Nanofluids

Next, the thermal conductivities of alumina nanofluid at a temperature range of 15 °C to 35 °C were measured using a KD2 Pro Thermal Properties Analyzer by Decagon Devices which measures thermal conductivity based on the transient hot wire (THW) method. Transient hot wire method is determined as one of the most robust and reliable techniques for the determination of thermal conductivity in nanofluids and was utilized by various researchers such as Dehkordi *et al.*, Wen and Ding, Ghadimi, Patel *et al.*, and Halefadi *et al.* [14, 15, 21, 22, 23]. A total of 5 readings of thermal conductivities at an average of 15-minute interval was recorded for each temperature measurement and was averaged out to minimize error and ensure data reproducibility. The uncertainty of the measurements of thermal conductivity was within 5% under the conditions of this work. In order to regulate the temperature of the suspension, a

refrigerated bath circulator manufactured by WiseCircu with an accuracy of ± 0.1 °C was used. The results obtained are shown in Fig. 1, where it was observed that thermal conductivity increases almost linearly with the rise of temperature. As the preparation technique of nanofluid was performed in accordance to the works of Dehkordi [4], the results were compared with the results of Dehkordi as well as ASHRAE data [24]. Results have shown comparatively lower but good agreement of results with Dehkordi, with a maximum discrepancy of 3.75% at 30 °C. On the other hand, the experimental thermal conductivity was found to be relatively higher than ASHRAE data, where the highest discrepancy was recorded as 2.24% at 20 °C.

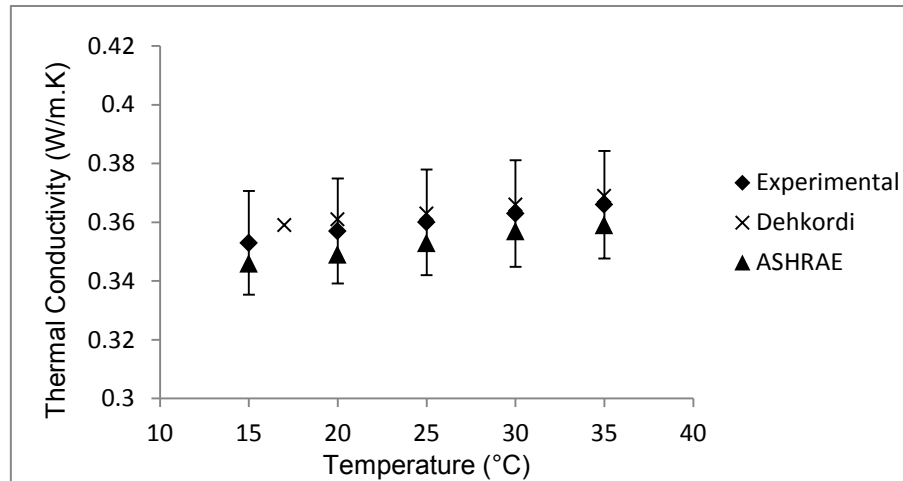


Figure 1. Effects of temperature on the thermal conductivity of alumina nanofluids

2.2.2 Viscosity of Nanofluids

The viscosity of alumina nanofluids were also measured at the mentioned temperature range of 15 °C to 35 °C by using a Vibro Viscometer by A&D Company (Model SV-10) with an uncertainty of $\pm 3\%$. The regulation of temperature was also performed by using the same bath circulator manufactured by WiseCircu. The results obtained are shown in Fig. 2, where it was observed that the viscosity of alumina nanofluids decreases with increasing fluid temperature.

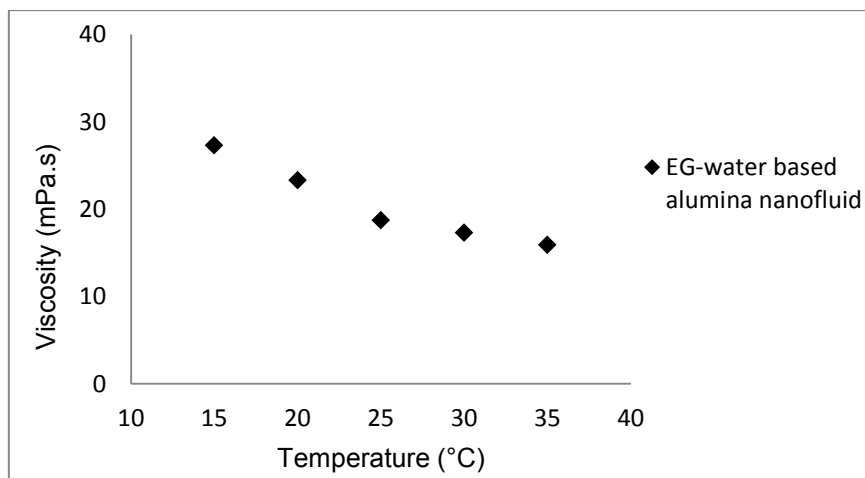


Figure 2. Viscosity of alumina nanofluids as a function of temperature

2.3 Experimental System

The experimental system constructed to measure convective heat transfer coefficient is shown in Fig. 3. The experimental loop consists of a nanofluid reservoir tank, a peristaltic pump, a heat transfer section, a data acquisition system, a cooling system and lastly a DC power supply. The peristaltic pump used for this investigation was manufactured by Longerpump (Model BT600-2J) with an attachable pump head (Model YZ1515x) and a rotating diameter of 0.056 m with adjustable rotating speed. The heat transfer section on the other hand consists of a copper tube of 1.54 m in length and 3.53 mm in inner diameter. Four K-type thermocouples with a precision of 0.1 °C were mounted on the heating section along the copper tube at axial positions from T_1 to T_4 of 78 mm, 443 mm, 689 mm and 1191 mm, respectively from the inlet in order to measure wall temperature distribution. Two K-type thermocouples (T_{in} and T_{out}) were also installed at the inlet and outlet of the test section to measure bulk temperature. The heating section was heated with a silicon rubber flexible heater linked to a DC power supply with a maximum power of 90W manufactured by Watlow Electronics. In order to obtain a constant heat flux condition, the copper tube was insulated with a thick thermal isolating layer to minimize heat loss. Lastly, the inlet temperature of the heating section was manipulated by using a cooling system consisting of a thermal water bath and a heat exchanger. The range of temperature and velocity performed in this experiment falls from 15 °C to 35 °C and from 0.35 m/s to 0.75 m/s, respectively due to experimental limitations. The experiment was carried out according to a set of runs determined by the design matrix generated by Design of Experiments software and all the data collected for the experiment were logged using a Graphtec data logger.

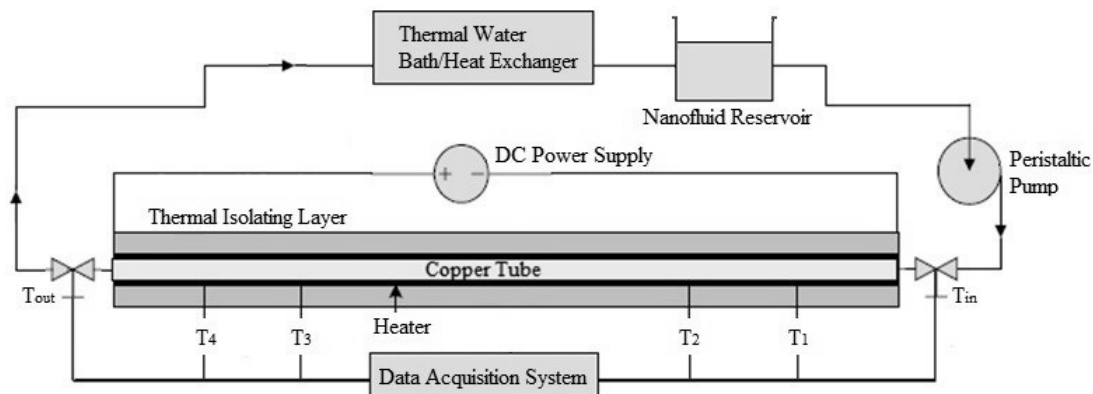


Figure 3. Schematic diagram of experimental setup

2.3.1 Calibration of Experimental Setup

Prior to the experiment, calibration was performed in order to evaluate the accuracy and reliability of the experimental system. The experimental setup was tested using deionized water as the working fluid and the obtained results were evaluated with the predictions of the well-known Shah equation under the state of constant heat flux and laminar flow regime [25]:

$$Nu \begin{cases} 1.953(RePr \frac{D}{x})^{1/3} & (RePr \frac{D}{x}) \geq 33.3 \\ 4.364 + 0.0722RePr \frac{D}{x} & (RePr \frac{D}{x}) < 33.3 \end{cases} \quad (1)$$

The comparison of the heat transfer coefficient between measured data and Shah equation is presented in Fig. 4, where the experiment was performed at $Re = 1157$.

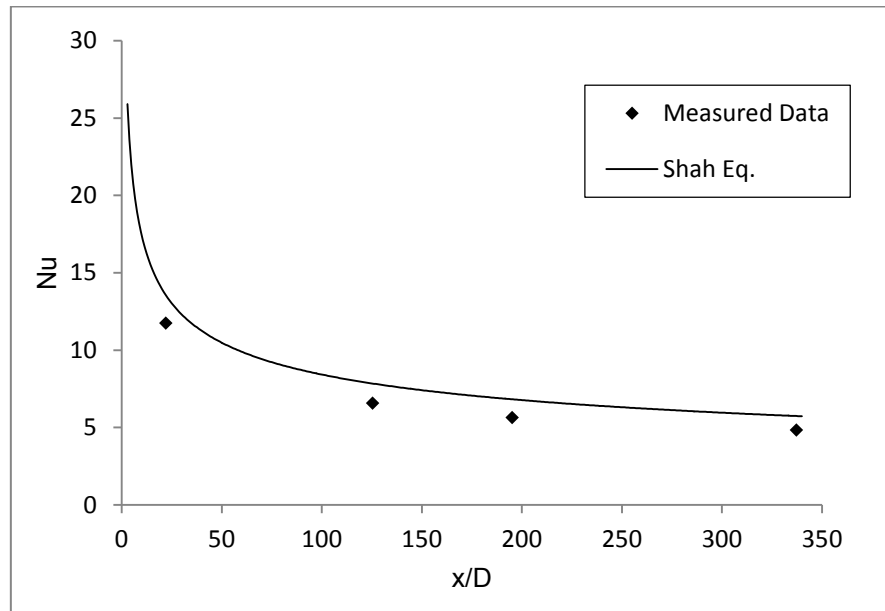


Figure 4. Comparison of heat transfer coefficient between measured data and Shah equation at $Re = 1157$ using deionized water

From Fig. 4, a reasonably good agreement was observed between measured data and Shah equation, with a maximum deviation of 16% observed at $x = 78mm$. The reason for this deviation may be due to the difference in tube sizing, as Shah equation was formulated on the basis of large channel tubes, but the copper tube used in this experiment is much smaller in comparison [15, 25].

2.4 Data Processing

Once sufficient data was collected from the experiment, the calculation of heat transfer coefficient, Nusselt number and Reynolds number were performed. Initially, convective heat transfer coefficient was calculated by following the Newton's law of cooling equation as:

$$h = \frac{q''}{T_{out} - T_{in}} \quad (2)$$

Parameters involved in calculation of Eq.2 include q'' , T_{out} and T_{in} which represent heat flux, outlet temperature and inlet temperature, respectively. Heat flux used throughout the experiment remains constant at a constant supply of power at 67.5W. With the convective heat transfer coefficient obtained, the representative dimensionless group of heat transfer, the Nusselt number was determined by:

$$Nu = \frac{hD}{k} \quad (3)$$

In this equation, parameters D and k denote the inner diameter of copper tube and thermal conductivity of alumina nanofluid, respectively. Lastly, Reynolds number was also calculated by:

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

Parameters ρ , V , and μ in this equation constitutes to the density of alumina nanofluid, velocity of fluid flow and viscosity of alumina nanofluid, respectively. Upon obtaining the heat transfer coefficient, Nusselt number and Reynolds number, optimization using Design of Experiments was then performed.

2.5 Optimization using Design of Experiments

The Design Expert (version 7.0) software was used to perform the statistical design of experiments and data analysis. In this investigation, a five level two factor central composite design (CCD) and Response Surface Methodology (RSM) were utilized to optimize the two operating variables: temperature and velocity. The ranges of variables were as mentioned earlier at ranges of 15 °C to 35 °C and from 0.35 m/s to 0.75 m/s. On the other hand, the responses were determined as Nusselt number and Reynolds number.

Consecutively, analysis of variance (ANOVA) was performed to evaluate the adequacy of the mathematical models. ANOVA determines which factors or interactions between factors have a significant effect on the responses by using Fisher's statistical tests (F-test). Effects calculated using ANOVA that falls below a confidence level of 95% was discarded to improve regression model. In contrary, effects which exceed the confidence level of 95% were considered significant. Once the model was validated, the relationships between the factors and the corresponding responses will be graphically illustrated as a 3D response surface plot using RSM in order to obtain the exact optimum values of parameters.

3. Results and Discussion

3.1 Average Convective Heat Transfer of Alumina Nanofluids

Upon calibration of experimental setup, the experiment was performed to determine the average convective heat transfer, Nusselt number and Reynolds number of alumina nanofluids. The results obtained were tabulated in Table 1, where the runs of the experiment were randomized in order to minimize the error of uncontrollable factors.

Table 1. Experimental results in accordance to the random runs randomized by CCD

Runs	T _{in} (°C)	T _{out} (°C)	Velocity (m/s)	h (W/m ² K)	Nusselt No.	Reynolds No.
8	25	33	0.65	493.4	4.72	136.0
3	15	22.9	0.75	499.7	4.89	107.5
13	25	33.6	0.55	459.0	4.39	115.0
11	25	33.8	0.55	448.6	4.29	115.0
1	15	26.6	0.35	340.3	3.33	50.1
6	30	38.3	0.55	475.6	4.50	124.3
5	20	29.4	0.55	419.9	4.06	92.3
12	25	33.7	0.55	453.7	4.34	115.0
4	35	41.5	0.75	607.3	5.67	184.5
7	25	34.2	0.45	429.0	4.10	94.1
9	25	33.7	0.55	453.7	4.34	207.3
2	35	44.7	0.35	406.9	3.80	86.1
10	25	33.7	0.55	453.7	4.34	207.3

From the experimental data tabulated in Table 1, a design matrix was then generated using CCD with factors of temperature and velocity in both coded and actual values, and their respective responses of Nusselt and Reynolds number. The design matrix comprises of 4 factorial points, 4 axial points and 5 replications of center point as illustrated in Table 2. The objective of the replications of center points (Runs 13, 11, 12, 9 and 10) is to obtain a good estimation of experimental errors.

Table 2. Design matrix generated using CCD of variables temperature and velocity and respective responses of Nusselt and Reynolds number

Run	Factor A Temperature (°C) (Coded Value)	Factor B Velocity (m/s) (Coded Value)	Response 1 Nusselt Number	Response 2 Reynolds Number
8	25 (0)	0.65 (+0.5)	4.72	136.0
3	15 (-1)	0.75 (+1)	4.89	107.5
13	25 (0)	0.55 (0)	4.39	115.0
11	25 (0)	0.55 (0)	4.29	115.0
1	15 (-1)	0.35 (-1)	3.33	50.1
6	30 (+0.5)	0.55 (0)	4.50	124.3
5	20 (-0.5)	0.55 (0)	4.06	92.3
12	25 (0)	0.55 (0)	4.34	115.0
4	35 (+1)	0.75 (+1)	2.97	184.5

7	25 (0)	0.45 (-0.5)	4.10	94.1
9	25 (0)	0.55 (0)	4.34	115.0
2	35 (+1)	0.35 (-1)	3.80	86.1
10	25 (0)	0.55 (0)	4.34	115.0

Two quadratic polynomial equations for Nusselt and Reynolds number in accordance to the design matrix generated by CCD were developed to fit the experimental data using response surface methodology and are as shown respectively below in terms of coded factors:

$$\text{Nusselt No.} = 4.33 + 0.44A + 0.62B + 0.077AB - 0.22A^2 + 0.3B^2 + 0.24A^2B - 0.13AB^2 \quad (5)$$

$$\text{Reynolds No.} = 114 + 28.67A + 39.28B + 10.25AB - 17.06A^2 + 9.94B^2 \quad (6)$$

In both the equations, parameters A and B represent temperature and velocity, respectively. With the equations generated, analysis of variance (ANOVA) was then performed to determine the significance and to assess the “goodness of fit” for both the equations. Table 3 illustrates the results and evaluation of ANOVA performed on both Eq. 5 and Eq. 6.

Table 3. Statistical analysis of variance (ANOVA) for responses of Nusselt number and Reynolds number

Source	p-value, Prob. > F	
	Nusselt Number	Reynolds Number
Model	< 0.0001, significant	< 0.0001, significant
Factor A: Temperature	0.0002	< 0.0001
Factor B: Velocity	< 0.0001	< 0.0001
AB	0.0046	< 0.0001
A ²	0.0197	0.0025
B ²	0.0054	0.0315
A ² B	0.0042	eliminated
AB ²	0.0444	eliminated
Lack of fit	0.1654, not significant	not significant
R-squared	0.9986	0.9979
Adjusted R-squared	0.9967	0.9964
Predicted R-squared	0.9664	0.9620
Adequate precision	93.681	109.238

Referring to Table 3, it can be observed that both the models of Nusselt and Reynolds number were significant with p-values of less than 0.0001 (p-value < 0.05 is the indication of significance of model for 95% confidence intervals). The factors of temperature and velocity and their interaction effects (AB) were found to be highly significant for both models, as their p-values were all less than 0.0001. Besides that, the second-order effects (A² and B²) of both the models were also found significant. Lastly, the A²B and AB² factors were found significant for Nusselt number and insignificant for Reynolds number. All the insignificant factors will then be discarded in order to improve the regression model and optimization results. The lack of fit,

which describes the variation of data around the fitted model, is not significant for both the responses. This implies that the model is fitted well to all data. On the other hand, an R-squared value of close to 1 and a reasonable agreement between predicted R-squared and adjusted R-squared is desirable. For both models, both the criteria were achieved, indicating a satisfactory adjustment of quadratic model to experimental data. Lastly, adequate precision of greater than 4 represents adequate model discrimination, which was achieved by both equations of Nusselt and Reynolds number.

Upon validating both the models, two three dimensional graphs were plotted based on the mathematical models using Response Surface Methodology (RSM) to evaluate the effects of temperature and velocity. As seen in the figures, both the Nusselt and Reynolds number increases when the values of temperature and velocity increase. The optimum operating conditions for temperature and velocity to operate in order to deliver the highest values of Nusselt and Reynolds number according to Fig. 5 and Fig. 6 is at 35 °C and at 0.75 m/s. The maximum values of Nusselt and Reynolds number were predicted at 5.67 and 184.5, respectively. The obtain results have shown reasonable agreement from researchers such as Ding *et al.* [17], Heyhat *et al.* [18] and Kwon *et al.* [19] on the effects of temperature and velocity on the Nusselt number.

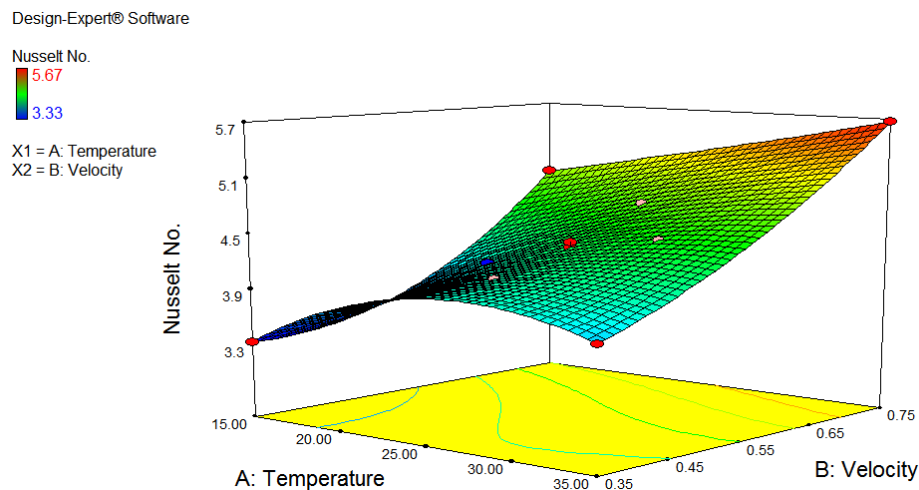


Figure 5. Response surface plot in the studied range of variables for Nusselt number

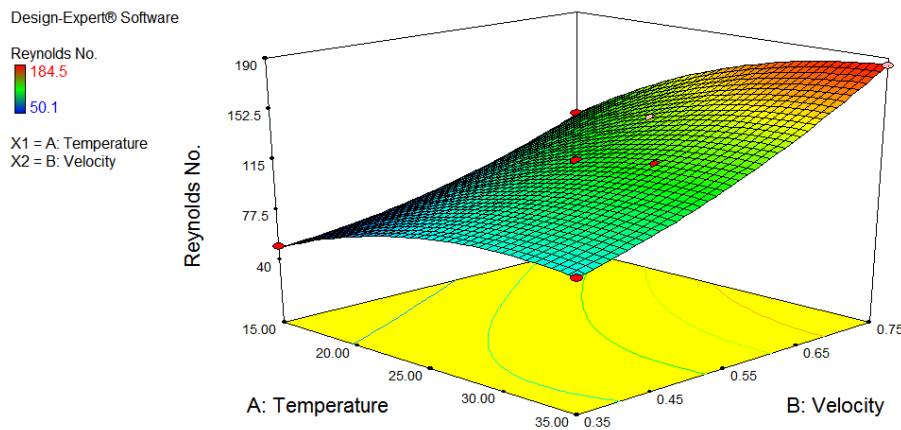


Figure 6. Response surface plot in the studied range of variables for Reynolds number

3.2 Convective Heat Transfer Enhancement

In order to evaluate the convective heat transfer enhancement of alumina nanofluids, the convective heat transfer coefficient and the Nusselt number of base fluids were firstly determined. The convective heat transfer coefficient and Nusselt number were compared on the basis of Reynolds number; hence the Reynolds numbers obtained from Table 1 were adapted. The reason for the comparison being done under the same Reynolds number instead of velocity is that Reynolds number takes the viscosity effects of the fluid into account, therefore providing a more realistic and higher accuracy of results. The repetitions of the center point previously done were excluded as CCD and RSM methods were not used in evaluating the heat transfer enhancement. Table 4 below depicts the results obtained from the experiment performed using base fluids.

Table 4. Experimental results of base fluids based on similar Reynolds numbers

No.	T _{in} (°C)	T _{out} (°C)	Reynolds No.	Velocity (m/s)	h (W/m ² K)	Nusselt No.
1	25	37.8	136	0.24	308.4	3.02
2	15	27.9	107.5	0.28	306.0	3.06
3	25	39.1	115	0.20	279.9	2.75
4	15	38.4	50.1	0.13	168.7	1.69
5	30	44.4	124.3	0.19	274.1	2.67
6	20	33.8	92.3	0.21	286.0	2.83
7	35	46.3	184.5	0.24	349.3	3.37
8	25	41.1	94.1	0.16	245.2	2.40
9	35	55.9	86.1	0.11	188.9	1.82

From the results obtained, the heat transfer enhancement of alumina nanofluids were then determined in terms of percentage in enhancement of convective heat transfer coefficient and Nusselt number, respectively. The results were illustrated in Table 5.

Table 5. Heat transfer enhancement of alumina nanofluids at varying temperature and velocity

No.	T _{in} (°C)	Reynolds No.	h_{nf} (W/m ² K)	h_{bf} (W/m ² K)	h (%)	Nu_{nf}	Nu_{bf}	Nu (%)
1	25	136	493.4	308.4	60.0	4.72	3.02	56.3
2	15	107.5	499.7	306.0	63.3	4.89	3.06	59.8
3	25	115	453.7	278.0	62.1	4.34	2.75	57.8
4	15	50.1	340.3	168.7	101.7	3.33	1.69	97.0
5	30	124.3	475.6	274.1	73.5	4.50	2.67	68.5
6	20	92.3	419.9	286.0	46.8	4.06	2.83	43.5
7	35	184.5	607.3	349.3	73.8	5.67	3.37	68.3
8	25	94.1	429.0	245.2	75.0	4.10	2.40	70.8
9	35	86.1	406.9	188.9	115.5	3.80	1.82	108.8

As seen in Table 5, the enhancement of convective heat transfer coefficient ranges from 46.8% to 115.5%, whereas the enhancement of Nusselt number ranges from 43.5% to 108.8%. The maximum heat transfer enhancement of alumina nanofluids were both observed at a temperature and Reynolds number of 35 °C and 86.1, respectively. This enhancement percentage reported is significantly higher as compared to the results of previous researchers such as Wen and Ding [15], Lai *et al.* [16] and Kwon *et al.* [19] who performed alumina nanofluids at different temperatures, concentrations and Reynolds numbers. From the results, it can be concluded that the interaction effects plays a significant role in influencing the heat transfer characteristics of alumina nanofluid and should not be neglected.

3.3 Optimization on Heat Transfer Enhancement

Upon determining the heat transfer enhancement of alumina nanofluids, optimization in order to investigate the optimum operating conditions was performed. Optimization is a process that determines the optimum desirability depending on the boundary conditions, or “goals” set for each of the factors and responses. In the present investigation, the goal for temperature was set to “in range”, where it means that temperature is desirable at any point. On the other hand, the goal for velocity was set to “minimize”, whereas the goals for Nusselt and Reynolds number were set to “maximize”. The main reason why velocity was limited to a minimum value is because as the velocity increases, the pumping power required in pumping nanofluid will also augment, ultimately increasing the operational cost and thus deemed undesirable. Upon setting the boundary conditions, the 3D desirability plot and contour plot were then generated using RSM as seen in Fig. 7 and Fig. 8, respectively.

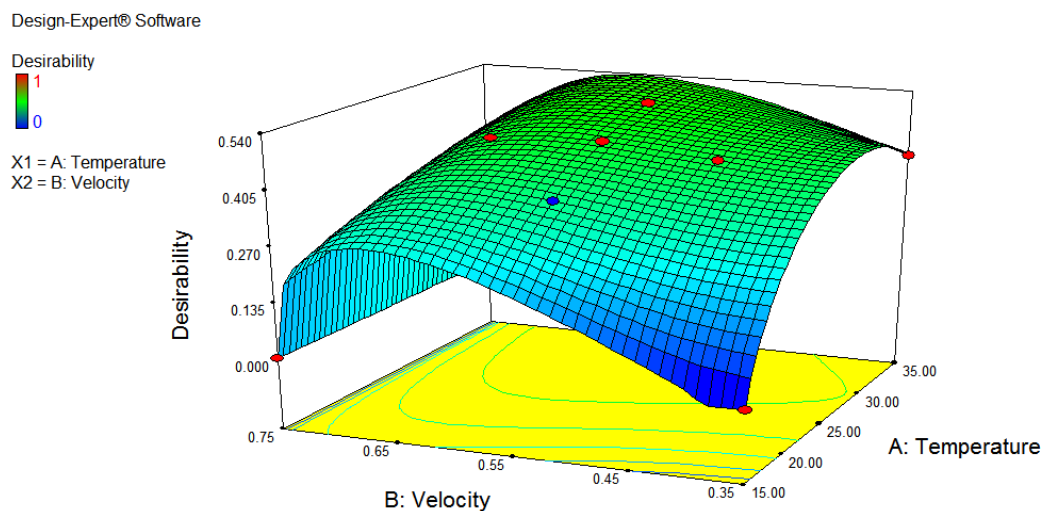


Figure 7. 3D desirability plot for optimum heat transfer enhancement of alumina nanofluids

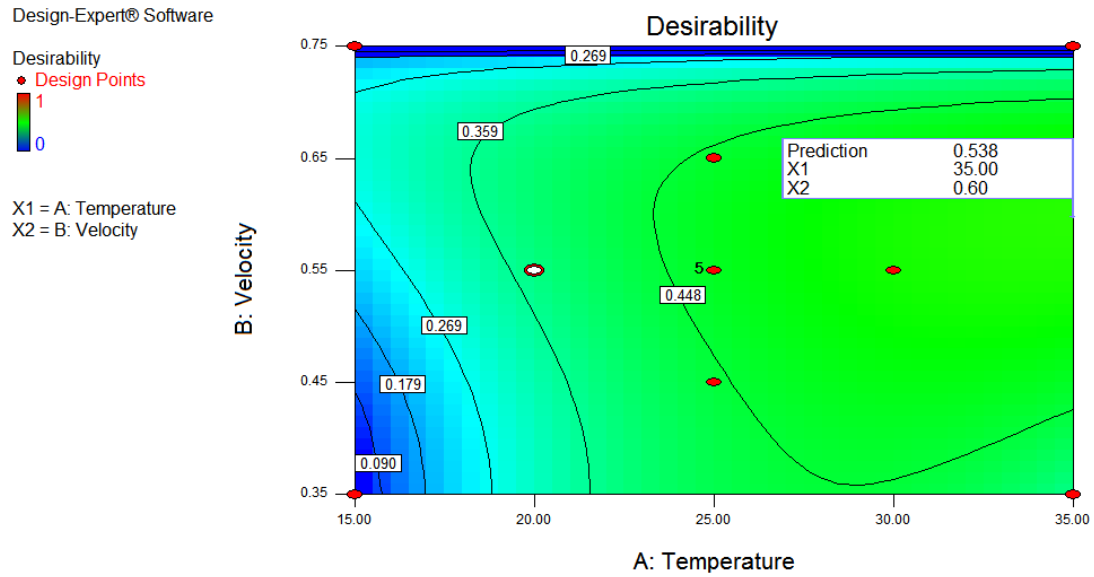


Figure 8. Contour plot for optimum heat transfer enhancement of alumina nanofluids

As seen in the figures, the highest desirability was determined at a value of 0.538 at the temperature and velocity of 35 °C and 0.60 m/s, respectively. In order to evaluate the accuracy of the prediction, the experiment was re-performed with alumina nanofluids at the mentioned parameters in order to determine the uncertainty. Table 6 illustrates the predicted desirable points, experimental results and the uncertainty of the prediction.

Table 6. The evaluation of goals and predicted points for corresponding factors and responses of alumina nanofluid

Factor / Response	Goal	Lower Limit	Upper Limit	Desirable point predicted	Experimental Data	Error (%)
Temperature	In range	15	35	35	35	-
Velocity	Minimize	0.35	0.75	0.6	0.60	-
Nusselt No.	Maximize	3.33	5.67	4.8	4.74	1.27
Reynolds No.	Maximize	50.1	184.5	138.6	138.6	-

The results obtained in Table 6 shows that the modeling and optimization performed in this investigation were able to predict the aforementioned conditions of nanofluid successfully up to an accuracy of 1.27%. Therefore, it can be concluded that all the results obtained were deemed adequate and accurate, and the optimum operating condition in accordance to the desired goals falls at a temperature and velocity values of 35 °C and 0.6 m/s, respectively.

4. Conclusions

This investigation is concerned with the optimization of temperature and velocity on the heat transfer enhancement on non-aqueous alumina nanofluid using both experimental and analytical techniques. In terms of experimental study, the investigation was performed with nanofluids flowing through a circular copper tube under a constant heat flux condition and a laminar flow regime. The experiment was performed according to the design matrix generated using Design Expert (version 7.0) with varying ranges of temperature from 15 °C to 35 °C and velocity of 0.35 m/s to 0.75 m/s. Nusselt number and Reynolds number were chosen as responses. In terms of analytical techniques, Central Composite Design (CCD) and Response Surface Methodology (RSM) were applied. Statistical analysis of variance (ANOVA) was also performed in order to evaluate the significance of models created.

In conclusion, a stable suspension of 1% alumina nanofluid was prepared and was observed to be stable for more than a week. Thermal conductivities and viscosities of alumina nanofluid were measured at different temperatures and have achieved good agreement of results with Dehkordi. On the other hand, the heat transfer enhancement of alumina nanofluids was evaluated by using CCD and RSM, where the highest heat transfer coefficient and Nusselt number was determined at values of 607.3 W/m²K and 5.67, respectively at the temperature and velocity of 35 °C and 0.75 m/s. From ANOVA, the interaction effects between temperature and velocity was found to be significantly high in influencing the heat transfer enhancement of alumina nanofluids. The maximum heat transfer enhancement was recorded at a value of 115.5% for heat transfer coefficient and 108.8% for Nusselt number, which are both significantly higher than the results reported by previous researchers, hence further proving the significance of the interaction effects between temperature and velocity. Optimization was performed to determine the optimum desired operating conditions, where factors temperature and velocity were set to “in range” and “minimize”, respectively and the goal of both the responses of Nusselt and Reynolds number were set to “maximize”. Results have shown that the optimum operating condition in accordance to the desired goals as mentioned is at a temperature of 35 °C and a velocity of 0.6 m/s. Lastly, error analysis was performed and an uncertainty of 1.27% was determined, hence validating the modeling and optimization performed in this investigation.

Future work beyond this study would be to resolve the instability of nanofluids after a certain period of time. Although nanofluids are able to maintain stability throughout the experiments performed, long-term stability remains a challenge for nanofluids and this is one of the major hurdles that remains nanofluids from widely commercialized in industries. Therefore in the future, research can be performed to propose an alternative preparation method which has the ability to exceed the stability of nanofluids produced using both one and two step methods. Another recommendation of future would be to perform multifactorial design method and optimization on other factors influencing heat transfer properties of nanofluids such as concentration, particle size, etc. As reported in this investigation, the interaction effect between temperature and velocity on the heat transfer enhancement was significant and the enhancement results were found to be significantly higher than previous researches. Therefore, using multifactorial design method and optimization of other factors should also be considered to evaluate the interaction effects and optimum operating conditions in order to achieve the highest productivity and cost efficiency in a heat transfer system.

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Personalized Learning in the Engineering Curriculum: Web-based Approach

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Abstract

Field of engineering is one of the toughest field of studies and students often do not enjoy every subject provided in this course. Each person might have their own unique learning styles and personality traits. By taking this information about those students and learning about their personalities and intelligence types, it would be easier to grasp their interest towards a particular subject; by providing personalized learning to them. In order to do this, firstly a subject which students would find both uninteresting and more challenging in the engineering curriculum had to be found to work with. This subject had to also be of important value in the industry. After going through different surveys done by Taylor's University's School of Engineering students over this matter, the subject of Mechanical Vibration was chosen to work with in its 2014 August intake. After much research on different personalized learning techniques, Howard Gardner's Theory of Multiple Intelligences which divides learners into 7 different groups was chosen to be worked with. Mainly for two reasons; firstly that it covers different type of learners and when the focus is put on one particular group out of the seven, the results can be more accurate and effective and secondly because no research of this method has been done on core engineering subjects in the mechanical engineering curriculum before to the knowledge of the authors. A keynote to be discussed is that this project focuses on a web-based approach to personalized learning. This is done to evaluate the results to see if a positive outcome is achieved and hence if the same model could be applicable for other learning groups and hence on a bigger scale throughout all engineering schools. The personalized learning took place for couple of group of learners with positive feedback which shows this kind of web-approach interaction could be achievable with students if the needed resources are funded and applied.

Keywords: Personalized Learning, Engineering Curriculum, Education, Learning Styles, Multiple Intelligences.

1. Introduction

One of the main missions in education as a whole is to educate students in a good competent manner in which the student themselves take interest in particular subjects. This holds true in all bases of education and the engineering curriculum is no different than others. Therefore one of the main focuses in the engineering curriculum must always remain to be educating competent engineers who would be able to apply their knowledge truly well in the industry and are also able to adapt to technological advances. With the advancement of technology in recent years and the youth's dependency on them, such as computers and tablets, the question permits that would it be possible to relate their learning process with use of our current technology in a web-based approach? Furthermore, how could this learning process be more effective than the current methods carried out in engineering schools around the world. That is why this project focuses on personalized learning through a web-based approach. The question that remains to be answered is, can personalized learning be delivered effectively through a web-based approach in the engineering curriculum? In order to answer that question, it is initially crucial for one to clearly have a grasp of what personalized learning is and what it provides to the students rather than the regular learning methods currently being carried out.

Not only in the School of Engineering, but every classroom in every course at all universities and even on school level consists of more than a few inattentive students who do not find the class or the subjects being taught interesting or compelling. This leads to them being often bored and wondered in the classroom meaning a struggle lies ahead for the lecturer of that particular to grab their interest and have their attention. This does not necessarily has to do with how good or bad the lecturer presents the class and what subject it is, but more so with all the different personalities the lecturer has to deal with.

The lecturer could present the material in an organized and articulate fashion, but that still wouldn't guarantee the full attention of all students. A scenario like this could lead to several different outcomes. Of course it is still possible for students to review the subjects taught before the exams take place and practice on their problem solving skills. Having said that, these kind of practices are not ones that produce competent engineers for the industry or educational matters later in their career. Hence even if the results do not backfire in the exams and students are able to score well in them with the right techniques, it would not be considered as a successful educating process as it is only a temporary way to fix things and students have not undergone a learning process in which they were driven by their own interest towards the subject to have a complete grasp over the particular subject and completely gain intellectual knowledge over the said subject. This is where personalized learning can come into action to help with the process.

One of the main reasons to this problem is that many educators are mostly professionals with degrees in their own profession and have had limited training in teaching practices. According to J. Holvikivi [1] engineering educators and those who teach it to aspiring future engineers are mostly professional engineer and scientists that have mastered their profession and its demands in the engineering curriculum but only have a very light training in educational sciences. They are well

aware of their own field of science but not entirely familiar with behavioral sciences and their didactic methods are often superficial. This is considerably more important in case of engineering education due to a more challenging multidisciplinary field and difference in epistemological views of learning sciences. So a challenge lies ahead for the educators to reach out to their students. A challenge which could be tackled by implementing a successful plan in shape of personalized learning for students. This project focuses on different methods of personalized learning processes and different profiles of learners by conducting different surveys and delivering the right tools for a better learning environment. It focuses on how to reduce this lack of inter-disciplinary understanding by learning more about the students which in return would help for an improved communication that eventually leads to didactic methods in engineering.

Different students have their own unique learning styles and personality, but it is important to find out what the common learning methods that would be interesting to the majority and different groups of students are; for the sake of delivery of that specific module or topic to them according to their learning abilities. Some students might initially be interested in certain fields of physics or chemistry, but teaching and learning methods play a big role in their pursuit of maintaining that interest as well as understanding those certain fields. It is crucial for the right methods to be chosen, because if not, it might be an initiative to drive these students away from the particular subject and perhaps the field as a whole. So it is important to firstly learn about students, their characters and their unique learning styles and deliver the educational knowledge according to their learning abilities, hence delivering personalized learning. According to a research paper done by N. Orhun [2] it is conducted that being aware of different learning styles would provide a better engineering educational experience for the students as well as helping instructors to relate and understand their students better. But it remains to be answered in what ways the instructors could reach out to the students and in what manner they could deliver their educational knowledge to them.

While different kind of books and indoor classroom activities specific to students' learning abilities are methods used for personalized learning, a web-based approach in some fields of study have shown to be a very useful learning method and with the right implementation, can be considered as the perfect method of delivery for personalized learning. In recent history, e-Learning has become a very active field of research with huge investments from around the world in it. [3] E-Learning represents the web-based delivery of contents which links the learners with the instructors. E-Learning is not specific to one type of teaching and supports different manners of learning. Not only that, but sometimes it becomes the only possible method of learning where there is absence of teacher or the student due to different reasons. In this case it is mainly important since it can be used for instructors to apply different personal teaching approaches and students to implement personal studying approaches.

According to Gilbert and Han [4] a traditional classroom consists of a single instructor and several learners which is a one-to-many relationship. Instructors may present the information at hand with their own personal style of learning or instructing which might not be suitable for every student. So this is where the method of "learning styles" can be carried out for better results. In Kolb's famous and old method of "learning styles" there are different kind of learners. In D. Kolb's research

for effectiveness of these styles [5] learners are put in 4 different groups of learners; Accommodators who feel and do. Divergers who learn by feeling and watching. Convergers whose learning style is by thinking and doing and lastly assimilators whose style is mostly thinking and watching. Also in a research done by Kuri, [6] it states that students have a broad range of learning preferences and vary in their performance in the courses they take which feature different teaching approaches. Lecturers usually use different methods and techniques to reach out to their students for this matter. Factors affecting engineering students' performance in a course are related to how their learning preferences fit with the teaching styles provided for them. Learning styles is also affected by the students' method of studying the learning materials. Based on this method and its findings, a research was conducted by N. Caligtary [7] which is directly related to learning style. Based on this research, when students take on their preferred learning styles, their performance was later on reflected in their academic studies. This study inspected the relationship of engineering students' take on learning styles with their performance. The experimental group for this study consisted of 285 students whom learning styles were measured by using learning style assessment tool. Four years later upon graduation, their performance was compared with their learning styles. The study showed that most students were assimilators followed by divergers (those who diverge) and convergers (those who converge) with accommodators being in the last place. This can be considered a good indication of what kind of learners mostly exist in an engineering curriculum to be referenced on, with assimilators being in the first place. The final result of this study did in fact show that the theory of learning style has the potential for guiding students for better individual performances.

Other studies have been done by M. Alseddiqi and S. Abdulrasool [8] to improve learning effectiveness in engineering curriculum where method Technical and Vocational Education (TVE) was taken. The purpose of this experiment was to examine available approaches of learning in TVE and learning styles preferred by TVE students. The results showed that teachers did not use to apply enough methods of teaching and on the other hand TVE students had a wide variance of learning preferences. The experiment allowed students to learn the subjects in their own learning choices and relate what they were learning into industry applications by using diagrams, videos, pictures, animations and virtual simulations. It has to be mentioned that other researches which stand against personalized learning also has been done. E. Howe and R. Kekwaletswe [9] raise a point in their research that at university level where there is a strict class schedule, it is hard to maintain a personalized learning among students with the limited number of class time they have. Furthermore it is discussed why a web-based approach is the most suitable solution for this method.

Based on J. Hung's research, [10] the instructional value of web-based educations has been an important area of research in information systems education and we-based education or e-Learning has been a big part in college education in recent years and is growing rapidly. M. Martinez Cartas' study [11] focused on a personalized learning with various models including e-Learning in field of chemical engineering and subject of fuel technology which had interesting outcomes which shows not only grades of students and the passing percentage improved when put in the personalized learning environment, but it also helped increase the optional activities done by students in the

field since more of them realized which activities they are mostly adapted to, based on their intellectual skills.

The researches done previously, show that when personalized learning took place in the classrooms, the instructor tried to mix different learning styles in one class. This would mean at each stage different students would find it interesting. Same thing happened in the e-Learning approach as well. This project on the other hand focuses on a personalized learning which dedicates each class to a specific group through a web-based approach. It must also be noted that Howard Gardner's Theory of Multiple Intelligences [12], a theory which divides student into seven different groups where each individual characteristic traits are taken into account in a manner that indicates which of those complement each other in order to best deliver the personalized learning experiment. Also to add to the effectiveness of the approach, unlike previous researches this project tends to make the learning experiment more personalized by having the students of specific learning style with specific characteristic traits watching a complete different tutorial class to those of another group, rather than trying to fit it all into one tutorial. Since there can't be multiple classes for students in the campus for each group, a web-based approach is the best way to deliver these courses to these students.

2. Research Methodology

It was initially crucial to completely understand the work ahead and highlight the key missing areas and gaps as there have been a lot of researches done in this field. After finding those gaps, it was decided the Howard Gardner's Theory of Multiple Intelligences can be considered as one of the best ways to approach a core engineering subject to personalized learning, something that has not been thoroughly focused on before. It was quite crucial for this research to find the right subject to be studied. Depending on the engineering school, the number of subjects provided for a bachelor's degree is different, but usually varies around 40 subjects. Among all these subjects, it was important to find out which subject is best suited for this experiment. There are a few criteria which was decided to be looked at in order to find this subject.

1. How challenging the students find the subject?
2. Which subjects do the student find more uninteresting and unappealing in the mechanical engineering curriculum?
3. In what ways is a thorough understanding of the subject important in the industry?

Looking at these three important factors, a survey was conducted among mechanical engineering last year students who had took majority of the subjects provided in the school of engineering to indicate which subjects they find most challenging and less appealing. This survey was done among 26 students detailed in Table 1.

Table 1. Number of Students Taking the Survey

Total Students	Students in Semester 7	Students in Semester 8
23	7	16

The students who already had took the core scientific and other elective subjects provided in the engineering curriculum, took the survey which in return indicated set of subjects that could have been worked with based on the 3 factors provided. Having said that, the 3 mentioned factors are not the sole consideration for choosing this subject. On top of that, a list of subjects that were to be offered in Taylor's University's School of Engineering's August 2014 intake had to be reviewed to see if any of the chosen subjects are found there to be worked with.

Upon finding the suitable subject to find the right experimental group, the next step was always to differentiate different group of learners and learn about their profiles. Based on Gardner's Theory of Multiple Intelligences, seven learner's profiles abilities and a short description of them are shown in Table 2. [13]

Table 2. Intelligence Types and their Short Description

Intelligence Type	Description
Linguistic	comfortable with writing or speaking
Logical - Mathematical	Solve problems with detecting patterns and scientific reasoning
Musical	Appreciate the use of sound and voices in rhythmic patterns
Bodily - Kinesthetic	requires a learning method that gets the learner involved physically in the process with manual dexterity and physical agility and balance
Spatial - Visual	Interpretation of things is done through creation of visual images, pictorial imagination and expressions.
Interpersonal	Able to relate to others and understand relationships between people and their situations
Intrapersonal	Have personal cognizance and objectivity and the capability to understand oneself.

These intelligence types provide pivotal and inescapable indication as to people's preferred learning styles, as well as their behavioral and working styles, and their natural strengths. [14] The types of intelligence that a person possesses not only shows that person's capabilities, but also the manner or method in which they prefer to learn and develop their strengths as well as how to develop their weaknesses.

Looking back at Table 2, a questionnaire had to be created to capture students' dependency on different intelligence types. This was done by asking total of 42 questions, 6 for every intelligence type, about simple everyday life matters which in return would indicate their intelligence type. Figure 1 shows part of one of the questionnaires answered by one of the students.

Score the statements in the white boxes only	Score		Q#
I like learning more about myself		3	1
I am able to play a musical instrument	0		2
It's easiest for me to solve problems when I am doing something physical		4	3
I often have a song or piece of music in my head	3		4
Budgeting and managing my money easy for me	2		5
I enjoy crosswords, word searches or other word puzzles	1		6
I enjoy logic puzzles such as 'sudoku'	1		7

Figure 1. Sample of Handed Questionnaire about Types of Intelligences

As Figure 1 shows, there are different questions dedicated to each intelligent type without students knowing which type they belong to when rating. The white boxes is where the students rate their approval or disapproval of the statement from 0 to 5, with 5 being the highest rate of approval. For example question 6 is showing a student's assessment of their capability in linguistic learning style while on the other hand question 5 and 7 rates their logical and mathematical thinking ability. This in return shows where each students' capabilities are and students' intelligences can be broken down into different sections and they also can be divided to different groups of learners with personalized learnings of different kinds being delivered to each group as well as evaluation one personalized learning with different groups to see its evaluation. Adding to that, this method can fill the void where the weaknesses of students are. For example if someone has lower capabilities in mathematical intelligences and higher bodily intelligence, a mathematical subject can be delivered to them via physical learnings. But whether or not this method can be achieved via a web-based approach is to be discussed.

After the survey was completed and feedback was gotten, a graph of multiple intelligence was designed for each student. This graph takes the total rating of all intelligences for each students and takes percentage of different intelligence types and shows how in which intelligence types they mostly are comfortable with. Also another method was chosen where highest scored intelligence would put the student into a particular group of learner where in total 7 different groups were designated for students. It has to be emphasized that with limited sources, knowledge, funds and time, it would be unrealistic to deliver an effective personalized learning to all seven set of learners who are part of the classroom. So the focus was always to work with one or couple of these groups with the available sources through a web-based approach and evaluate the results to see if a positive outcome is achieved and hence if the same model could be applicable on a bigger scale throughout all engineering schools. Adding to that, these methods were tested on other learners to evaluate the results and see if they could be relatable.

So after getting the results and having different group of learners, an experimental group was chosen. A group that based on their intelligence type, is getting personalized learning tutorials through the web, where the effectiveness of the experiment is evaluated through qualitative surveys. It has to be emphasized that this experiment is not done for the sake of students improving their grades alone, as that could be achievable with any kind of extra tutorials. There would be no grade comparison of before and after, but instead of how the experiment drove the students toward showing more interest in learning of the said subject and if not, finding out how could it be more effective based on their intelligence type. Adding to that, the strict policy of not revealing the students' grades by Taylor's University's School of Engineering adds its backing for the approach to solely be about grade improvement.

Upon completing all the necessary surveys to learn about students' profiles, it was necessary to carry out the project for results. The feedback gotten from students lead each student to have their own graphics and multiple intelligence breakdown. Adding to that, students' names were written on each graph to know where they belong. On the other hand, a virtual class where interaction with students could be reached was necessary. Initially a Facebook group where this interaction could be carried out was

chosen but later a MOOC class was also created for better interaction with the students. Apart from videos released for the highest found intelligence group, the interaction with the students helped for a better delivery of a personalized learning. In this virtual class, students would reach out for their problems highlighting where they have problems in understanding. Then the profile of the student who left the comment was checked from the feedback gotten back from the class to learn about their learning profile. The video provided tried to focus on the strengths of that person in learning and cover up their weaknesses with the right approaches. For example, Figure 2 shows some of the students' comments on the virtual class in MOOC. All names are blanked out for privacy protection of the participants in this project.

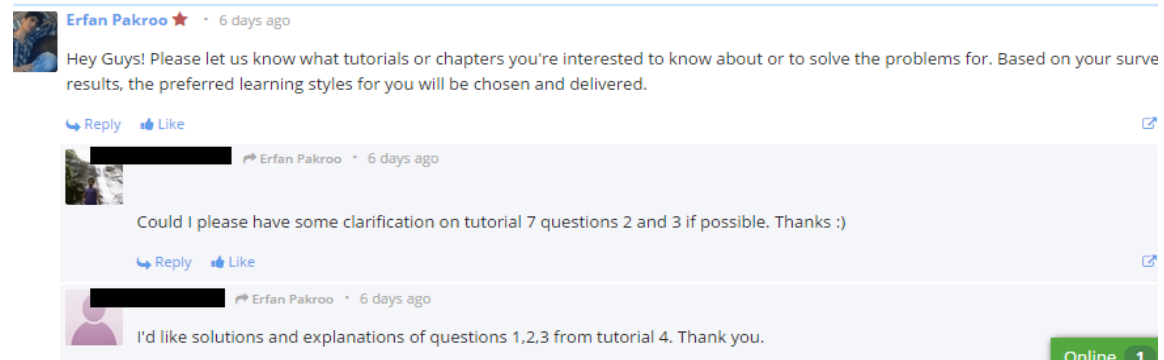


Figure 2. Interaction with Students in a Virtual Class

The interaction with students was not via MOOC alone and it continued on email forum as well as a Facebook group, since not all students were comfortable with using MOOC.

On the other hand the videos delivered to the students based on their learner's profile, were uploaded via YouTube and Vimeo. Figure 3 shows an example of this in MOOC.

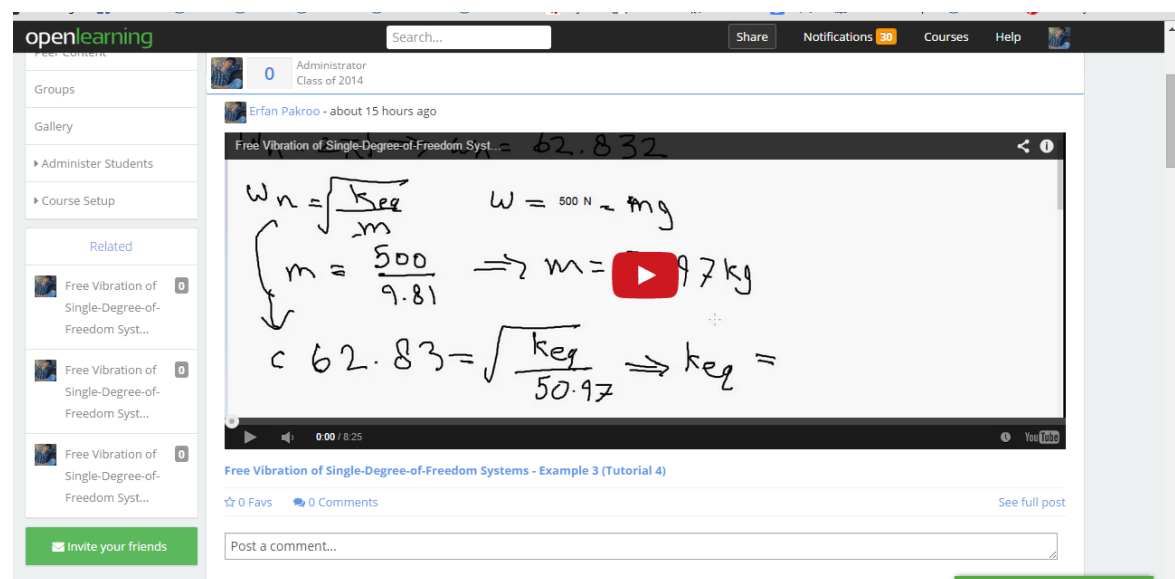


Figure 3. Video Tutorial based on Student's Request

Since it would defy the purpose of the project to have a grade comparison before and after delivery of video lectures as well as boundaries in the way to have access to these grades due to privacy issues, qualitative surveys had to be carried on later on to find out if the students found these methods useful. These surveys could evaluate the effectiveness of the approaches taken and find out what improvements can be done for a better learning environment based on personalized learning.

3. Results and Discussion

As discussed in the methodology section, students were initially undergone surveys to find which subject is suitable for the experimental group to be chosen based on a few factors. Table 1 shows different students who took this survey while Table 3 indicates the results of this survey where the 23 students rated different subjects in order to find the more challenging and uninteresting subjects. In this survey rating of 1 was indication of the least challenging and 5 the most challenging. The ratings were not in ascending or a descending order and students were allowed to rate each section to their desire rate of 1-5.

Table 3. Students' Rating of Engineering Curriculum's Subjects (1 being the Least Challenging and 5 the Most Challenging)

Type of Subject	Rating of 1	Rating of 2	Rating of 3	Rating of 4	Rating of 5	Mean Rating
Project-Based Subjects	8	9	5	2	0	2.13
Mathematics	2	7	7	5	2	2.91
Core Scientific Subjects	0	2	5	7	9	4.00
Computer Based Subjects	4	6	5	5	3	2.87
Elective non-scientific Subjects	7	8	6	1	1	2.17

All 23 students who took part in this study rated each field individually based on their experience with these subjects. The mean rating of each category is found by equation 1.

$$\text{Mean Rating} = \frac{(n1 \times C1) + (n2 \times C2) + (n3 \times C3) + (n4 \times C4) + (n5 \times C5)}{N} \quad (1)$$

Where n indicates number of people and C is the coefficient of how much that score weighs, where C1 = 1, C2 = 2, C3 = 3, C4 = 4, C5 = 5.

N is the total number of people in the experiment which is 23.

Furthermore, the students were asked to write 3 additional subjects for each category that they rated 4 or 5 which they find the hardest. Taking these subjects into account, Advanced Thermo-Fluids was found to be one of the top rated subjects in terms of difficulty, but since it was one of the subjects not provided in Taylor's University's August intake, it was not taken into consideration. Next subjects holding a tie were Theory of Machines and Mechanical Vibration which the latter was chosen at the end since it was both a provided subject in this intake and an important one for industry related work.

In deciding the learner's profiles and where they belong and evaluating their multiple intelligences, the surveys that Figure 1 holds an example of, was handed out. These surveys were sent online to all students to take part in. The sample returned with the result was not very big as some of the completed surveys were void due to wrong assessment and filling the boxes with similar numbers by some students. So a better approach had to be taken and therefore the survey was retaken later by attending a Mechanical Vibration class upon consulting with the class's lecturer. This time a sample of 30 students were surveyed. The results of the survey can be interpreted in a few different ways. While taking this survey, students were asked to write out their name with their privacy being protected, in order to be able to have everyone's learning profile. Having said that some students still did not feel comfortable to share their information. Figure 4 shows some of the results of this process with students' name being blanked out and the highest intelligence of the student highlighted.

A	B	C	D	E	F	G	H
Student Name	Linguistic	Logical-Mathematical	Musical	Bodily-Kinesthetic	Spatial-Visual	Interpersonal	Intrapersonal
1							
2	22	19	14	14	15	14	19
3	17	26	18	25	14	21	25
4	6	14	23	23	14	17	16
5	26	22	21	16	18	21	24
6	25	20	23	20	23	16	20
7	18	18	11	17	16	14	21
8	7	14	11	13	12	15	18
9	18	17	14	18	8	17	24
10	23	22	24	13	20	16	24
11	16	15	11	18	15	22	20
12	18	23	11	18	19	19	17
13	17	24	13	20	19	16	19
14	19	23	5	26	11	18	24
15	17	18	16	15	14	16	16
16	17	17	16	26	13	19	20
17	13	19	18	17	20	14	19
18	18	22	16	20	15	12	18
19	20	25	13	19	16	17	20

Figure 4. Feedback of Student Surveys on their Multiple Intelligences

While scattering the students in 7 different groups based on their dominant intelligence type can be a good indication of their learning styles, it might not be the most accurate way to determine it as there can be other intelligence types which score close to the dominant ones but don't get mentioned. For that reason, cumulative and average score of all intelligence types by these students can be found in Table 4.

Table 4. Scores Indicating Students' Multiple Intelligences

Score	Linguistic	Logical-Mathematical	Musical	Bodily-Kinesthetic	Spatial-Visual	Interpersonal	Intrapersonal
Cumulative	522	601	452	539	485	491	576
Average (out of 30)	17.4	20.0	15.1	18.0	16.2	16.4	19.2

Table 4 shows that the dominant intelligence type among students is the Logical - Mathematical intelligence type. This kind of result is understandable since more

people of this group are driven towards the engineering curriculum. Following that are group of Intrapersonal learners. These learners are the ones who understand one's own interests and goals themselves. Intrapersonal learners tend to shy away from others. They're in tune with their inner feelings having wisdom and motivation with a strong will, confidence and opinions. They are independent learners that and can learn through introspection. Since they are most independent of learners, they need books and creative materials, as well as privacy and time. [15]

A personalized learning of Logical – Mathematical method can be beneficial to both groups mentioned. Logical learners because obviously that is what they respond to and enjoy the most learning about. Logical – Mathematical learners might have it easier with this subject, especially if the right techniques are shown to them. How this group works, as the name of the profile suggests, is by detecting patterns and scientific reasoning; therefore logical thinking. They like to analyze problems and perform mathematical calculations. They are well aware and understand concepts based on relationship between cause and effect towards a tangible outcome or result. The learners of this group are more inclined to perform mental arithmetic calculations and create processes to measure difficult things. Creating these kind of processes, analyzing machines and such and assessing value of propositions falls in the category. [16] This method of learning is especially very well suited for engineers and often times engineers belong to this group. Having said that, not all engineers fall into this group and can have other learning styles. Since the subject at hand (Mechanical Vibration) is very much related to logical and mathematical problems, this profile became crucial; because most learners belonged to this group, it was easier to work with. When student's intelligence is not dominated by this group or they have scored very low in this segment, the personalized learning delivered must be based on their other intelligences. But since it is a mathematical and logical module after all, it has to be connected to this intelligence type at some point for the best outcome.

Second highest group, are intrapersonal learners. Intrapersonal learners are often individual learners themselves, so a web-based learning where they can put their focus on the videos and learn about it more individually would help them. Hence the main personalized learning delivered to the students was done with the logical - mathematical method.

The next two highest ranked groups of this study group are the linguistic and kinesthetic learners. Linguistic learners, are comfortable with things being explained, and interpreted to them via language. This group understands relationship between communication and meaning. Activities that are better done with this set of learners is following a set of instructions by reading them. They are good with written piece of works and commenting on events and communication skills. Approach that has to take place for teaching of Mechanical Vibration for this group may not have the easiest correlation, but can be done to perfection based on their other skills while mixing it with linguistic approaches.

The third favored group as the survey suggests, are kinesthetic learners where its practices requires a learning method that gets the learner involved physically in the process with manual dexterity and physical agility and balance. The need for one to be kinesthetically involved to learn things falls under project based learning in the engineering curriculum. This of course is very common in engineering school and

practiced commonly. The problem that was faced in this section was connecting the learning technique of providing Mechanical Vibration tutorials to a web-based project.

So based on these results the provided video tutorials for students were mainly focused on the logical and mathematical learners. The personalized learning environment set for students based on their learning abilities is of course one of the main catalyst to drive them towards studying the subject more ambitiously and therefore increasing their grades, but having said that, results of how suitable these personalized learning environments have been for students is done through qualitative surveys and not grade comparison. This is both because these results are prohibited information from students as well as not missing the key point of motivating students towards the subject rather than train them for tests and exams. The provided leaning assessments and videos through the web to the students were assessed by the students. As mentioned earlier in the paper, providing all lectures based on all intelligence types for every individual would be next to impossible due to limited sources, knowledge, funds and time. So the evaluation of the effectiveness of the method was done where students gave their opinions on the video lectures provided to them and comparing their feedback with their intelligence type.

On the other hand, as mentioned in the methodology section, students were encouraged to enquire about different parts of their subject through the virtual class. For example, when student #4 enquired about part of their course to be taught to them, this method was taken. Profile of student #4 as shown in Figure 4 (row #5) was looked at. As mentioned, a graph of intelligence for each student was made for them to better understand their intelligence type as well. Figure 5 show the graph for multiple intelligence of student #4. In this graph the x-axis is indicated by numbers which are different intelligence types listed by 1) Linguistic, 2) Logical-Mathematical, 3) Musical, 4) Bodily-Kinesthetic, 5) Spatial-Visual, 6) Interpersonal, 7) Intrapersonal,

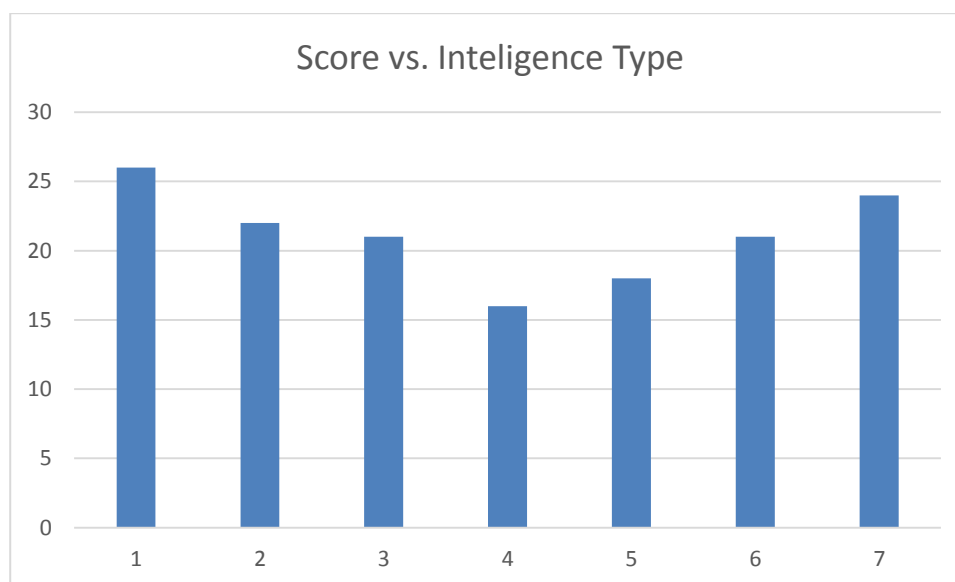


Figure 5. Bar Graph of Student #4 Intelligence Types

Accordingly, each intelligent type was taken percentage wise compared to other intelligence scores to draw a line graph to see the scatter among different intelligence types. Figure 6 indicates one of the examples for student #4.

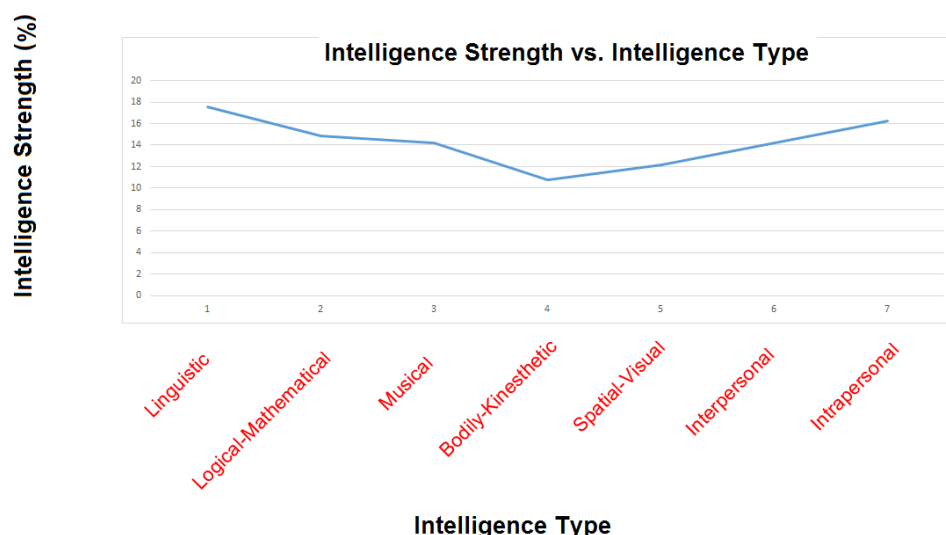


Figure 6. Line Plot of Student #4 Multiple Intelligences

Looking at student #4's feedback, it can be interpreted that this student's intelligence is dominated by linguistic intelligence, followed by intrapersonal and logical thinking. So the lecture provided to them was through this personalized learning of focusing on linguistic teaching, but mixing it with logical and mathematical approach at times to best deliver the lecture.

The process of looking at the feedback results for every students and their data and graphs was done for every student who enquired about different parts of their subjects via MOOC, Facebook and e-mail as different students were more comfortable with different interaction methods.

Upon completing these virtual classes, those students who participated in the experiment were surveyed to find out the effectiveness of this process. First important factor was to see if these students felt they were assigned to the right personalized learning methods. This can be interpreted by two methods were first students were asked their best learning methods which later on was compared to their preferred learning methods obtained from the surveys. So the students were asked to identify their dominant intelligence type based on what they believed to be true. Only 3 of the students thought they are not well identified by their dominant intelligence type which is a good indication that majority of the students were put into the groups that they feel is best suited for them as well groups and the survey results are quite accurate.

Firstly, the survey required about the efficiency of web-based lecture videos to students to see if it was useful. All students found these videos useful as they had a source to solve their problems and work on their problem solving skills. Having said that, evaluation of the personalized learning had yet to be done. Apart from the personalized learning delivered to students who inquired about it in the virtual class, the videos uploaded in general took an approach in logical – mathematical style of teaching since that group dominated the class. Evaluating these results among students, it is found out that these videos were found useful by all students but not completely relatable to their personalized intelligence for about half of the students. This is understandable as only 40% of the students' intelligence was dominated by logical – mathematical intelligence. On the other hand when students individually

commented in the virtual classroom or emailed requiring about a specific topic, their profiles were studied and the lecture was delivered to them based on their score. When these students were surveyed it was concluded that this kind of learning suited their style perfectly and they were able to comprehend and have a grasp on the subject by undergoing this experiment, even if limited topics of the subject was covered. Linguistic learners who enquired about a certain topic in the subject, were asked if they found the delivered lecture more suitable for them than the other video which focused on logical method of teaching. 4 out of 5 of the learners of this group responded in which 3 responses were positive into thinking the second approach suited their intelligence better. The last student, student #30, even though put in the linguistic-dominant intelligence group, found the logical approach more suiting for them. After coming to this realization, profile of student #30 was looked back at along with its graphs. Figure 7 shows a bar graph of this student's results.

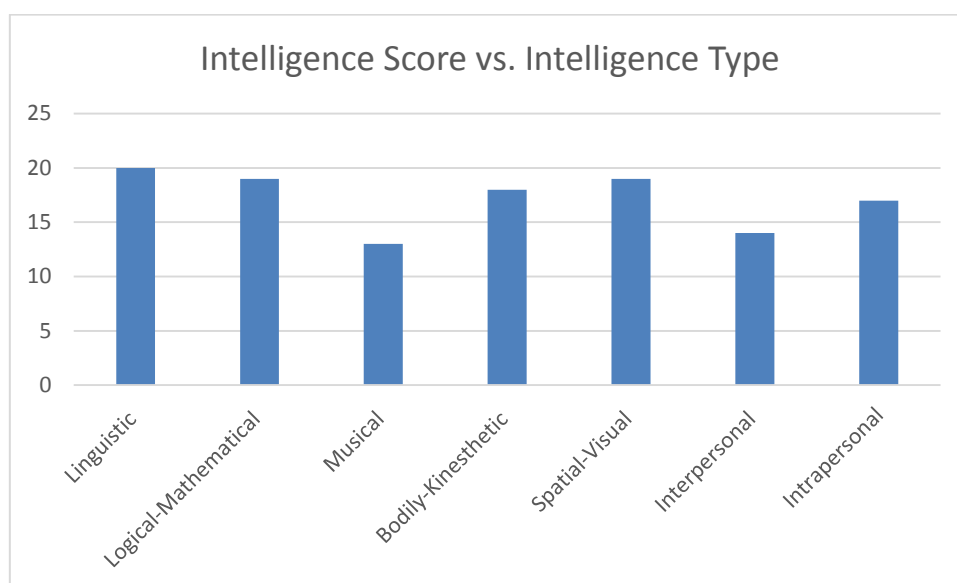


Figure 7. Bar Graph of Student #30 Intelligence Types

Looking back at Figure 7, it is visible that even though the dominant intelligence of this student is indicated by linguistic, his logical – mathematical thinking has scored only 1 point less than linguistic, so it is not far from reality that this person is more comfortable with logical methods. This is why it is important in this method of personalized learning not to focus on the dominant intelligence type and take all intelligence types into account and deliver a personalized learning based on all those factors. This is why it is important to have a virtual class where students can talk about their problems and with focus on their profiles, best personalized learning methods to be delivered to them.

Of course it would not be realistic to deliver an effective personalized learning to every single individual based on their profile, but a better method that can be used other than setting people into 7 different groups by their dominant intelligence type is to put them into different groups by adding cumulative scores of two different intelligences. This way a more accurate indication of their intelligence can be looked at. For example if a person is both good at visual and logical intelligence, a method where the main focus is on these two intelligence types would be more efficient.

4. Conclusion

To sum it up, personalized learning is a method of learning which has had a lot of research and focus towards itself. It's a very old method which has been around for a very long time now and researches done about it show that whenever students are undergone an experiment which focuses on their abilities of learning, it often has had positive results. . This is basically because every person have their own characteristic features, own way of thinking and own way of learning. So basically in a regular classroom, the lecturer is having a direct relation with dozens of different minds and hence different learning abilities and it is impossible to keep it interesting for everyone. Researches done so far indicate how a classroom which features different learning styles can be interesting to more people, but this project completely focuses on a particular intelligence model and deliver it based on those characteristic traits only, to increase the effectiveness of the learning. Of course it has to be mentioned that with limited sources, funds and time it would be unrealistic to deliver an effective personalized learning to all seven set of learners who are part of this classroom. So the focus was to deliver the class based on the dominant intelligence type of the class while evaluating different students' profiles and upon their request in a virtual classroom, look at their profiles and deliver a personalized learning based on their profile. Doing this for 2 different intelligence types had a positive reaction since students found them both interesting and useful. Having said that, focusing on one intelligence alone was not the key decider in those individual lectures. The focus was put into all of the student's capabilities and the lecture was delivered combining their top scored intelligences if they had close scores to each other.

Delivering lectures based on the dominant group of learners in the classroom mainly kept one group happy, the group that were identified by that intelligence. This of course proves that personalized learning is a positive approach. Later on when linguistic learners went on that kind of learning specific to them, majority of them were more interested with that approach and found it more suiting, further proving personalized learning is helpful for majority of the students. Having said that, the question that how can it be delivered for all different groups in an effective manner is a more complicated one that needs a bigger work. This kind of tuition cannot be done with a single educator, certainly not an unqualified one, but there are works in the future that can be done to tackle this issue. The method where the students can partake in a virtual class and have an educator deliver the lecture based on their profile might not be the most efficient way of teaching since there would be lot of different groups in one class, much more than 7 groups. So a system where students can be participants in this virtual classroom and be part of the educators can be one of the ways universities can approach this method in the future. Adding to that a longer survey which identifies different intelligences that one might possess in order to better understand their learning styles is encouraged.

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Effectiveness of Contrast Therapy on Muscle Recovery

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Abstract

Human often suffered muscle pain and soreness due to the excessive stress on their body due to intense training or workout. It is very hard to maintain high level performance and physical strength of an athlete without the intervention of recovery. There are many studies show that the result of separate heating or cooling temperature on muscle recovery. A new idea came up with a combination of successive heating and cooling which performed in a cycle. To ensuring the appropriate results, a comprehensive study on the muscle physiology and designs has been carried out to develop the effective heating-cooling cycle instrument associated with the massage therapy. The effective timing cycle and its duration for the contrast cycle are still subjected to uncertainty. Therefore, the aim of this research is to investigate the ideal time cycle and effectiveness of the contrast therapy. In this project, an experiment is carried out to investigate the appropriate timing ratio for the contrast cycle and its effectiveness. A sample of twenty male futsal players has been chosen to participate in this experiment. Each participant performed the contrast therapy with different timing cycle of 3-, 5-, and 8-minute hot/cold cycle. The statistical data shows that a 5-minute cycle is the best while the 3- and 8-minute cycle shows very little change. The result suggests that both cycles are either with not enough time or too much unnecessary time. The study also shows that most of the participants are willing to adhere to the new technique departing from their traditional techniques after the physically practiced the new technique.

Keywords: Human muscle, Nerves system, Heating/Cooling device, Thermoelectric properties, Massage therapy.

1. Introduction

Muscle fatigue is one of the common problems which suffered by most of athletes who always involved in high intensity activities. Many athletes train extremely hard without giving their body time to rest which can lead to overload and poor performances (Mackinnon and Hooper, 1991). One of the most important aspects of any exercise and strength training program is the recovery which defined as 'the return of the muscle to its pre exercise state following exercise' (Tomlin and Wenger, 2001). Human muscle tends to breakdown and rebuild after performing repetitive or high intensity activities. Progressively overload and putting excessive stress on the muscle without rest could lead to tiny injuries and muscle pain. Therefore, recovery or proper treatment is absolutely necessary to maintain a high level performance and reduce the risk of getting injuries.

Currently there are many physical therapies that can be used to accelerate the recovery from fatigue after intense workout or physical training. Cryotherapy (cold therapy) is one of the common techniques which used to reduce the muscle swelling and inflammation. Few researches have pointed out that it might have some value in recovery system muscle contractile disarrangement that caused the delayed-onset muscle damage (Bailey et al., 2007; Eston & Peters, 1999; Yanagisawa et al., 2003a). While thermotherapy, also known as heat therapy is a physical therapy which is using the application of heat to relief the muscle pain and improve the blood circulation of the body (Prentice, 1999; Brukner & Khan, 2001; Zuluaga et al., 1995). It can be perform by using heating pack, hot water, ultrasound, and so on. Sports massage is another technique which has been used to reduce the muscle spasm and soreness. A proper massage to the affected area could helps in muscle relaxation and minimizes the muscle contraction. Acupuncture is among the oldest healing therapy which originates from China. It is performed by inserting the extremely thin needles to the specific injured point along the skin. It is commonly used to treat lower back pain, myofascial pain, headache, tennis elbow, and osteoarthritis of the knee by medical acupuncturists in US (Diehl et al., 1997).

Recently the alternating heating and cooling (known as contrast therapy) has the potential to cure the muscle pain and recover from muscle fatigue. Alternating hot-cold water immersion is one of the alternating heat and cold techniques which widely used and still used in aiding recovery after intense workout or physical training. Basically it is a water treatment whereby immersing a limb or the entire body into ice water and then immediately in warm water for several cycles. Applying cold temperature could reduce the muscle pain and inflammation of the affected area. Followed with the warm temperature could help enhancing the blood circulation and hence improving the *regeneration* process. However, it causes inconvenient to transfer a person from cold water to warm water and back to cold water again which lack of flexibility. Setting up all the necessary equipments for the muscle treatment or therapy is wasting a lot of time and efforts. It is also very inconvenient to transfer an athlete who suffers muscle pain in the middle of the training or competition to a clinic or hospital in order to receive the appropriate muscle treatment. Besides, using lots of ice or water for each muscle treatment is a waste of money and natural resources. Water immersion technique covers all body without a distinctive location which may give mixed signal to the brain about the recovery. Furthermore, the prices for each treatment or repetitive treatments are very costly and unaffordable by most of the

people. Until now there is no solution yet that can perform the alternating hot and cold treatment efficiently and effectively. Therefore, the challenge of this research is to propose a new technique with competitive, or even much better, performance compared to other traditional physical therapies with better flexibility and portability. At the same time, the new technique is expected to perform the muscle treatment with less expenses and better environmental sustainability without wasting any water or ices.

The new idea of combining the heating and cooling together requires two important issues: one is to have extensive study on muscle and nervous systems to see the best reaction, and second to designing a portable heating/cooling cycle instrument which is capable to perform the contrast therapy consisting of alternating applications of heat and cold in continuous cycles. The new idea is expected to relieve muscle pain and improve muscle recovery from fatigue efficiently.

The purpose of this study was to investigate the effectiveness of new contrast therapy with different hot-cold timing ratios. The research questions are to examine the effectiveness of this contrast therapy in reducing the muscle pain and soreness. Secondly is to estimate physically the ideal timing ratio for the contrast cycle. This study contributes to the literature on contrast therapy and provides evidence that support the use of contrast therapy as an effective modality for muscle recovery. The results of this research will also determine the ideal timing ratio for the contrast cycle and serves as a reference and comparable data for the future development and work.

2. Physiological Effects of Contrast Therapy

Recovery is defined as '*the return of the muscle to its pre exercise state following exercise*' (Tomlin and Wenger, 2001). During the recovery stage, oxygen is used to restore the muscle to its pre-exercise condition. Basically the idea of recovery is to increase the supply of oxygen into the muscle tissue and remove the lactate and other metabolite wastes (Barnett, 2006; Draper, Bird, Coleman, & Hodgson, 2006). According to Stephens and Taylor (1972), muscle converts 80% from fatigue within 90 seconds with the normal blood circulation and no sign of recovery without the existing of blood flow. Tomlin and Wenger (2001) claimed that the fast recovery period occurred when there is a rapid drop in rate of oxygen consumption and heart rate.

Thermotherapy makes a significant impact on muscle recovery by causing vasodilatation (widening of small blood vessels) and vasoconstriction (narrowing the blood vessels). Applying cooling temperature to the acute injuries could limit the amount of swelling by preventing less blood flowing into the cooling muscle region. Enwemeka *et al.*, (2002) has explained that the decrease in tissue temperature would cause vasoconstriction on the sympathetic fibres by stimulating the cutaneous receptors which decrease the swelling and inflammation thus lower the risk of the injury.

According to Cochrane (2004), the production of *lactate* is the sign of exercising and the intensity and duration affects the amount of production. The increase of blood lactate level and H⁺ affecting the muscle contractile performance and hence develop muscle fatigue. In the studies of Banfi *et al.*, (2007) found that the contrast and cold water immersions could increase the creatine kinase washout and

blood lactate removal of rugby players. A study by Monedero and Donne (2000) has proved that active recovery was the best in lactate removal compare with passive recovery, massage, and combined recovery (active recovery and massage). However, several studies show that there is no significant impact on the accumulation of the muscle lactate. According to McArdle *et al.*, (2001), this complex process still depends on the local blood flow, chemical buffering, movement of lactate from muscle to blood, lactate conversion in liver, muscle and heart.

Cochrane (2004) proposed that applying cooling temperature could flush away the lactic acid level in the blood as the accumulation of the lactic acid is believed to be the primary cause of muscle fatigue. Wilcock *et al.*, (2006) has suggested that cold immersion could reduce the cell necrosis as well as reduce the metabolism and nerve conduction velocity which results in lowering the risk of secondary damage. The recent study from Ascensão (2011) has shown that the cryotherapy has positive impact on reducing some biochemical functional and repairing the damaged muscle after a one-off soccer match.

Heat has an opposite effect which could help in muscle relaxation and enhance blood circulation at the same time. Thermotherapy has shown increasing tissue temperature could increase the blood flow circulation and muscle elasticity which causing local vasodilation and hence increase the metabolite production and reduce muscle spasm (Prentice, 1999; Brukner and Khan, 2001; Zuluaga *et al.*, 1995). Habash *et al.*, (2006) proved that a hot pack can improve the blood circulation in the muscle. Improving the blood circulation increases the rate of oxygen supply to the muscle for muscle recovery. However, applying heat to the swelling part would cause inflammation. Applying heat after the swelling gone could improve blood circulation and helps in muscle relaxation (Masset *et al.*, 1998).

Currently, the effectiveness of the contrast therapy and its physiological effects is still subjected to debate among researchers and medical members. Few studies has shown that the combination of alternating hot and cold constitute a thermal modality which has positive impact on the regeneration and alleviation of muscle pain and soreness (Masuda *et al.*, 2005; Breger *et al.*, 2009; Shih *et al.*, 2012). The common practiced ratio for warm to cold water for injury treatment ranges between 3:1 or 4:1 with the hot temperature ranging from 37°C to 43°C and 12°C to 15°C for cold (Bell and Horton, 1987; Myrer *et al.*, 1994; Brukner and Khan, 2001; Halvorson, 1990). Some studies also shows different time ratios for the heat and cold cycles, e.g., 1:1, 2:1, 3:1, 4:1, and 5:5 warm to cold ratio (Vaile *et al.*, 2007; Coffey *et al.*, 2004; Fiscus *et al.*, 2005; Hamlin, 2007). Higgins and Kaminski (1998) suggested that the duration of the treatment is recommended to repeat twice daily for 20-30 min. Lehmann *et al.*, (1974) suggested that for physiologic effects to take place the muscle must reach at least 40°C.

Studies from Masuda *et al.*, (2005) have shown that the repeated thermal therapy was able to improve from fatigue, pain, sleep disturbance, and low-grade fever. According to the studies of Breger *et al.*, (2009), 100 therapists were chosen and 70% of the respondents use the contrast hot-cold water immersion technique also known as contrast baths as a treatment intervention with different timing, duration, and temperature. The remaining 30% respondents do not use contrast baths and 69% of this group explained they do not use contrast baths as there was no evidence to

support the use of the contrast baths (Breger *et al.*, 2009). Shih *et al.*, (2012) also claimed that contrast baths with repeated alternation of heat (38-40°C) and cold water (10-18°C) immersions was able to increase blood flow to the injured point by a type of “pumping” action without causing any accumulation of additional edema. Shih *et al.*, (2012) further explained that the increase in blood flow could be primarily attributed to the fluctuations of blood flow velocity which transferring more nutrition and oxygen for the soft tissue to repair during the alternating heating and cooling cycles.

However, Hing *et al.*, (2008) in their review have shown that the evidence regarding the efficiency of the contrast baths for physical recovery is still insufficient. There are also some disadvantages for using the contrast baths as a treatment for muscle recovery. One of the disadvantages is the flexibility of the contrast baths. It is not easy to control and switch during the intervals between hot and cold as it might affects the outcome of the result. The contrast bath is using the water immersion technique which covers all body without a distinctive location which may give mixed signal to the brain about the recovery. Furthermore, setting up the equipment for the contrast baths takes a lot of effort and time. Therefore, a controllable heating/cooling cycle device will be fabricated to overcome the problems above.

In this study, the controllable heating/cooling cycle device is able to perform the switching between the hot and cold intervals easily. Besides, the timing ratio cycles and the duration are adjustable in this device which improves the flexibility of the treatment. The device will only cover the distinctive injured location of the patient which improves the accuracy of the signal sent to brain for recovery. However, more research is required to investigate and prove the effectiveness of the contrast hot-cold therapy. An experiment will be carried out to investigate and clarify the effectiveness of the contrast therapy in human muscle recovery.

3. Research Methodology

An experiment is carried out to investigate the effectiveness of the contrast therapy with different timing ratio and duration for the treatment. In this project, a controllable heating/cooling cycle device is fabricated that serves as the heating and cooling protocol for the contrast therapy. The heating-cooling cycle device is designed in such a way that is capable to provide heating and cooling cycle with different output temperature range and time interval per cycle. With the aids of this device, the desired range of temperature and the time interval per cycle for the contrast therapy can be adjusted accordingly.

3.1 Questionnaire

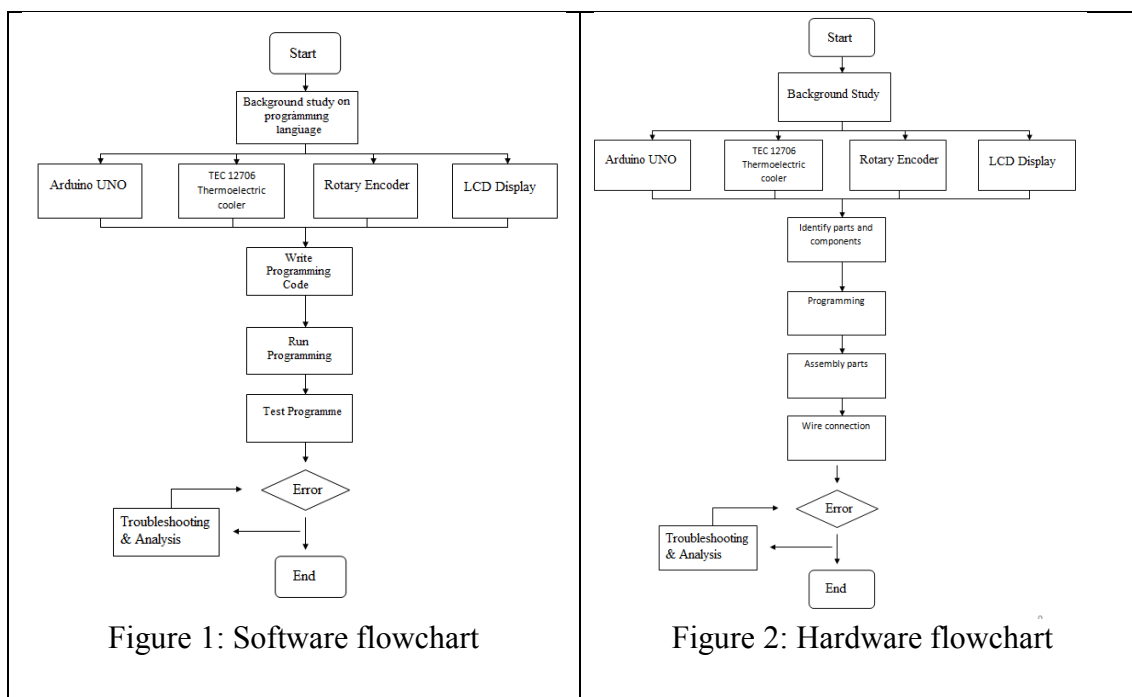
A questionnaire is prepared to assess the outcome of the study. The questionnaire consists of three parts: part one has yes/no questions about general information; part two is multiple choice style questions that serve to evaluate the conditions of the patients before the treatment; and thirdly, part three consists of three methods of treatment to evaluate the effectiveness of the each method. The questionnaire then provides all possible elements that are needed to statistically analyze the outcome of this experiment.

3.2 Subjects

Twenty-male futsal players (aged 18-24 years) who suffered of calf muscle pain were randomly chosen to participate in the study. Each subject was given the contrast therapy for 3 different sessions. In the first session at 3 minutes, 5 minutes and 8 minutes for each cooling or heating cycle. A questionnaire was constructed and given to the subjects to record the effects of the contrast therapy after each treatment. The experiment was conducted in the laboratory of the Taylor's University and lasted for a few days.

3.3 Theoretical Framework

Figure 1 and 2 show the soft and hardware flowchart, respectively. For the software flowchart (Figure 1) shows the programming language for the Arduino UNO. Then, a suitable programme is designed and tested by running the simulation. Troubleshooting is required to produce an appropriate programme code to carry out the function.



For the hardware flowchart (Figure 2), the project starts with literature review and background study on the 4 important components which consists of Arduino UNO, thermoelectric cooler, rotary encoder, and LCD display. The availability of the materials has been checked and all the datasheet of every component that needed to fabricate the project have been gathered. After the design has been outlined, all required components are purchased.

In this project, Arduino UNO has been used to control the sequencing cycle for the heating and cooling intervals of the project by providing appropriate functioning. The programme is written in such a way that user is capable to input the desired hot and cold intervals of the contrast therapy. A thermoelectric cooler is associated with the Arduino UNO to produce heating and cooling cycle for the muscle

treatment. Besides, rotary encoder serves as an input key for the user to regulate the desired hot and cold intervals while the LCD display will be used to display the time for each interval.

Having completed all requirements, a prototype was built by assembling and wiring all components into breadboard. The written programme is downloaded in to the Arduino UNO and a test for outcome of the prototype is carried out. Troubleshooting takes care of all errors developing during the testing procedure. The project becomes ready for use.

3.4 Instrumentation

3.4.1 *Arduino Uno*

The Arduino Uno (Figure 3) is a microcontroller board based on the ATmega328. This microcontroller is very easy to program and interface with variety of devices. It consists of 6 analog inputs and 14 Digital I/O pins which suitable for the need to interface with LCD display, rotary encoder, and thermoelectric cooler. It required low input voltage to the device which ranged between 7-12V. It consists of 16 MHz Clock Speed and 32k Flash Memory.

Arduino Uno was selected for its flexibility, portable, low cost, small size, and light. The device powered by USB interface and requires no power supply.



Figure 3: Arduino Uno

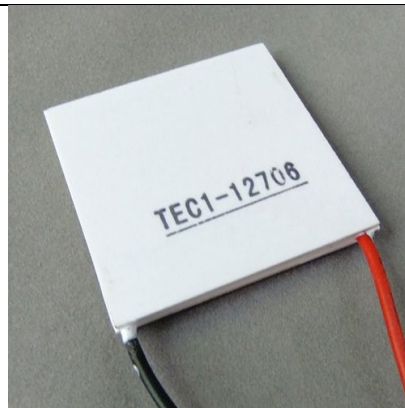


Figure 4: Thermoelectric cooler

3.4.2 *Thermoelectric Cooler*

A semiconductor device (TEC1-12706) is used for the contrast therapy. The 5x5cm 'P' and 'N' type semiconductor has cold and hot side. By adjusting the input current of the power supply, the output temperature could easily change according to the current input, see Figure 4.

3.4.3 *LCD display*

A 2x16 LCD display (Figure 5) is used to display adjusting time by make interface with the Arduino and can be programme.

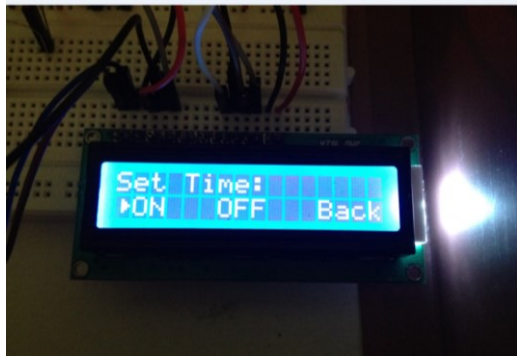


Figure 5: LCD display

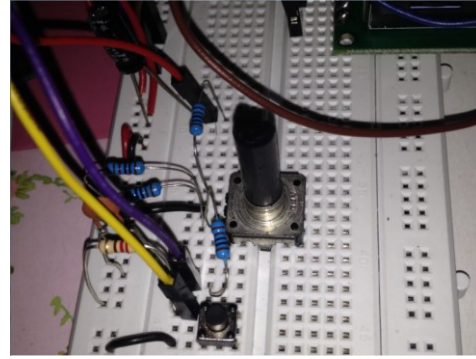


Figure 6: Rotary Encoder

3.4.4 Rotary Encoder

A rotary encoder (Figure 6) chosen for its flexibility is able to produce 4 combinations of 2 bit grey code which are 00, 01, 10, and 11.

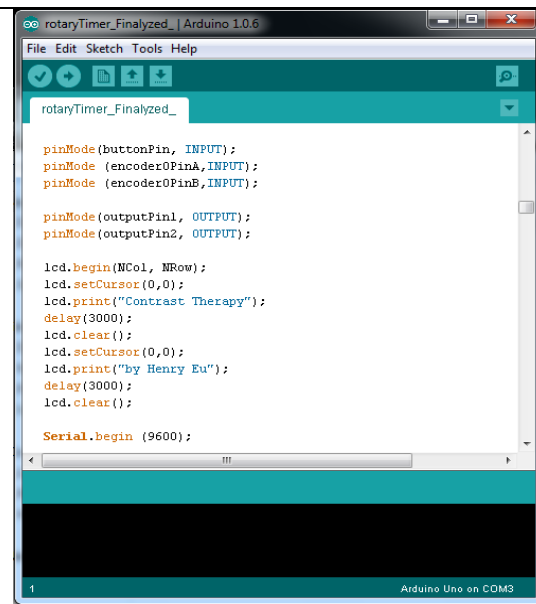


Figure 7: Programme code for contrast therapy

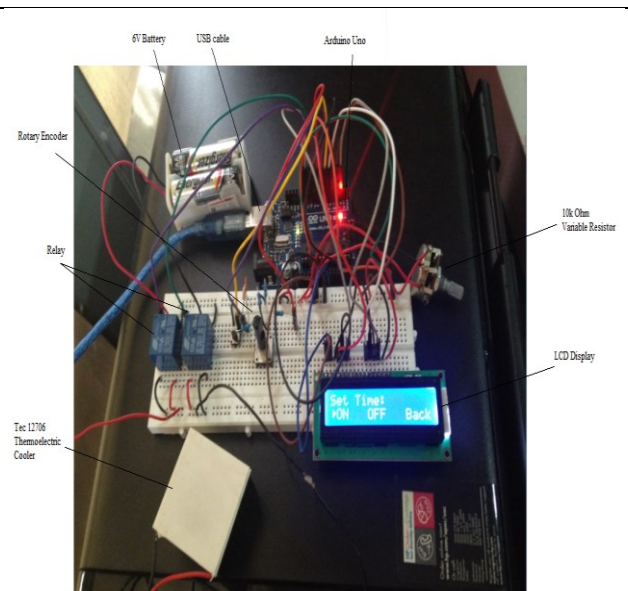


Figure 8: Heating-Cooling Cycle Instrument

3.4.5 Software Integration

Arduino 1.0.6 software (Figure 7) is used to program, using Java language, the heating-cooling cycle instrument and it is compatible with Windows, Mac OS X, and Linux. It also allows user to write, compile, and upload the code to the arduino board to perform desired function.

3.4.6 Overall Design of Heating-Cooling Cycle Instrument

Figure 8 shows the overall design of heating-cooling cycle instrument which consists of a 6V battery, LCD display, Arduinio UNO, thermo-electric cooler, and rotary encoder.

3.5 Procedure

Experiment was set up as shown in Figure 9. The thermoelectric cooler was attached to the calf muscle area of the participant by wrapping it using a special fabric. The temperature was adjusted between 18°C (cold) and 40°C (hot). In the first session, 3 min cycles time was applied to the calf area of the participant for duration of 9 min to study the effect of the contrast therapy. The experiment was repeated with 5 min cycles time with duration of 15 min and 8 min cycles time with duration of 24 min for the following second and third sessions. Each participant was given a questionnaire form to record the effect of the contrast therapy after each treatment. An error of about $\pm 3\%$ is estimated based on the following parameters that were used in the experiment: estimating the time, estimating the time for contact, power variation of the power supply, and the human error. Data was collected, tabulated and statistically analyzed.



Figure 9: Experiment Setup

3.6 Statistical Analysis

In this study, two types of statistical analysis were performed. First, descriptive analysis was to compare the number, percentage, standard deviation, and mean of the data groups. Secondly, one-way analysis of variance (ANOVA) was used to investigate the significant effect of the timing cycle and the interaction effects. In this analysis, significance of 5% was considered.

4. Results

Table 1 shows the statistical analysis for the first part of the questionnaire which is about the general information. The study was conducted on males only. There are 85% of the participants suffer of lower leg pain while the rest of 10% suffer of numbness and only 5% suffer of swelling. All participants (100%) were suffering of muscle pain prior to this study. The data shows that only 10% have used the contrast while the rest of 90% were never used this technique. Regarding to be touched by someone during the treatment, 75% answered with yes while only 25% answered no. The result of this estimation could be change after the treatment which

is conducted on the basis of “no touch” therapy. As this treatment is new procedure, 90% of the patients are willing to try it while only 10% are still with old fashion technique. Regarding the number of previous visits to the therapist, mostly (80%) have more than three visits. The participants who were conducted therapy are divided into three categories: 50% for six months, 35% for a year, and 15% for one month. The participants who got injured in the last week is 25%; 65% in the last two weeks; and 10% in the last month.

Table 1. Distribution of Sociodemographic Characteristic of Studied Sample Part 1

Sociodemographic data	(N=20)	%
Age:		
Mean±SD	23.45±1.538	
Gender:		
• Male	20	100
• Female	0	0
Sympton		
• Lower leg pain/sore	17	85
• Numbness/weakness	2	10
• swelling	1	5
Usually suffer muscle pain/soreness		
• Yes	20	100
• No	0	0
Do you use contrast to reduce muscle soreness and pain		
• Yes	2	10
• No	18	90
Do you like to be touched by someone		
• Yes	15	75
• No	5	25
Do you like an alternative procedure for muscle and soreness pain		
• Yes	18	90
• No	2	10
How many times you have been visited a physical therapist		
• Once	1	5
• Twice	3	15
• Three of More	16	80
When was your last visit to a physical therapist		
• One Month	3	15
• Six Months	10	50
• One Year	7	35
How long you have been injured		
• One week	5	25
• Two weeks	13	65
• One Month	2	10

Table 2 shows the results of the treatment for three cycles. The 10-point scale is divided into four categories for the pain that still exists after the treatment as 1 (very

painful); 2 (painful); 3 (less painful); and 4 (very less painful). For the 3-minutes cycle, the mean of 2.15 suggests that the pain is still under the category of painful. For the cycle of 5 minutes, patients were recovered better as the mean of 3.00 moves to the category 3 which is less painful. When it come for the cycle of 8 minutes, patients felt a little better as the mean moves to 3.10 which is still in same category.

Table 2. Means and Standard Deviations of Pretreatment and Post treatment on Total Pain Score

Time cycle	Mean $\pm$ SD	F	P-value
3 min	2.15 $\pm$ 0.366	1.00	>.05
5 min	3.00 $\pm$ 0.562	31.67*	<.05*
8 min	3.10 $\pm$ 0.641	33.32*	<.05*

*indicates significance differences.

Table 3 shows the one-way ANOVA statistical analysis. The analysis for the whole group shows a standard deviation of 16.35 while the standard deviation within the individual group is 10.90. The analysis also shows that *F*-value is 19 which is much higher than the *F*-critical value of 3.1588.

Table 3. One-Way Analysis of Variance for

Source of Variation	SS	df	MS	<i>F</i>	P-value	F crit
Between Individual Groups	10.90	2	5.45	19	4.757E-07	3.1588
Within the whole Groups	16.35	57	0.286842105			
Total	27.25	59				

5 Discussion

In Table 1, only 10% of the participants have used the contrast therapy while 90% were not exposed to this type. This figure suggests that the new method is relatively very new which agrees with the most published papers where traditional therapy is the common one. The new technique used here could even influence the results to be even less than 10% who were exposed to this type of the therapy. When the participants were asked about being touched by someone else, 75% of the patients have no objection to do so. The result suggests the psychological influence of treatments where usually being touched by other people since in their mind that they never be exposed to any treatment in which massage was done without a hand on their body.

In contrast to the previous finding, the statistics shows that 90% of the participants are willing to try the new technique. The number of participants who are familiar with the therapy is 80% who, at least, have three visits to the therapists. This high percentage is encouraging as those participants are familiar with the process and their judgment about the technique is really valuable and could be relied on. The last two statistical data show that half of the patients were in the physical therapist place about six months ago despite the fact that one-quarter of them got injured in the last week. The two results suggest that most of the patients have lost interest in the traditional therapy due to its ineffectiveness.

Table 3 shows the one-way ANOVA statistics for the three cycle time categories of the treatments. The cycle of 5 minutes (total of 15 minutes) is seemingly is the best cycle and shows the recovery could be classified as very good category. The data shows that the 8-minute-cycle has almost no effect as expected. Unfortunately, there is no previous results that might be used for comparison. The only close result was provided by Stephens and Taylor (1972) as the recovery takes place after 90 seconds of hot-bath immersion. The standard deviation shown by ANOVA of 10.90 and 16.35 are encouraging and they are within the acceptable results. The F -value of 19 is really encouraging as the hypothesis set for this statistics was not rejected; but was strongly accepted.

The statistical analysis and experiment results were used to answer the research questions:

1. Is contrast therapy effective in reducing the muscle pain and soreness?

The null hypothesis of this research question suggested that the contrast therapy does significant impact on muscle recovery. According to table 4-2, the results indicated that there were statistical significances in improvement from painful category to less painful category. Table 4-3 also has shown that the F -value is 19 which is much higher than the F -critical value of 3.1588. This indicates the contrast therapy does significant impact on muscle recovery. Therefore, the null hypothesis of this research question is accepted which stated that contrast therapy is effective in reducing the muscle pain and soreness.

2. What is the ideal timing ratio for the contrast cycle?

The null hypothesis of this research question suggested that at 5 minutes cycle has the higher effect on muscle recovery. Table 4- 2 shows the results of the treatment for three cycles. For the 3-minutes cycle, the mean of 2.15 suggests that the pain is still under the category of painful. For the cycle of 5 minutes, patients were recovered better as the mean of 3.00 moves to the category 3 which is less painful. When it come for the cycle of 8 minutes, patients felt a little better as the mean moves to 3.10 which is still in same category. The results proven that the 5 minutes cycle has the higher effect on muscle recovery. Thus, the null hypothesis of this research question is accepted.

5.1 Limitations

However, there are several limitations that might affect the accuracy and reliability of the results which have to be considered. One of the limitations that have to be considered is the human body reaction as different people having different rate of metabolism. A person with higher metabolism rate might have a better rate of digestion and elimination of waste product. Nevertheless, it is impossible to have all the patients with same metabolism rate.

The participants of this study were mainly those who suffered calf muscle pain and there was a chance that different size of muscle affects the muscle recovery rate. Different size of muscle group might have different time of healing. This might have affected the effectiveness of the contrast therapy.

The time of day that the participant undergoes the contrast therapy might have affected the accuracy of the results. Participants were conducted in different times of the day depending on the meeting time for contrast therapy. A person at different times of the day might have different rate of metabolism and body reaction which affected the rate of recovery. Thus, the difference in rate of recovery might have affected the accuracy of the data.

Another possible limitation that might have affected the result is this study contained small sample size. The results measured and calculated might not reliable to prove the effectiveness of contrast therapy as it only consists of small sample size. The actual effect of the contrast therapy might have not shown within the small sample size. The small group of patients could be increased for more reliable analysis and better results.

6. Conclusions

Muscle fatigue is one of the common problems which suffered by most of athletes who always involved in high intensity activities. From the literature review, it has been discovered that there is lack of study shows that the appropriate timing ratio and duration that does significant impact on human muscle recovery effectively. This study is crucial to determine the effectiveness of the contrast therapy with different hot-cold timing ratio.

This research shows that the new methodology for therapy is encouraging and more studies are needed in the future to explore the importance of the new therapeutic technique. This study has shown that the contrast therapy is effective in reducing the muscle pain and soreness and the results have shown statistically improvement from painful category to less painful category. The effectiveness of this new contrast therapy is very clear in the statistical data as the null hypothesis set by the experiment was strongly accepted. The statistical analysis has shown the depth of dissatisfaction amongst patients regarding the traditional therapy. The willingness of patients to adhere to the new technique was not surprising at all. This study also determined the ideal timing ratio for the contrast therapy and the results have shown that 5 minutes is the best timing ratio for the muscle treatment. This study contributes to the practice of physical therapy by providing more evidence to support the use of contrast therapy as an effective modality for muscle recovery.

6.1 Future Work

There are some areas of improvement and future work that can be done in this study. Since this research only limited to the individuals with calf muscle pain and soreness, further studies on the effectiveness of contrast therapy with different muscle groups would improve the reliability of the results and data. Besides, the small group of patients could be increased for more reliable analysis and better results as the actual effect of the contrast therapy might have not shown within the small sample size. Researchers also can explore more into the different combinations of the timing ratio and validate with the results of this study to determine the best timing ratio for the contrast therapy. In addition, more research is required to examine the ideal temperature, duration, and time ratio for the muscle treatment. In the future work, the

researchers can also consider the effect of contrast therapy on nerves system and the thickness of the skin to the muscle.

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Dynamic Modeling of Solar Thermal Air Conditioning

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Abstract

Air conditioning has evolved over the years to become a large percentage of global power consumption especially in developed countries with large infrastructure. With global warming still on the rise and the population across the globe continuing to rise, the need for a more sustainable approach to heating, ventilation and air conditioning is growing. Air conditioning systems require four major components; an expansion valve, an evaporator, a compressor and a condenser. Of those four mentioned, the compressor is the component that consumes the most amount of power and is the focus of many studies and efforts to make more efficient in hopes of improving the overall efficiency of air conditioners. In this project, solar thermal energy will be used to heat the coolant through the piping system before it enters the compressor to slightly increase the pressure going into the compressor. This helps save power from the compressor power load. To verify the feasibility of this approach, the air conditioning cycle was subjected to a computational fluid dynamics (CFD) simulation as well as an experiment. The experimental setup consisted of a copper piping system and a digital water bath that simulates the heat energy received from the Sun. As for the CFD analysis, the ANSYS Workbench 15.0 software was used to model the copper pipe that holds the air conditioning coolant. That model was then used to calculate the pressure change across the horizontal pipe when positive heat flux is added to the system. However, the experimental data collected did not reflect the hypothesis made due to a number of errors in the setup. The CFD simulation results, on the other hand, did correlate with the hypothesis of coolant pressure increasing along horizontal pipes with solar thermal energy introduced. The economic feasibility of such an application still requires more experimental data for verification and any future endeavors in this research subject would require improved experimental setups and procedures.

Keywords: Computational fluid dynamics, air conditioning, solar energy, vapor compression, volume of fluid method.

1. Introduction

1.1 Background

The need for a comfortable workspace is universal and a major part of what makes an environment comfortable to work in is temperature. Indoor temperature is one of several factors that lead to a comfortable environment such as humidity, air cleanliness, workspace layout, lighting and so on. Air conditioning has played a huge role, especially in hot tropical countries, to allow for a more enjoyable working experience be it in hospitals, offices, classrooms or courtrooms. That being said, air conditioning also contributes to a large portion of energy demand all across the world, more so in developed countries. Heating, ventilation and air conditioning (HVAC) systems are being improved and optimized more and more as the need for higher energy efficiency becomes a priority [1]. As the world becomes more developed, air conditioning will continue to grow in demand as will the global population, giving rise to a struggle to meet power generation demands whilst mitigating the effects of global warming [2].

The first documented air conditioning unit was invented by Willis Carrier in the early 1900's and has since progressed and evolved into a technology that is essential to modern day living. Large HVAC units and systems can be seen used in countless buildings; industrial warehouses, commercial office blocks, and various residential buildings across the globe. Many of the HVAC units currently in use in shopping malls, offices and houses are vapor compression refrigeration systems that circulates a coolant through a cycle of expansion and compression that draws heat from a source and dissipates heat out of the target area [2].

The growing market for air conditioners has its benefits but does contribute to the global warming issue through the emission of greenhouse gases, namely chlorofluorocarbons like Freon-12. On top of that, the amount of power required to sustain an air conditioned society will continue to grow with the number of air conditioners being used daily. The amount of raw materials and energy that is needed to match the energy consumption of HVAC systems will only grow larger. According to the Saudi Electric Company, SCECO, in the year 2002 the use of air conditioning in residential areas alone contributed to an estimate of 60% of the total residential power used [3]. With temperatures in tropical countries rising ever so slightly over time, demand for air conditioning will only increase.

The experimental analysis will examine the hypothesis of the project that is the pressure of a fluid, which is coolant in this case, flowing through a horizontal pipe subjected to heat will increase by a small degree. By running simulation in CFD as well, the two sets of data can be compared and verified.

If proven successful, this alternative source of energy, however small in scale, will be a welcome addition to the vast array of alternative energy solutions available to air conditioning units and systems. Given that the feasibility is found to be low, this method could still be examined further or installed in small scale applications such as personal air conditioning units in rooms or vehicles.

1.2 Literature Review

1.2.1 Air conditioning

Air conditioning in essence is the heat transfer through a coolant that draws heat from a source (indoors) and dissipates that heat to a heat sink (outdoors). This process is also known as the refrigeration cycle or Carnot cycle. There are two different types of refrigeration cycles being implemented in air conditioners today; vapor compression and vapor absorption.

Vapor compression is the most commonly used of the two cycles in air conditioning and refrigeration systems [4]. In a vapor compression cycle, there are four major components; the compressor, expansion valve, condenser and evaporator. A liquid coolant is moved through this system to absorb and release heat in the targeted areas [5]. By comparing the two different cycles, vapor compression almost always uses more power than a system running on vapor absorption. This is due to the fact that vapor compression requires large amounts of power for the compressor unit and that power load scales with the load of the air conditioning system, whereas a vapor absorption system requires low amounts of power for the absorbent pump. The absorbent pump does not require additional power to cope with a higher cooling load as compared to vapor compression.

Vapor absorption runs on the same principle as that of the vapor compression cycle with one major difference; the mechanical compressor in vapor compression is replaced by a thermal compressor or pump [6]. Vapor absorption has an advantage over vapor compression when it comes to energy usage. For vapor compression cycles, the energy source must be electrical, no other energy types can be used. Vapor absorption, however, is able to run on heat energy which can be supplied by excess heat of another system like a heater, engine or boiler. In the case of cooling loads of a large scale, vapor compression systems are still much more suitable.

1.2.2 Compressors

The function of a compressor is to increase the pressure of fluid in a specific volume by compression. To do this, the compressor requires electrical energy to transform into mechanical energy that presses the fluid into a small volume. In an air conditioner, the compressor represents the most crucial part of system in terms of power as majority of the power supplied to the air conditioner is used by the compressor [7].

Compressors used in air conditioning can be segregated into different types, one of which is the reciprocating compressor. The reciprocating compressor is actually the oldest type of compressor, appearing in the 1600's. Very much like a piston, a reciprocating compressor draws in low pressure vapor as the piston head moves downwards. On the upstroke, the intake valve is closed and the vapor is then compressed. The pressure will reach a value that allows the release valve to open, thus allowing the compressed fluid to exit the chamber. However, this reciprocating motion does produce high noise levels in the air conditioner as well as produce heat. The excess heat energy, as a result, can lead to reduced performance [8].

The scroll compressor is comprised of interleaved scrolls that rotate in relation to one another, producing pockets of compressed fluid along the scrolls. Invented in the 1900's, the scroll compressor has been improved into what it is today [9]. Another type of compressor is the rotary compressor, which can be further separated into constant speed compressors and variable speed compressors. As opposed to the reciprocating compressor, rotary compressors increase in efficiency with increasing operating frequency [10]. This means that rotary compressors work better at high loads whereas reciprocating compressors would be less efficient at higher loads. Rotary compressors that operate at low frequencies, however, is found to be inefficient and results in fluctuating temperatures. To address this, dual rotary compressors have been introduced to increase the efficiency at low load operations while maintaining the high load efficiency [11].

Compressor efficiency largely affects the efficiency of the entire air conditioning unit. The measure of efficiency for an air conditioner is called the Coefficient of Performance (COP) and it features the power supplied by the compressor as a major variable. COP is the ratio between the amount of heat that can be drawn by the evaporator and the amount of power supplied to the system, which is the power used by the compressor. However, in theory the COP of an ideal air conditioner should be measured by the mean temperature of input temperature and output temperature, assuming there is no heat loss [12].

1.2.3 Computational fluid dynamics

Air conditioning has been researched in several different ways. One of the methods used in this project is computational fluid dynamics with the ANSYS simulation software. CFD has been used to investigate specific parts of an air conditioner [13], the fluid flow in the air conditioner [14, 15] as well as the presence of leakage in ducts [16], and has grown to become a reliable tool to improve air conditioning performance and efficiency. The industrial sector has gradually increased its use of CFD as the previous barrier to utilize the technology; large amounts of memory and hardware to run simulations and modeling, is now being slowly eradicated. Development of CFD coding also has improved from a place where it was deemed too unreliable and not user friendly [17]. As a result, the use of CFD is much more evident now as a viable research tool.

There are various disadvantages to performing analysis using CFD. Studies have shown that estimation and approximation of flow around turbulent and inner regions can be met with errors [14]. Also, there can be limitations in approximation of the effects of buoyancy as well as humidity in the flow of a fluid [15]. That being said, CFD still provides very accurate calculations and is deemed appropriate for this application in this project.

Aside from using CFD as a base to research air conditioning, one can also conduct experiments on various aspects of an air conditioning unit. Most experiments can be very complicated and requires a large amount of time and energy to monitor and execute. Furthermore, the possibility of human error in experimental setup, data collection, calculation and analysis can dampen the effectiveness and accuracy of the experiment. However, experimental data is still crucial and almost absolutely necessary to verify and validate any research approach. For this project, an

experiment will be conducted on the compressor and the coolant flow that is directed towards the compressor.

1.3 Project Aim

By reducing the amount of power the compressor uses in an air conditioner, the overall efficiency of the air conditioner can be improved. In this project, solar energy in the form of heat will provide additional compression for the coolant, hence reducing the load of the compressor. This is similar to how solar thermal refrigeration systems utilize thermal energy generated by the sun to heat the refrigerant in the solar collector array [18]. The aim of this analysis is to investigate the feasibility of this method using CFD and experimental data.

2. Methodology

2.1 Experimental method

The premise of the experiment is a horizontal pipe that carries the refrigerant will be subjected to a heated water bath in order to simulate the solar thermal energy received from the Sun. A closed pipe system was designed to carry the refrigerant through a water bath and is powered by a simple pump. The material used for the pipe is selected as copper, firstly because the pipes that carry the refrigerant in most split air conditioners in the outdoor condenser unit are made of copper.

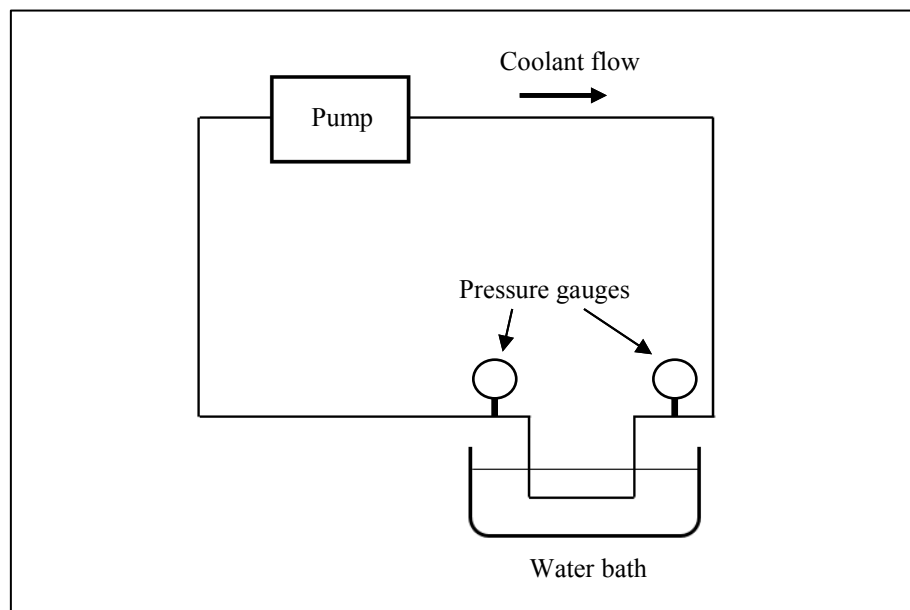


Figure 1: Experimental setup schematic diagram.

Fig. 1 above shows a simplified diagram of the experiment that was conducted to show the change in pressure across a uniform, copper pipe when subjected to heat, which is provided by the water bath.

For the above experiment, a simple water pump was installed to ensure constant fluid flow throughout the pipe system. The liquid inserted into the system was ethylene glycol, which is a readily available car air conditioning coolant liquid. Refrigerant gas was not used due to safety reasons as well as being extremely difficult

to handle. Although using refrigerant gas would provide a more accurate result, the difficulty and complexity of working with it warranted a different type of coolant to represent the air conditioner refrigerant.

The piping system was installed using copper elbows and connectors, and thread seal tape was applied where necessary to ensure the entire pipe system is sealed and would not leak. The liquid was inserted using a copper T-elbow which had an opening that could be sealed when needed.

The water bath used was a digital water bath that was available in the university laboratories. The proper safety measures were considered and personal protective equipment were used at all times. The piping system would be removed from the water bath when the water bath is increasing its temperature, as the digital water bath requires time to calibrate the water in the basin to the exact temperature set. Therefore, the copper pipes are moved away during this process before being placed back in for data collection.

The experimental procedure starts with the setup of the equipment. The water bath is turned on and set to the desired temperature. The experiment was performed at increasing temperatures of intervals of 5 °C starting with 40 °C. When the temperature of the water bath reached the temperature set, the pipe system was placed into the water bath and the water pump was turned on. After allowing the readings of the pressure gauges to stabilize for a minute or two, the pressure at the start of the submerged copper pipe and the pressure at the end of the submerged copper pipe was recorded. The water pump was then turned off and the piping system was then removed from the water bath and allowed to cool. This procedure was repeated for increasing temperatures; 45 °C, 50 °C, 55 °C and 60 °C.

2.2 Numerical Method (CFD)

The numerical method, or empirical method, involves the calculation of algorithms and approximation of values that help determine the necessary variables. In this project, using only the numerical method would be extremely time consuming and tedious. However, computational fluid dynamics can provide the solution as the numerical method provides the basis on how CFD calculates and estimates the change in properties of the material in question. The quantitative research using CFD will enable the investigation of the change in thermodynamic properties of the coolant in the portion of the piping system leading up to the compressor of the air conditioner. The software utilized for this research was ANSYS Workbench 15.0.

A CFD simulation starts with the creation of a geometry model in either 2 dimensions or 3 dimensions. Once a geometry model is completed, the meshing can be defined and controlled by the user. The next step after meshing would be to start setting up the solver by defining the boundary conditions, materials, input and output parameters, and solver method. Initialization of the solution is done once the model goes through a final check, after which the calculation can begin.

The CFD simulation is designed as a horizontal, uniform pipe and the pressure at the inlet and outlet of this area are recorded. The relationship between the change in pressure across the heated region and the amount of heat energy received by

the coolant across the pipe. The pipe is modeled in the 2-dimensional realm and is 20 cm long and 2 cm high, which represents a diameter of 2cm.

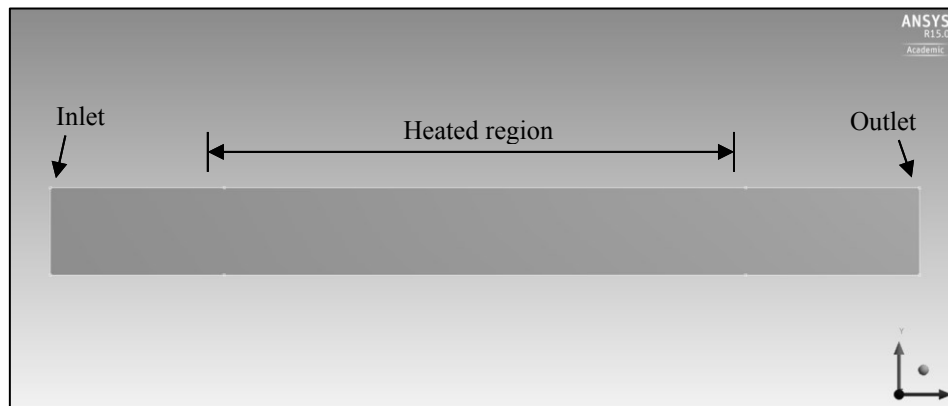


Figure 2: Geometry model of the CFD simulation.

The model seen in the above Fig. 2 shows the sectioned pipe where the middle portion is representing a heated region, where the upper and lower walls are given a positive heat flux property similar to the previous CFD simulation. In actuality, the copper pipe that holds the coolant is much longer than 20 cm. However, the scale was reduced to allow comparison of the results to the experimental data. The mesh was then generated with similar settings, with number of divisions mesh control and bias factor along the y-axis.

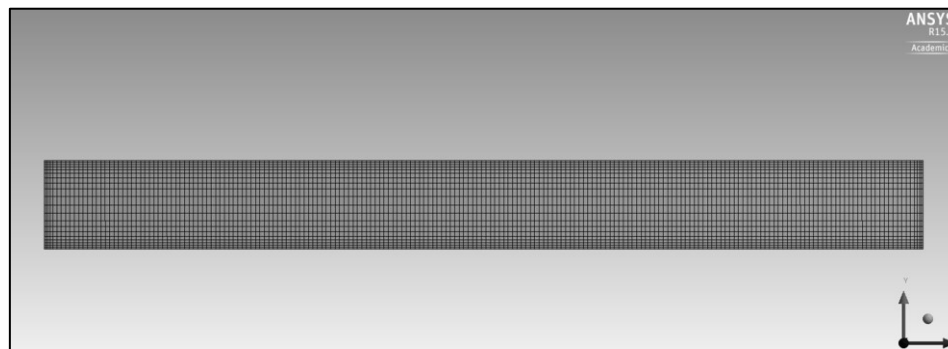


Figure 3: Mesh of the geometry model.

The solver in the solution setup is set to pressure-based and steady state, with absolute velocity formation enabled. The models that were enabled for the simulation was the k- ϵ turbulence model with standard wall functions on. The materials in the model are defined as copper for the pipe walls and difluoromethane (R32) as the refrigerant. The surface body was given the material properties of difluoromethane, which was edited with a density setting of compressible liquid.

The boundary conditions of the inlet are set to pressure-inlet with a gauge pressure of 100 Pa and the boundary conditions of the outlet are set to outlet-vent. Solar thermal energy is simulated as heat flux along the heated region just as the previous simulation conditions. The solution monitors are set to display the facet average along the vertical column before and after the heated region, which are named pressure_input and pressure_output. The simulations were repeated for increasing heat flux for the heated region from 0 W/m² to 400000 W/m², with intervals of 50000 W/m² at a time.

4. Results & Discussion

4.1 Experimental Results

Table 1: Results from the experimental simulation of uniform copper pipe.

Water bath temperature (°C)	Inlet gauge pressure (psi)	Outlet gauge pressure (psi)
40	1.2	1.2
45	1.4	1.4
50	1.6	1.5
55	1.7	1.7
60	1.9	1.8

Table 2: Results from the experimental simulation of uniform copper pipe in converted units.

Water bath temperature (°C)	Inlet gauge pressure (kPa)	Outlet gauge pressure (kPa)
40	8.27	8.27
45	9.65	9.65
50	11.03	10.34
55	11.72	11.72
60	13.10	12.41

The results shown in the above tables were compiled using pressure gauges with low decimal count reading spacings which made determining the reading difficult. This may have contributed to possible errors in the results of the experiment. The experimental data ends at 60 °C due to the fact that the water pump started to malfunction due to slight pipe leakage at the connectors on the inlet and outlet of the pump.

Assuming a refrigerant temperature of 35 °C, dimensions of the pipe of 10 cm length and 2 cm diameter, and a thermal conductivity of copper of 399 W/mK, the heat flux calculated from a high temperature of 40 °C is approximately 50000 W/m². Therefore, the simulation procedures are done in intervals of 50000 W/m² for every increasing 5 °C.

4.2 CFD Simulation Results

Table 3: Results from the CFD simulation

Heat Flux (W/m ²)	Gauge inlet pressure (Pa)	Gauge outlet pressure (Pa)	ΔP (Pa)
0	89.34	68.15	21.19
50000	89.73	70.10	19.63
100000	90.29	72.87	17.42
150000	90.52	73.97	16.55
200000	90.66	74.70	15.96
250000	90.76	75.15	15.61
300000	90.82	75.47	15.35
350000	90.86	75.68	15.18
400000	90.89	75.84	15.05

4.3 Discussion

The results obtained from the experiment as shown in Tables 1 and 2 show the pressure of the coolant increasing with the increasing temperature of the water bath. However, the change in pressure from inlet to outlet is close to none across all temperatures. This could be due to the fact that the divisions of the pressure readings on the pressure gauge are too small and the decimal point accuracy of the true result cannot be read. The results could have a large amounts of errors due to human error in reading the results, the accuracy flaws in the experimental setup or measurement equipment, or the faulty experimental design. Furthermore, when compared to the results obtained from the CFD simulations at a glance, there seems to be no signs of any correlation whatsoever as the behavior of the results in both sets of data are different.

The results from the CFD simulation in Table 3 behave very differently as compared to the experimental results. Although both the gauge pressures at the inlet and outlet in both experimental and numerical results show an increasing trend, the rate at which the pressure increases differs from inlet to outlet. As opposed to the experimental results that has very close readings between inlet and outlet pressures, the inlet and outlet pressures in the CFD simulation differs by a substantial amount. The last column in Table 3 illustrates this by showing the difference in pressure from inlet to outlet. The difference in pressure decreases with increasing heat flux or solar thermal energy provided.

The most notable result is the outlet pressure recorded from the CFD simulations which increased at a higher rate than the inlet pressure. With 400000 W/m^2 of heat flux added into the pipe, the outlet pressure drops from 90.89 Pa at the inlet to 75.84 Pa at the outlet. The drop in pressure decreases as the heat flux was increased. This implicates that the pressure of the coolant after being exposed to solar thermal energy is higher than the pressure of the coolant if it was not given energy from the Sun.

This result validates the hypothesis that the fluid refrigerant pressure is increased when subjected to solar thermal energy as opposed to not being given that energy. However, the extent of the increase in pressure is not very high. Taking the results for zero heat flux and 400000 W/m^2 , the introduction of the positive heat flux increases the outlet pressure by 11.3%, with an inlet pressure is 100 Pa. It can be argued that, as the inlet pressure is increased, the outlet pressure may not increase by the same percentage.

Given the fact that the CFD simulation results does not have comparable results with any experimental data, due to the poor quality of the experimental results in this research, the conclusions that are drawn from these results need to be verified further. However, in this research, the inability to conduct a comprehensive experiment to mirror the simulation done in the CFD software has hurt the legitimacy of the results and data that has been collected.

5. Conclusion

The resulting data that was collected from this research project confirms the hypothesis that was made; that air conditioning coolant can increase in pressure from the introduction of solar thermal energy right before it reaches the compressor unit in the vapor compression cycle. However, the economic feasibility of implementing such an application has yet to be determined as the results from the experiments and simulations cannot draw such a conclusion.

Using solar thermal energy to directly heat and increase the pressure of the coolant flowing through the straight, uniform copper pipes that carry the coolant throughout the air conditioning cycle remains an option that can be explored. The decisions made in this research regarding the project scope and experimental procedures did not enable a comprehensive and conclusive study of the behavior of air conditioning refrigerant when the pipe system before the compressor is exposed to direct heat energy from the Sun.

It can be concluded that the hypothesis of the possibility of increasing pressure of air conditioning coolant with solar thermal energy is backed by CFD simulation results but requires more experimental results to verify. It is not recommended to continue the research with the same experimental and numerical methods and procedures due to the fact that the resulting data that was collected from the research was not conclusive or accurate enough to draw a meaningful conclusion. Any future work on this research subject would require more literature review and planning in the research design to ensure the experiments yield beneficial results.

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Effect of Aircraft Wing Geometry and Shape on the Lift at Low Subsonic Speeds

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Abstract

This research aims to develop empirical formulae that will quickly and yet accurately determine the lift produced by the wing based on a set of design requirements. Thus, in this particular research, Prandtl Lifting Line Theory is utilized and assisted with existing experimental data of two dimensional airfoils to develop empirical formulae. Experiments are conducted using low subsonic wind tunnel to generate experimental data to study the effect of aircraft wing models on the lift. The data collected are analyzed using Analysis of Variance to develop empirical formulae. The lift calculated from developed empirical formulae and known theoretical formulae are compared with the existing experimental data and analyzed. The final outcome of this research is the effect of aspect ratio on lift is evidenced to be significant at low subsonic speeds. However, the effects of taper ratio and wing shapes on lift are concluded to be extremely small at low subsonic speeds. Meanwhile, the empirical formula developed in this research is evidenced to be underestimating the lift generated by the wing. It managed to take into account the effect of aspect ratio on lift however, only yielded similar value of lift for all wing shapes and taper ratio.

Keywords: Low subsonic speed, Wing geometry, Lift, Airfoil, Aspect ratio

1. Introduction

Nowadays, investigations on the subject of aerodynamics characteristics of wing surface at low subsonic establishment was majorly due to the overall development of micro-air vehicles; enhanced via the responsiveness of the research community to conduct research on the respective subject. Commonly define as the smallest group of unoccupied air vehicle; micro air vehicle possess numerous latent applications stretching from terrestrial exploration to civil plus military related missions [1-3]. As do most aircraft, micro air vehicles also relies on the lift produced by its aerodynamic surfaces of aircraft wing in order for it to fly.

Eventhough the aerodynamic surfaces of aircraft wing have been specifically known to produce lift of an aircraft for the past few decades, they have been manufactured in various shapes and geometries. The objective to this is to allow the wing to meet a predefined set of design requirements in which, in aviation field, widely known as technical tactical requirements (TTR) [4].

TTR can be exemplified in a scenario where a missile is necessitated to fly over 1700 kilometres in distance at an altitude of 11 kilometres above sea level with a speed of Mach 3. These requirements provide significant aerodynamic performances that the missile must achieved. A missile which is designed under these specifications may not be able to achieve another set of TTR. For instance, a new set of TTR which required a missile to fly over 3000 kilometres in distance at an altitude of 9 kilometres above sea level with a speed of Mach 4 [4]

Performance of an aircraft in accomplishing its function is majorly influenced by the amount of lift produced by its wing configuration [5]. Every configuration on the other hand is unique and not universal which indicates that a wing designed for a Mach 3 speed is never to have same performances at Mach 4 speed due to nature of supersonic fluid flow [4]. Producing an appropriate configuration of wing is the main key to ensure an aircraft to successfully carry out its function.

However, designing, manufacturing and testing process of each configurations of wing are used to be very costly and time consuming. Therefore, there arises a need for empirical formulae that will directly analyse and provide the lifting force produced by the wing, to the manufacturer once the shapes and geometries of the wing have been decided. The empirical formulae will help aircraft designers to arrive at a conclusion sooner than experimentations on the multiple wings plan form.

Thus, the objectives of this research are to study the effect of aircraft wing geometries and shapes on the lift at low subsonic speed (Mach speed number less than 0.1) and also to develop empirical formulae that correlates the effect of aircraft wing shapes (rectangular, triangular, trapezoidal), geometries (Aspect ratio, taper ratio, span area) to the lift (lift coefficient).

1.1. Theoretical Framework

The theoretical framework of this research comprises of the general nomenclature of wings, specification of the wing geometrical characteristics investigated in this research and the simplification in the analysis of this research.

Firstly, the wing shapes selected as parameters in this research are rectangular, triangular and trapezoidal. These types of wing shapes were selected based on the common shapes seen to be utilized for aircraft design. For instances, the application of rectangular wing can be seen to be utilized by the early aircraft as built by Wright's brother's, while triangular wing can be seen to be utilized by the high speed aircraft like Concorde and lastly, the trapezoidal wing can be seen to be utilized by the passenger aircraft such as Boeing 747. The wing shapes tested in this research are illustrated in Fig. (1).

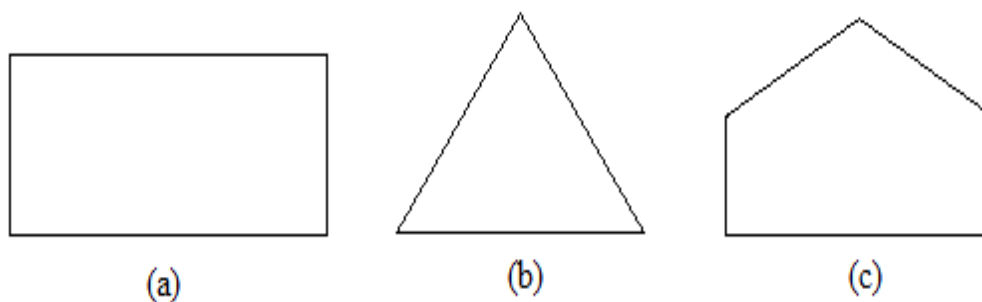


Figure 1: a) Rectangular wing shape b) Triangular wing shape c) Trapezoidal wing shape

The specific aerodynamic coefficient of wing investigated in this research is lift force. Lift force is a net upward force of an aircraft resulted by pressure differences between upper and bottom surfaces of an aircraft when streams passing through it. The direction of lift force on an aircraft is illustrated in Fig. (2).

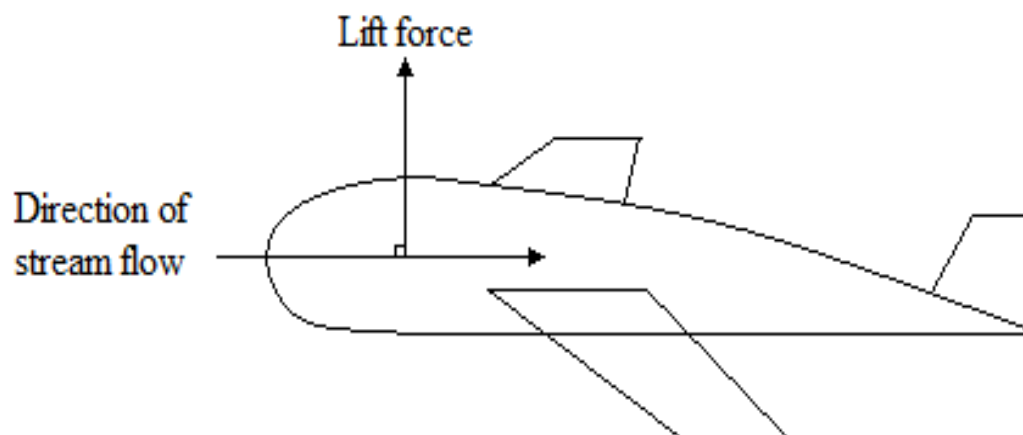


Figure 2: Direction of lift force on aircraft

Lift force generated by a wing relies on several wing geometrical characteristics. These wing geometrical characteristics are calculated based on several wing principal parameters. The general nomenclature of wing is provided in Fig. (3).

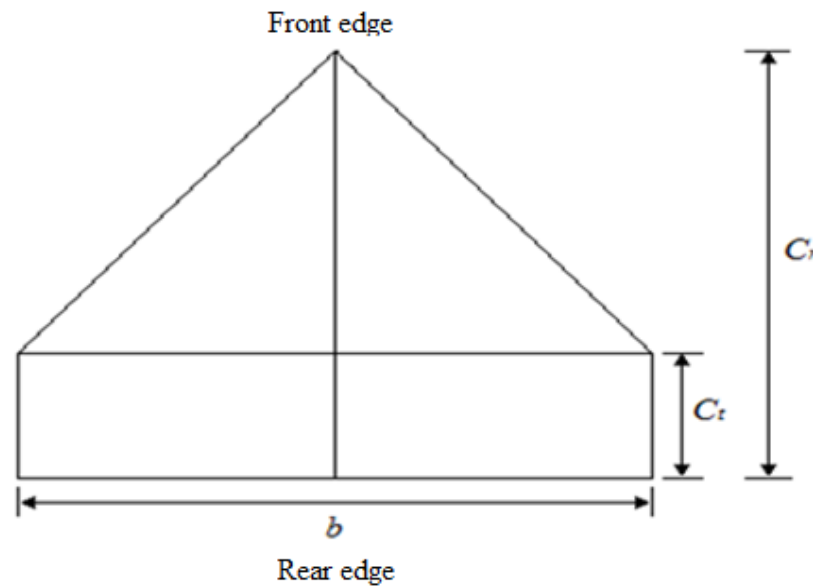


Figure 3: General Nomenclature of Wing

The wing principal parameters are given as followed [8]:

- a. Root chord, C_r
- b. Tip chord, C_t
- c. Wing Span, b

Meanwhile, the tested wing geometrical characteristics included with their calculations are given as followed [8]:

- a. Wing area, $S = \left(\frac{C_r + C_t}{2} \right) (b)$
- b. Aspect ratio, $AR = b^2 / S$
- c. Taper ratio, $\lambda = C_r / C_t$

Airfoil is a two dimensional section of a wing. The airfoil used in this research is a flat plate airfoil design. The selection of this type of airfoil was due to the simplification in analysis when compared with the existing experimental data. The design of flat plate airfoil used in this research is illustrated in Fig. (4).

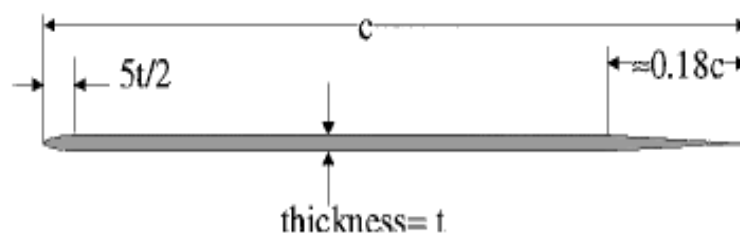


Figure 4: Flat plate airfoil [9]

Moreover, few generalizations have been made towards the implementation of the specific analysis in which the angle of attack was presumed to be zero or small as in below the stall angle magnitude. Meanwhile, the lift coefficient may figuratively be articulated in terms of lift force curve slope per radians due to objectifying the correlation of the effect of such parameters on the generated lift.

2. Methodology

The methods used in this research were semi-empirical method and experimental method. For the semi empirical method, known theoretical formulation was utilized and assisted with the existing experimental data in order to develop the empirical formulae. Meanwhile, for the experimental method, wing models were manufactured and tested inside the low subsonic wind tunnel in order to validate the empirical formulae developed.

2.1 Semi Empirical Method

The semi empirical method used in this research was the Prandtl's Lifting Line Theory, assisted by the experimental data of Alain and Thomas. Based on Prandtl's Lifting Line Theory, Eq. (1) was obtained [9]:

$$C_{L_a} = a = a_0 / \left[1 + \left(\frac{a_0 57.3}{\pi AR} \right) (1 + \tau) \right] \quad (1)$$

Where,

a_0 = Two dimensional lift curve slope

AR = Aspect Ratio

τ = Glauert parameter

Eq. (1) was applied to estimate the theoretical values of lift curve slope of all the wing models used in this research. Meanwhile, Glauert parameter is the estimation done by the Prandtl - Glauert transformation that as an aircraft is approaching the speed of sound, infinite pressures are likely to be experienced by the aircraft. The value of Glauert parameter, τ in Eq. (1) was taken to be 0.25 based on Alain and Thomas [9] in order to simplify the analysis.

Next, the value of the two dimensional lift curve slope, a_0 in Eq. (1) was also adopted from the experimental data of Alain and Thomas [1], in which the value was determined to be $a_0 = 0.0938/deg$ [9]. The value of the two dimensional lift curve slope mentioned was taken from the average value of the experimental data of two dimensional flat plate airfoils at Reynolds number ranging from 60000 to 200000. The value was used instead of the conventional value of $a_0 = 0.1/deg$ given by thin airfoil theory due to the good agreement obtained with the experimental data of Alain and Thomas [9].

On the other hand, the value of aspect ratio, AR in Eq. (1) was taken based on the geometry of the wing models manufactured. For this particular research, two aspect ratios of 0.5 and 1.0 have been tested to attain the research objectives.

2.2 Experimental Method

The experimental method used in this research was widely applied to study the effect of wing characteristics on lift, in which, testing the wing models inside the wind tunnel. Based on Sagar [1], the application of wind tunnel was preferred as the characteristics of flows within the wind tunnel can be controlled appropriately in order to achieve the objective of the research.

2.2.1 Experimental Apparatus

For this particular research, the wind tunnel application used is a form of low speed wind tunnel; specifically of the model TDA_M630/12AA/7/28 whereas fine tuning can be perform up to an amount of 38.35 m/s from 3.33 m/s range with the supplementary data of 4145 V/50 Hz, 63 mm in diameter fan and 3 HP [10]. Besides, the wind tunnel is profiled as an open type wind tunnel proportioned to a contraction ratio of 3.4:1 as well as installed with a small scale rectangular designed test section with dimension of 0.885 m long plus 0.303 mx 0.303 m in cross section. Furthermore, the data acquisition apparatus of the wind tunnel encompasses of a Gamma DAQ F/T transducer; a sensor that translates real time data into force and moment figures. Next, the usage of the DAQ power cable is due to forming a link between the sensors towards the DAQ transducer power supply. Finally, the installation of a NI PCI-6220 series PCI DAQ card onto the connected wind tunnel computer is a prerequisite as for the sensor to precisely record and display the force and moment figures.

2.2.2 Experimental Models

Wing models used in this research were designed by using three dimensional computer aided design software, Solidworks. The wing models designed in the Solidworks software were later fabricated by using the computer numeric control milling machine which is facilitated in Automated Laboratory of Taylor's University. All the wing models were made of a thick aluminium plate. The objective to this was to enhance the surface finish of the wing models hence, reducing the effect of boundary layer on lift due to the surface roughness of the models [11]. The number of wing models manufactured was five, in which comprises of two rectangular wing models, two trapezoidal wing model and two triangular wing model. The rectangular wing models have semi aspect ratio of 0.5 and 1.0 respectively. Meanwhile, the trapezoidal have taper ratio of 0.66 and 0.72 respectively and lastly, the triangular wing models have a similar aspect ratio and surface area with the rectangular wing model of aspect ratio of 1.0. The reason to this was to isolate the effect of investigated parameters from the other potential effect of wing geometrical characteristics on lift such as sweep angle plus percentage of cambered.

2.2.2 Experimental Setup

Experimental setup discussed in this investigation played a pivotal role in achieving the research objective as few alterations based on extensive research were made to the overall setup. The experimental setup used in this research was by positioning the wing model inside the rectangular test section of the wind tunnel. This was done by mounting the model on a pushrod and later connecting the pushrod to the load cell. The experimental setup used in this research is illustrated in Fig. (5)

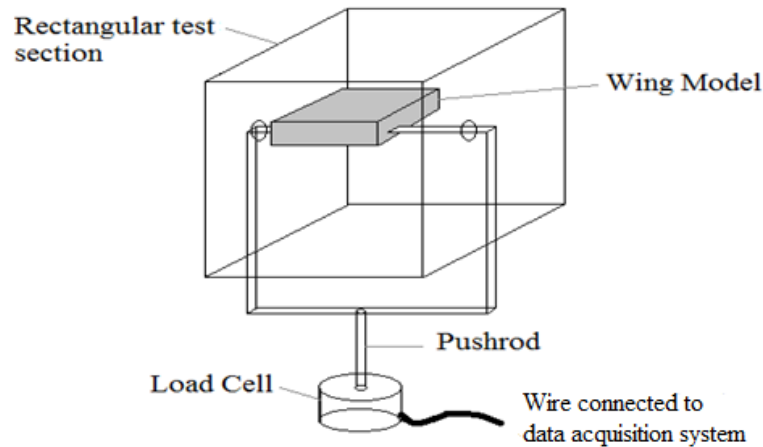


Figure 5: Experimental Setup of Wing Models Experiment

Based on this setup, the airstream with specific velocities adjusted by using wind tunnel's drive system were let passing through the model. The stream flow passing through the model created pressure differences over the top and bottom surface of the wing. This pressure differences were resulting in the lifting of the wing and these lifting forces were captured and later converted into an electrical signal by the load cell. The electrical signal was then translated and displayed on a computer through the interface software.

$$C_L = \frac{F_L}{0.5 \rho_p V_p^2 A_p} \quad (2)$$

Where,

ρ_p = Density of air within the wind tunnel

V_p = Velocity of air within the constant area of test section

A_p = Characteristic frontal area of body of model

All the data provided by the interface software were in form of force and moment values in three different axes. Therefore, Eq. (2) was applied in order to estimate the lift coefficient of the wing models. In order to simplify the analysis, the 20^o C recorded temperature within the test section was assumed to be constant during the entire experiment.

2.2.3 Calibration of Wind Tunnel

The wind tunnel used was calibrated with several different set of procedures before conducting the main event experiment. The objective to this is to determine the accuracy and uniformity of adjusted stream velocities along the rectangular test section [12,13]. The equipment used for the calibration process, precisely to measure the stream velocities, was a hot wire equipment (model: Delta OHM – AP471S1)

which comprises of a hot wire and an anemometer. Several parameters that were tested to achieve the purpose of the calibration were the operational frequency of wind tunnel's drive system, x – coordinates of rectangular test section and operational duration of wind tunnel's drive system. The calibration of wind tunnel setup is illustrated in Fig. (6).

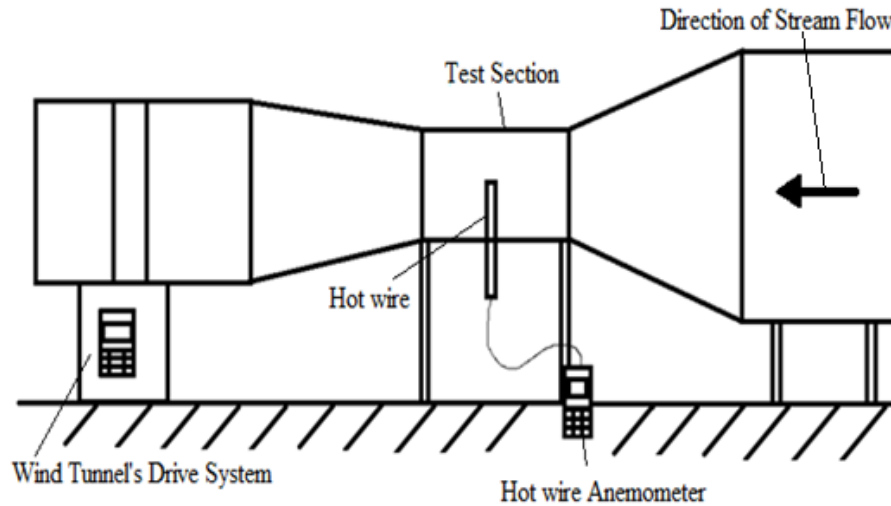


Figure 6: Experimental Setup for Calibration of Wind Tunnel

The calibration of wind tunnel setup illustrated was used for the entire calibration purposes experiments however, with different set experimental procedures. For determining the relationship between the wind tunnel drive system's frequency and the stream velocity generated within the test section, the hot wire was fixed to measure the stream velocities at the center of the test section while the operational frequency was adjusted to 60 Hz from 0 Hz frequency with the increment of 5 Hz. Next, for determining the accuracy of stream velocities generated along x – axis of test section, the operational frequency was fixed to operate at 40 Hz while the hot wire location was repeatedly changed from one end of the test section to the other end of the test section with the increment of 10. Then, the similar procedure was adopted at different operational frequency.

Lastly, for determining the relationship between the operational duration of wind tunnel's drive system and the stream velocities generated within the test section, the operational frequency and the location of hot wire was fixed at 40 Hz and center of test section respectively. Then, the stream velocities were recorded after 5, 10, 15, 20, 25 and 30 minutes of operational duration.

As a result, for the first calibration of the wind tunnel, It was found out that the stream velocity produced within the test section exhibits the linear relationship characteristic with the operational frequency of wind tunnel's drive system. Hence, the overall data was represented by the linear equation form, which the setting of specific operational frequency will be specifically adjusted towards the corresponding stream velocities inside the test section.

Meanwhile, for the second calibration of wind tunnel, few observations can be noted. Firstly, the stream velocity within the test section varies with respect to

different position along x – axis and particular operational velocity of the test section. Secondly, the velocity variations at the preliminary section of the test section were recorded as positive magnitudes whereas the velocity variations on route to the ending segment of the test section become negative units. However, the velocity dissimilarities are exceedingly small and negligible. Thirdly, the velocity variation gradient along x-axis revealed an almost similar pattern behavior for all operational velocities. Thus, this concludes of the stream velocity distribution is uniformly scattered within the wind tunnel’s rectangular test section.

Lastly, for third calibration of wind tunnel, it was found out that the maximum velocity disparities had occurred after 10 minutes of operating time and the minimum velocity variation occurring after 25 minutes throughout the wind tunnel operation time window. Since every interval of the velocity variations is very small and negligible, it confirms that the velocity variation along the test section is not exclusively dependent on the time taken for wind tunnel operation. Consequently, the velocity deviation in the test section does not have substantial variation at diverse duration of operation. However, in order to eliminate this bias factor, the lift generated by the wing models will be collected after 10 minutes of operational duration since the velocity distributions within the test section seems to obtain steady state.

3. Research Outcomes and Discussion

The first set of experiment was conducted by using NACA 0012 airfoil in order to determine the accuracy of the research methods used. The experimental data obtained were later validated with the experimental data of Abbott [19] as presented in Fig. (7).

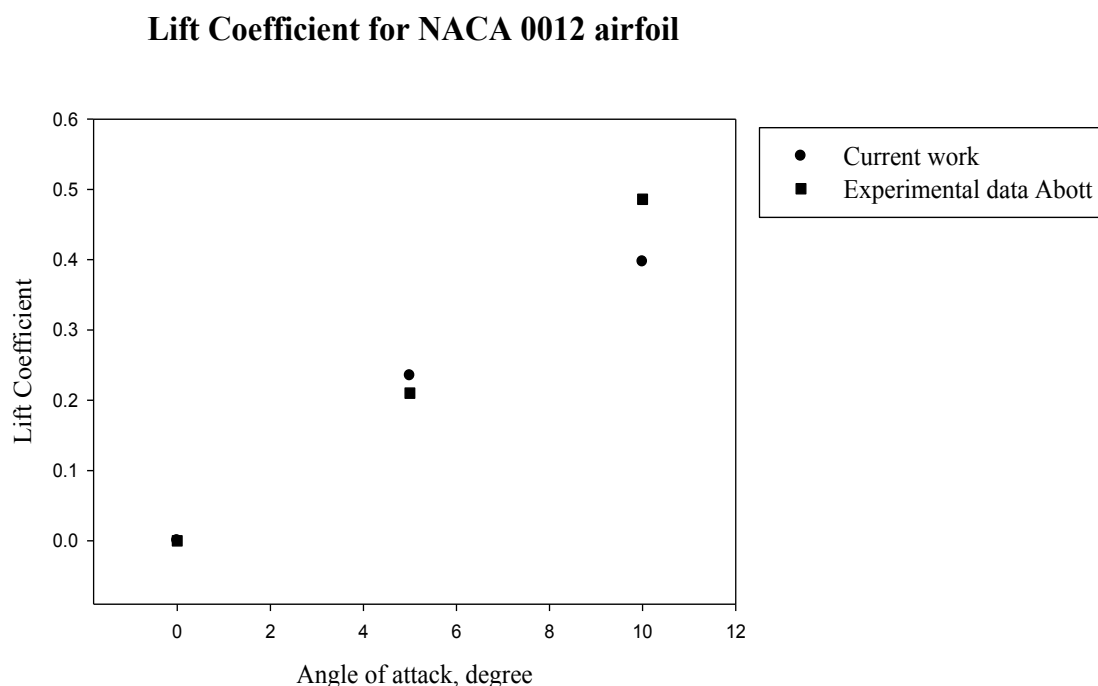


Figure 7: Lift Coefficient for NACA 0012 airfoil at 200000 Reynolds number

Based on Fig. (7), it can be seen that the experimental data obtained had an average deviation of 12% at 5° angle of attack from the experimental data of Abott [19]. In addition, the deviations of the data can be seen to be increased to 19% at 10° angle of attack. The reasoning to this might be due to the sensitivity of the designed test rig towards the vibration. Even though the load cell was tested to be able to determine precisely the value of load when the load was placed on top of the test rig in a static condition, the test rig seems to be vibrating as the wind tunnel was operated.

This assumption was supported with the increasing of data deviation as the increasing angle of attack. This is because as the angle of attack is increases, the drag force generated by the wing model will also be increases. Therefore, the large amount of drag force tend to push the wing model further backward resulting in the inability of the designed test rig to precisely capture the lift force generated by the wing model.

Another set of experiment was conducted in order to determine the mentioned behavior. The experiments were performed by using rectangular wing models, both having flat plate airfoil however, with different aspect ratios which were 0.5 and 1.0. The experimental data were later validated with the experimental data of Alain and Thomas [9] as illustrated in Fig. (8).

Lift Coefficient for flat plate airfoils

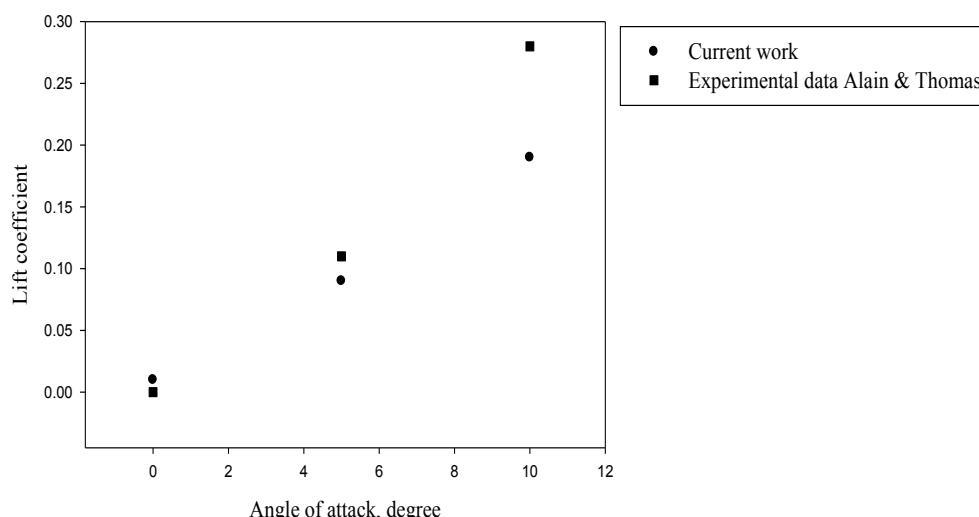


Figure 8: Lift Coefficient for various aspect ratios Rectangular wing models at 140000 Reynolds number

Based on Fig. (8), it can be seen that similar behavior of experimental data were obtained as the previous experimental data. Larger deviations can be seen to occur at 10° angle of attack than at 5° angle of attack. Therefore, this concluded that the designed test rig was sensitive towards the vibration. As an attempt to reduce the effect of this factor towards the reliability of the project, the further experiments were performed by fixing the wing models at 5° angle of attack.

Next set of experiment was performed by all the wing models having a flat plate airfoil however, with different aspect ratios which were 0.5 and 1.0 respectively. The aim of this set of experiment was to determine the effect of aspect ratio towards the lift generated by the wing models.

Based on the Fig. (9), it can be seen that the effect of aspect ratio towards the lift generated is significant. For instances, the rectangular wing model having an aspect ratio of 1.0 had generated 0.09 lift coefficient while the rectangular wing model having an aspect ratio of 0.5 only managed to generate 0.16 lift coefficient. This was expected as the higher aspect ratio means that the span of the wing is larger hence, the vortex flow effect that occurred at the wing tip is less exerted by the higher aspect ratio wing when compared to the lower aspect ratio wing [14]. As evidence, similar behavior was also predicted by Alain and Thomas [9]. This concluded that the effect of aspect ratio is significant at low subsonic speeds.

After that, another set of experiment was performed by all the wing models having a flat plate airfoil and 1.0 aspect ratio. However, unlike in previous set of experiment which was using rectangular wing models, this set of experiment was performed by using trapezoidal wing models with different taper ratios of 0.66 and 0.72 respectively. The aim of this set of experiment was to determine the effect of taper ratio towards the lift generated by the wing models at low subsonic speeds.

Lift Coefficient for various aspect ratios Rectangular wing models

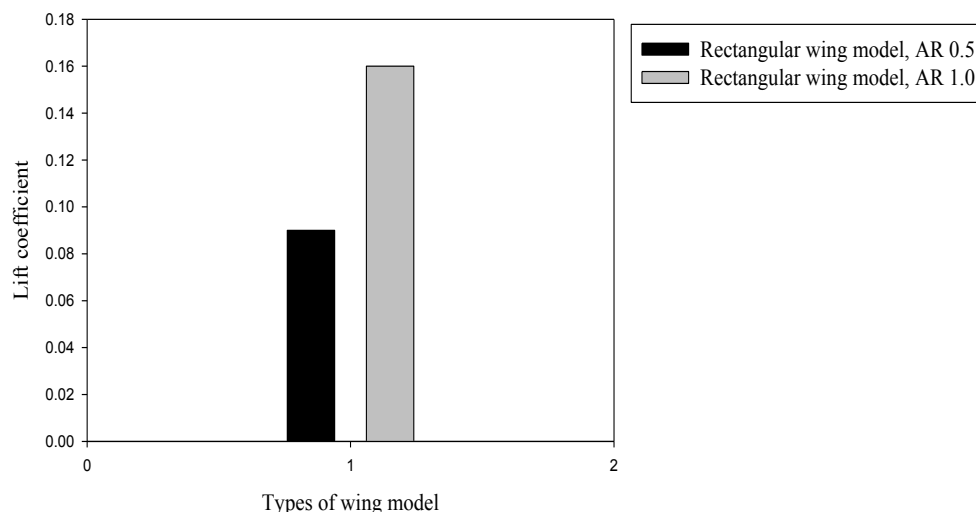


Figure 9: Lift Coefficient for various aspect ratios Rectangular wing models at 140000 Reynolds number

Based on Fig. (10), it can be seen that the more tapered trapezoidal wing had lower amount of lift generated compared to the less tapered trapezoidal wing. This is supported by the existing theory where it said that the more tapered wing should have lesser lift generated due to the less surface area that was chopped off from the wing [14]. Even so, it can be seen that only small differences in the lift generated between both trapezoidal wing models and the effect seems to be almost insignificant.

With regards to the small differences data, the behavior observed might be occurred due to insignificant effect of taper ratio at low subsonic speeds. As evidence, the tapered wings are usually used for high speed aircraft like Boeing and Concorde which the speed regimes of the flights are likely to be in higher subsonic or

supersonic speeds. Thus, the effect of taper ratio towards the lift generated at low subsonic speeds was concluded to be extremely small.

Next, another set of experiment was executed by using three different shapes of wing models with all having aspect ratio of 1.0; Rectangular, Trapezoidal and Triangular. The aim of this set of experiment was to determine the effect of wing shapes towards the lift generated by the wing models.

Lift Coefficient for various taper ratios Trapezoidal wing models



Figure 10: Lift Coefficient for various taper ratios Trapezoidal wing models at 140000 Reynolds number

However, problem arises during executing the experiment as the triangular wing model was designed to have a decreasing thickness along the wing span. This caused difficulties when trying to drill through the wing model in order to fit in the support rod within the wing model. Therefore, as a solution, the triangular wing model was redesigned by having a vertical plate welded at the center, on top of the wing model. Next, the vertical plate was drilled to enable the support rod to be fitted in, in order to hold the wing model within the test section. The entire experimental data were presented in Fig. (11).

Based on Fig. (11), it can be seen that the triangular wing model had significant deviations from the other shape of wing model. The experimental data seems to conclude that the triangular wing model had the lowest lift generated. It was indeed strange as the trapezoidal wing model and the rectangular wing model had almost insignificant effect due to the different shapes. As the triangular wing model was the only one to have an addition feature than the others, the experimental data was suspected to be affected by some errors.

Therefore, as the triangular wing model was seems to be having a vertical fin, a thorough investigation was performed focusing on the effect of vertical fin on the distribution of flow passing through it. Based on the existing theories, the vertical fin is used by most aircrafts nowadays in order to stabilize the aircraft from rotating side to side. This rotation from side to side is widely called as the yawing moment [20]. In

an attempt to stabilize the aircraft, the vertical fin must be designed straightly aligned possible on the center of the aircraft body in order to prevent the aircraft from having a yaw moment.

Lift Coefficient for various shapes of wing models

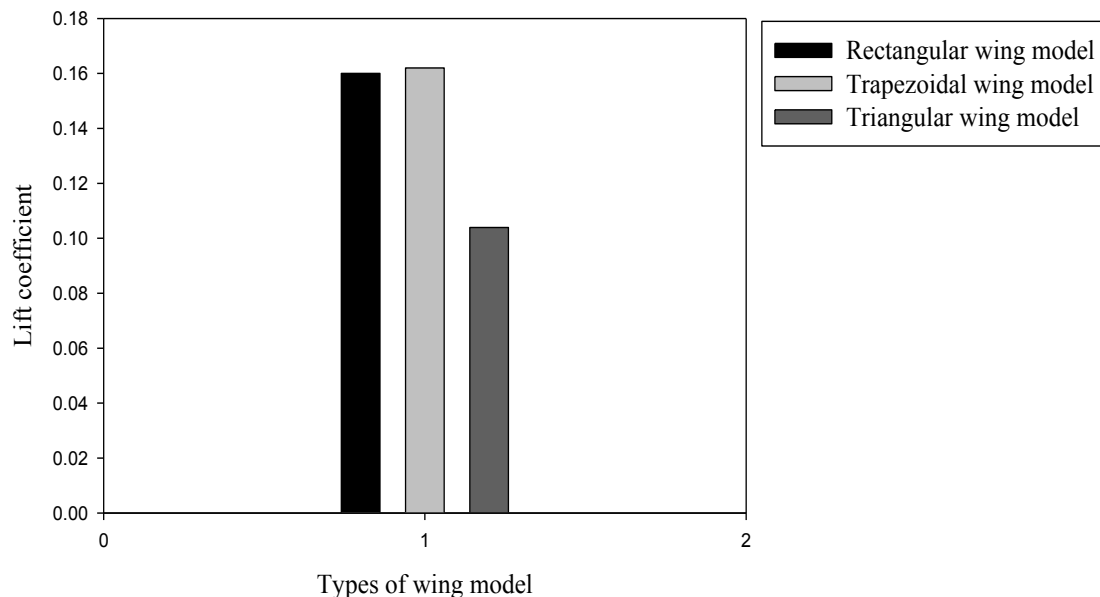


Figure 11: Lift Coefficient for various shapes of wing models at 140000 Reynolds number

Thus, when rechecking the triangular wing model again, it was found that the vertical plate was not welded straightly aligned to the center of the wing model instead, having a slightly off towards the left direction. This might cause the triangular wing model to be yawed hence, causing the test rig to be vibrated unusually from the other experiments. As a result, the lift generated by the triangular wing model was unable to be precisely captured by the load cell. As these errors was affecting the experimental data of the triangular wing model, this set of experiment was concluded with the effect of different shapes of wing model is not significant at low subsonic speeds.

After that, several investigations were done in order to determine the accuracy of the semi empirical method in estimating the lift generated by the wing models at low subsonic speeds. For the first investigation, the experimental data for rectangular wing models with different aspect ratios were compared with the semi-empirical data obtained in this project. The comparisons of data are presented in Fig. (12).

Based on Fig. (12), it can be seen that the semi empirical method used in this project managed to estimate the lift generated by the 0.5 aspect ratio rectangular wing model. However, it can be seen that the semi empirical method used in this project was underestimating the lift generated by the 1.0 aspect ratio rectangular wing model. The reasoning to this might be due to the incapability of the semi empirical method to take into account the vortex induced lift effect. Vortex induced lift effect is the lift generated due to the flows that are vorticing around the wing. When streams are let passing through the wing model, at one point, the stream will starting to form a vortex

flow around the wing model. This vortex flow will increase the lift generated by the wing model. As this factor is not taken into consideration by the semi empirical method, the semi empirical method used in this project was unable to estimate the lift generated by the larger aspect ratio wing model. Therefore, it was concluded that the semi empirical method used in this project was able to estimate the lift generated by the rectangular wing model however, it tends to underestimate as the increasing of aspect ratio.

Comparison between experimental data and semi empirical data for Rectangular wing models

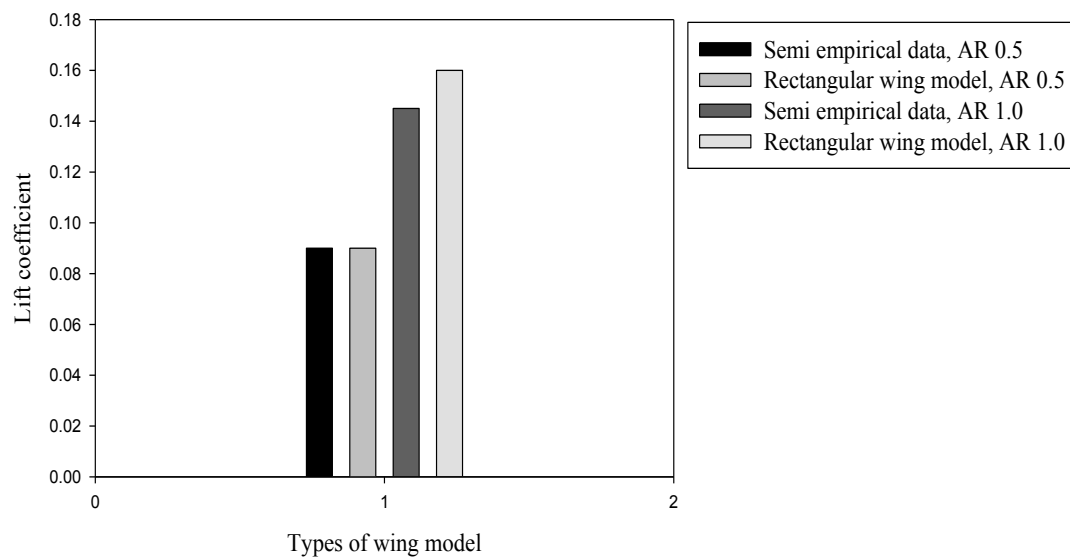


**Figure 12: Comparison between experimental data and semi-empirical data
 for Rectangular wing models**

For the second and the last investigation, the experimental data for all the wing models having aspect ratio of 1.0 were compared with the semi empirical data obtained in this project. The comparison of the data are presented in Fig. (13).

Based on Fig. (13), it can be seen that similar value of lift was estimated by the semi empirical method used in this project for all the wing models having 1.0 aspect ratio. The reasoning to this might be due to the incapability of the semi empirical method applied to take into account the effect of taper ratio and wing shapes towards the lift generated by the wing models. Based on Fig. (13), it can also be seen that the semi empirical method used in this project was underestimating the lift generated by all the wing models except for triangular wing model. The closest estimation by the semi empirical method for wing models having aspect ratio of 1.0 was the trapezoidal wing with having taper ratio of 0.72. The deviations between the data was only 0.01. On the other hand, the furthest estimation of the semi empirical method was occurred for the triangular wing model which illustrated 0.04 data differences. However, as the data for the triangular wing model was unreliable due to the several factors discussed previously, this indicates that the furthest estimation of the semi empirical method was occurred for the trapezoidal wing model having a taper ratio of 0.66. Again, this concluded that the semi empirical method applied in this project was unable to take

into account the effect of vortex induced lift, taper ratio and wing shapes when estimating the lift generated by the wing models at low subsonic speeds.

Comparison between the experimental data and semi empirical data for all the wing models having 1.0 aspect ratio

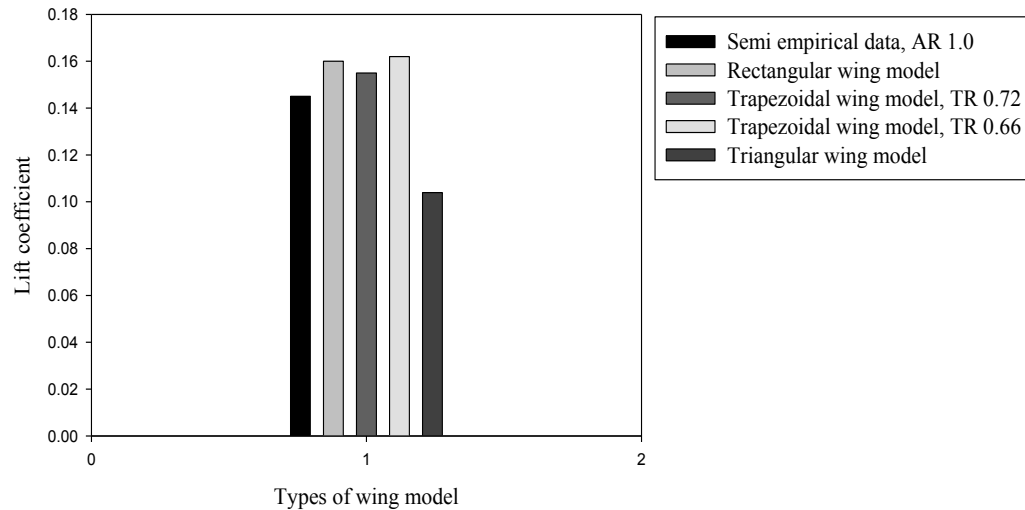


Figure 13: Comparison between the experimental data and semi empirical data for all the wing models having 1.0 aspect ratio

4. Conclusions

As a result, It was found out that the effect of aspect ratio towards the lift is significant at low subsonic speeds however, the effect of wing shapes and taper ratio towards the lift are extremely small. These behavior might be predicted at low subsonic flow. Also, the empirical formulae developed in this project was found out to underestimate the lift generated by the wing models. The reasoning to this is due to the incapability of the empirical formulae developed to take into account the effect of the vortex induced lift of the wing models. It was also found out that the empirical formulae developed was unable to take into account the effect of wing shapes and taper ratio as similar value of lift was yielded for all the wing models with having 1.0 aspect ratio.

As a recommendation for future works, the test rig used in this project can be redesigned to be mountly rigid to the ground in order to reduce the vibration of the test rig. This will helps in increasing the accuracy of the experimental data obtained. This will also allows further investigation on the effect of wing shapes and geometries on lift at low subsonic speeds at higher angle of attack. Along completing this project, several interesting areas were determined by the author to be investigated for future works; the investigation on the aerodynamic performances of micro air vehicle and the aerodynamic performances of a rotated aircraft due to crash.

Acknowledgment

The authors wish to deliver their appreciation to Taylor's University School of Engineering for granted permission to use the wind tunnel facilities in order to achieve the research objective.

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Thrust Generation Using Synthetic Jet

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Abstract

This study aims to explore new application of synthetic jet that utilizes the generated thrust for propelling purposes. The feasibility of synthetic jet as the propulsion system for a small underwater vehicle has already been proven. Nonetheless, there are few to none study validated its practicality as an airborne propulsion method. Hence, this study attempts to reveal the possibility of synthetic jet as a novel thruster of micro-air vehicle by investigating the capability of synthetic jet in term of thrust generation. Micro-air vehicle (MAV) is classified as aerial vehicle that has size restriction and deployed for various purposes comprising surveillance watching, military spying and others. This type of vehicle has developed since few decades ago as there is an on-going effort to study new techniques for air-vehicle propulsion. A helium-gas blimp with a volume of 0.5 m³ was referred to estimate roughly the needed thrust by calculating the drag force. A synthetic jet prototype was developed and tested. Its capable of producing thrust by pulsatile vortex ring was expected to overcome the blimp's drag force. To comply with the objective of this study, the prototype design replicates the scheme of micro-thruster which has several properties such as small-size, light-weight and low operating power. The performance of synthetic jet was assessed using direct thrust measurement. The result was verified with previous research data. In flight fundamental context, thrust generated by our synthetic jet is proven to overcome the drag force and the hypothesis is accepted; synthetic jet is a viable method for airborne propulsion. However, there are several factors (such as thrust-to-weight ratio, ratio of propeller size to propulsion power, and etc.) must be considered when dealing with micro-sized flying object and future work must consider those factors.

Keywords: Synthetic Jet, Thruster, Airborne Propulsion System, Micro-Air Vehicle, Direct Thrust Measurement.

1. Introduction

The science of flight stated four fundamentals which are lift, weight, thrust, and drag as shown in Fig.1 [1]. In designing an aircraft, engineers consider those elements to ensure the airplane travels through the air successfully. In a steady flight, the sums of all opposing forces are equal and thus complies with the conservation of momentum principle. Weight and lift force govern the altitude of the plane. To move the plane forward, the thrust must be greater than the drag [2].

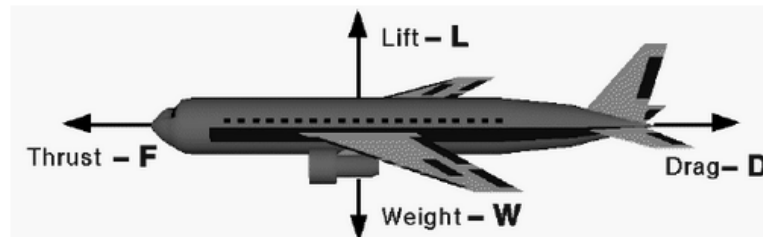


Figure 2. Four flight fundamentals [3]

Fluid dynamics define jet as fluid ejection from a duct into relatively large region through an orifice or nozzle [4]. Meanwhile, synthetic jet is a flow generated by alternate suction and ejection of the ambient fluid through an orifice with zero net mass flux. It has distinctive feature which is it enables the transfer of linear momentum to the flow system. The jet is different from synthetic jet as the net mass flux is not zero at one end where the fluid is supplied (mass inlet).

The study of thrust generation using synthetic jet has progressed since few decades ago. Its feasibility in various applications has been proven through a sensible amount of studies; an effective aerodynamic controller for airplane wing, effective chemical mixer replacing conventional agitator, viable propulsion method for underwater autonomous unmanned vehicle, and lastly efficient cooling device for electronic component [5-8].

Micro-air vehicle is an aerial vehicle flies in low Reynold's number at velocity up to 10m/sec [9]. It has numerous potential applications that benefit civilian and military. Usually, the propulsion system consists of electrical motor and power supply. The challenge of building this type of vehicle is maintaining the design compactness with electronic component installation to achieve mass restriction.



Figure 3. Example of micro-air vehicle with 7.3 cm wingspan [9]

There is an ongoing effort to study new techniques of micro-air propulsion [10]. To date, there are several methods of synthetic jet actuation, which is driven by piezoelectric, mechanical, electrostatic, plasma, and acoustic [5]. Each type has been tested experimentally as well as simulation using computational fluid dynamic software. However, not even single study had produced a scheme for airborne propulsion with concrete proof of its practicality when deployed together with air-vehicle.

This study tends to propose a new application of synthetic jet thruster. It has a potential to be deployed as thrusters for the flying surveillance camera. This type of air vehicle moves with slow speed because of low-thrust propulsion system and is suitable to be used in low wind interference surrounding such as shopping mall, examination hall and other places that fit to its capability. This idea is inspired by the immobility of surveillance camera that has a fixed position and limited view.

For that specific use, a synthetic jet prototype was constructed based on crude approximation of the thrust range needed to move a helium-gas blimp [11]. Helium gas inside the blimp provides the lifting force to carry payload. Meanwhile, the calculated drag force of the blimp ranges between 0.05mN to 1.36mN. If the thrust generated by synthetic jet prototype exceeds the drag force of the blimp, theoretically this air-vehicle will move forward [1].

A synthetic jet thruster will be placed at the bottom of a blimp parallel to the vehicle center of buoyancy. The thrust generated from thruster (F_{SJT}) will produce a reaction force (F_R) in the opposite direction. The force supplied from the thruster will initiate the movement of the blimp and cause it to travel in x-direction. Free body diagram showed in Fig. 3 provide a clear conception of the system.

The reaction force (F_R) generated from synthetic jet thruster will provide a force to the blimp, F_T . According to the Principle of Conservation of Momentum, movement will be initiated if the total thrust force greater than the total drag as equated in Equation 1. This blimp will travel at a constant speed when total forces of F_T and F_D are equal (Eq. 2).

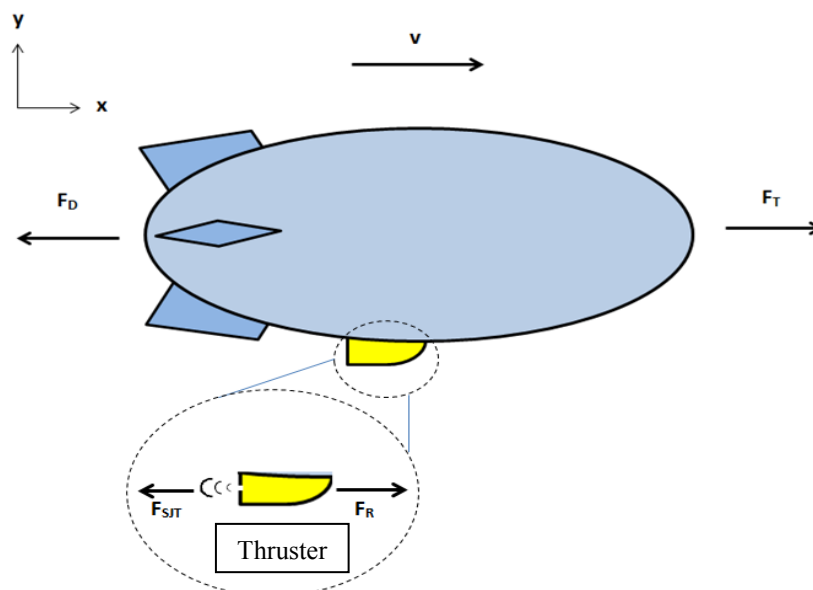


Figure 4. Free body diagram of blimp's propulsion system

$$\Sigma F_T > \Sigma F_D \quad (1) \text{ To initiate blimp movement}$$

$$\Sigma F_T = \Sigma F_D \quad (2) \text{ To blimp moves at constant speed}$$

As stated before, this study aims to develop the potential of synthetic jet as a thrust production device as well as to propose a new application of synthetic jet and identifies the range of application. Other than that, the objectives include:

- i. To identify the range of synthetic jet application as well as to clarify the gap within the area of study.
- ii. To design and build a synthetic jet prototype with optimum geometric configuration inspired from existing models.
- iii. To evaluate and select an appropriate method of measuring thrust specifically for synthetic jet prototype.

Usually, a synthetic jet model consists of cavity/chamber, diaphragm/membrane orifice and actuator (shown in Fig. 4) [12-13]. The actuator is used to synthesize jet flow meanwhile membrane is made up of elastic material which can deflect correspondingly to the frequency and amplitude of the actuator.

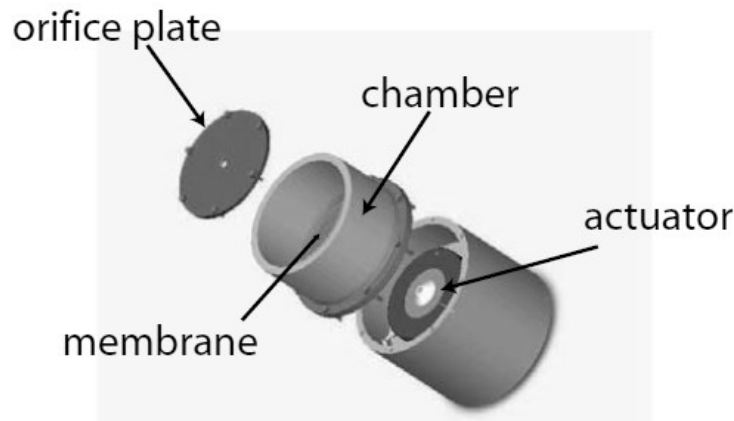


Figure 5. Parts of synthetic jet thruster [7]

When actuator stimulates movement of the diaphragm in oscillating manner, it will displace the cavity volume and lead to changes in mass of air inside the cavity. Mass flow rate flux inside the cavity resulted in pulsatile jet formation. Fig. 5 showed the formation of synthetic jet flow. (A) Intake stroke. (B) Ejection stroke. (C) Vortex pinched-off. (D) Successive vortex move away and the process repeats.

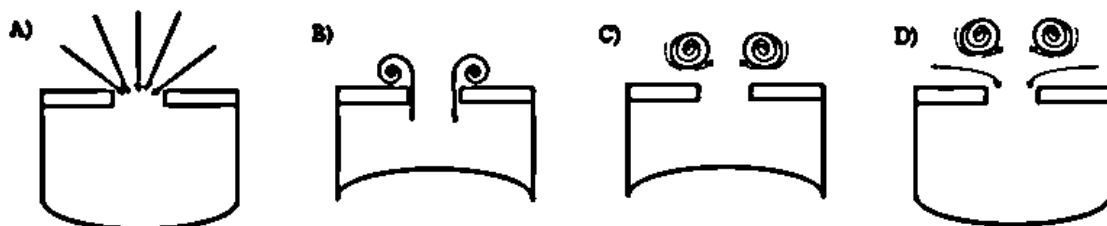


Figure 6. Synthetic jet formation [13]

2. Methodology

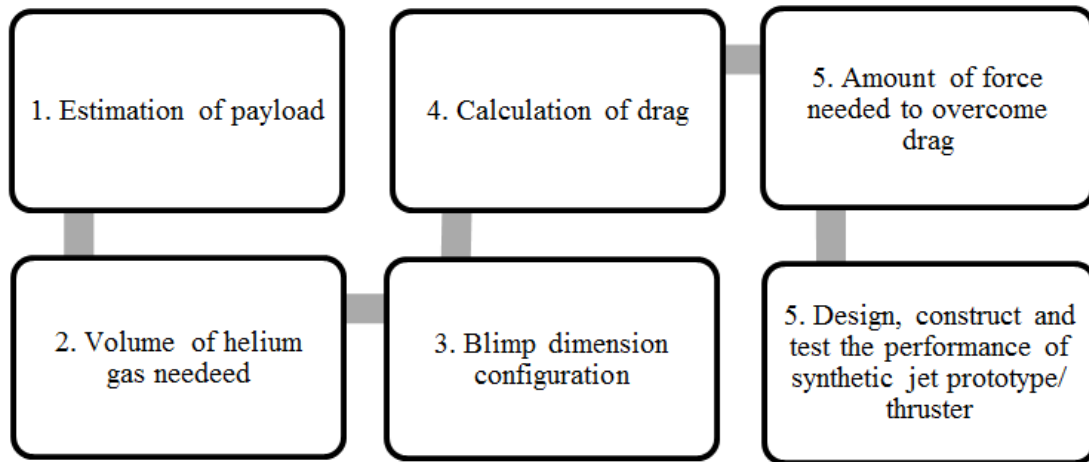


Figure 7. Propulsion system design procedure

To design a propulsion system of a blimp, it must follow the procedure as shown in Fig. 6 [11]. Firstly, estimation is made on the total weight of the payload by considering all possible components that build up the propulsion system. The system made up of thruster, electronics component and power supply. The total weight of the system is approximately 450g. Note that, the weights of all components were crudely estimated except for thruster, which used actual value.

The lifting force of helium gas is 1.02kg/m^3 at room temperature and atmospheric pressure at sea level [11]. From the total estimated payload, the required volume of the gas is about 0.45m^3 . Thus, the dimension of the blimp can be determined as well as the drag. Tayyab [11] proposed a dimension configuration of a 0.5m^3 blimp that has a total surface area of 3.474m^2 , a length of 2.07m and frontal area of 0.37m^2 .

By knowing the dimension of the blimp, drag can be calculated to determine the thrust need to be generated. Note that, the construction of the blimp is not included in this research; instead it is just a reference to generate an amount of thrust. The performance of the thruster can be determined from drag against velocity graph. It also determines the maximum speed of the blimp can move with the thruster

The synthetic jet prototype geometry was determined by rationing the diameter of the cavity to diameter of existing model [10]. Using the ratio of 15, our prototype was scaled down in size to achieve design compactness even though the actuation power is reduced. It consists of four elementary parts; orifice plate (overall diameter of 5cm and orifice diameter of 0.3cm), cavity/chamber (diameter of 4.5cm and height of 0.5cm), membrane/diaphragm (rubber) and actuator (speaker). Fig. 7 showed the prototype 3D drawing and end product.

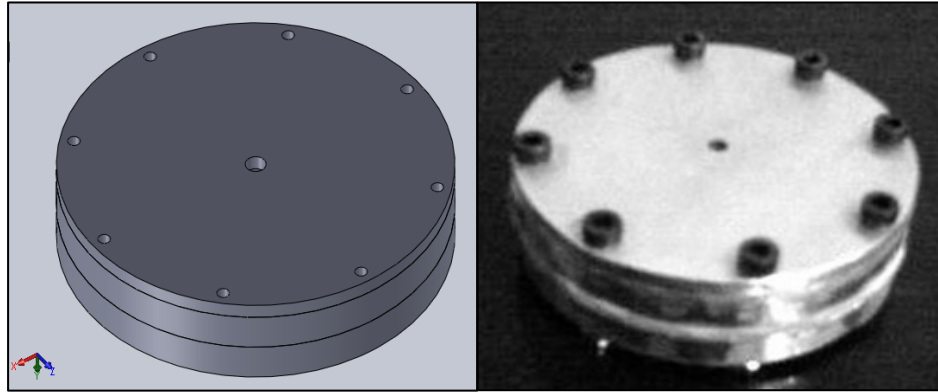


Figure 8. Synthetic jet prototype 3D Drawing using Solidworks (left) and manufactured prototype (right).

Since this area of study has not specified a standard scheme of thrust measurement experiment, we have selected the method based on a few factors; resolution, availability, and reliability. Hence, the performance of the thruster was assessed using direct thrust measurement in which the thruster was entirely mounted on an electronic balance [10]. The measurement of thrust was carried out in vertical direction. However, in real operation, the thruster will be deployed in horizontal direction.

The complexity of the prototype design and the actuation method has lagged this study. Other factors such as time-constraining research period (twelve weeks) and limited-budget has caused this research focused more on the construction and testing the actuation technique that produces a significant deflection to the membrane.

2.1 Synthetic Jet Thrust Calculation

There are several schemes of synthetic jet thrust calculation provided [7,10]. The fundamental of thrust calculation originates from a slug model (shown in Fig. 8) which represent stroke ratio denoted as L/D [5,12,13,14]. This non-dimensional analysis is the ratio of stroke length to the diameter of the ejected fluid. D is the diameter of the orifice and L can be obtained by integrating the centerline velocity (U_0) of the fluid within the period (T) of one successive ejection. The formula is stated below:

$$L = \int_0^T U_0(t) dt \quad (3)$$

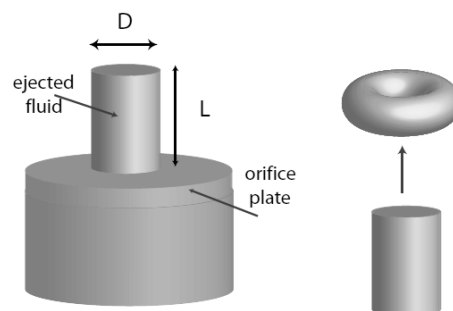


Figure 9. Slug model [7]

The ejected fluid travels away from the orifice at the velocity corresponding to the membrane actuation speed. It then forms a circle and creating impulse which determines the vortex strength [7]. The total circulation (Γ_o) can be calculated using Equation 4 [10]. Meanwhile, Equation 5 is the formula of synthetic jet thrust (T_h) related to the circulation. This formula contains the density of air (ρ), actuation frequency (f) and effective cross-section area of the jet orifice (A_{je}).

$$\Gamma_o = \frac{1}{2} \int_0^T U_o^2 dt \quad (4)$$

$$T_h = 2\rho\Gamma_o f A_{je} \quad (5)$$

2.2 Direct Thrust Measurement

Thrust measurement using analytic balance is not a new method. It replicates the practice of force measurement experiment using load cell or force sensor. It has been practiced by preceding work to directly measure the amount of thrust generated [7,10, 15]. This method uses the relationship between force and mass of Newton's Second Law ($F=ma$). As the acceleration of gravity is considered to be constant at all time, the force will increase corresponding to mass increment. An analytical balance with resolution of 0.001g was used to measure the thrust generated by the synthetic jet prototype.

The setup of the experiment is shown in Fig. 9 whereby the entire synthetic jet prototype was mounted on the electronics balance. The frequency was controlled by a function generator. Sine wave was used and the frequency slowly increased. The results obtained in a unit mass (gram) were recorded and tabulated for analysis. The measured mass was converted to unit Newton to obtain the thrust force.

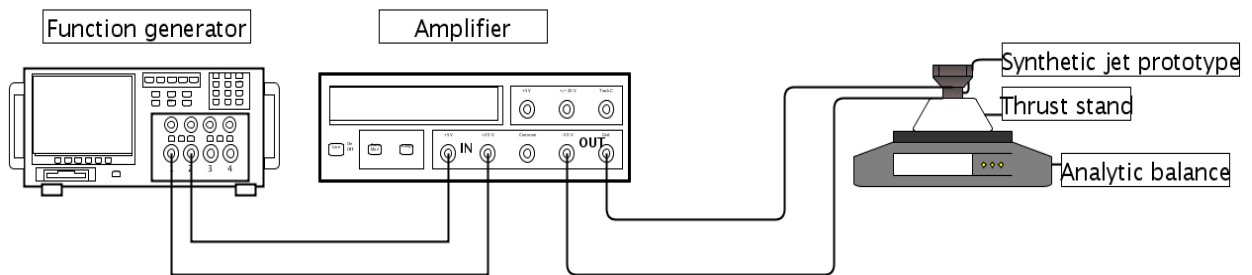


Figure 10. Schematic diagram of experiment set up

The prototype is oriented in y-direction for the thrust measurement purpose as shown in Fig. 10. However, in real operation, the thruster will be deployed in x-direction. When the synthetic jet prototype is actuated by the speaker, the membrane is deflected. This will cause alternate suction and ejection of ambient flow inside the cavity of the prototype. Then thrust (F_{SJT}) is generated through the orifice. The reaction force (F_R) can be measured by analytic balance in unit gram.

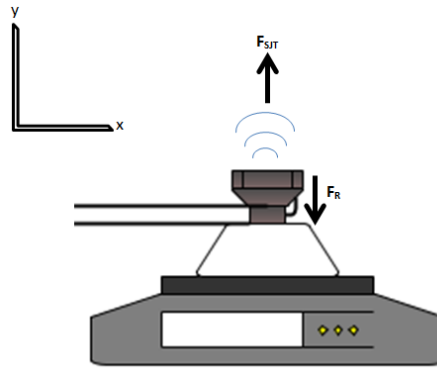


Figure 11. Synthetic jet prototype orientation in experiment set up

3. Results & Discussion

The graphs below show the relationship between actuation frequency and thrust generated. The graph on the left represents the experimental results (present work) and on the right is the previous experiment [10].

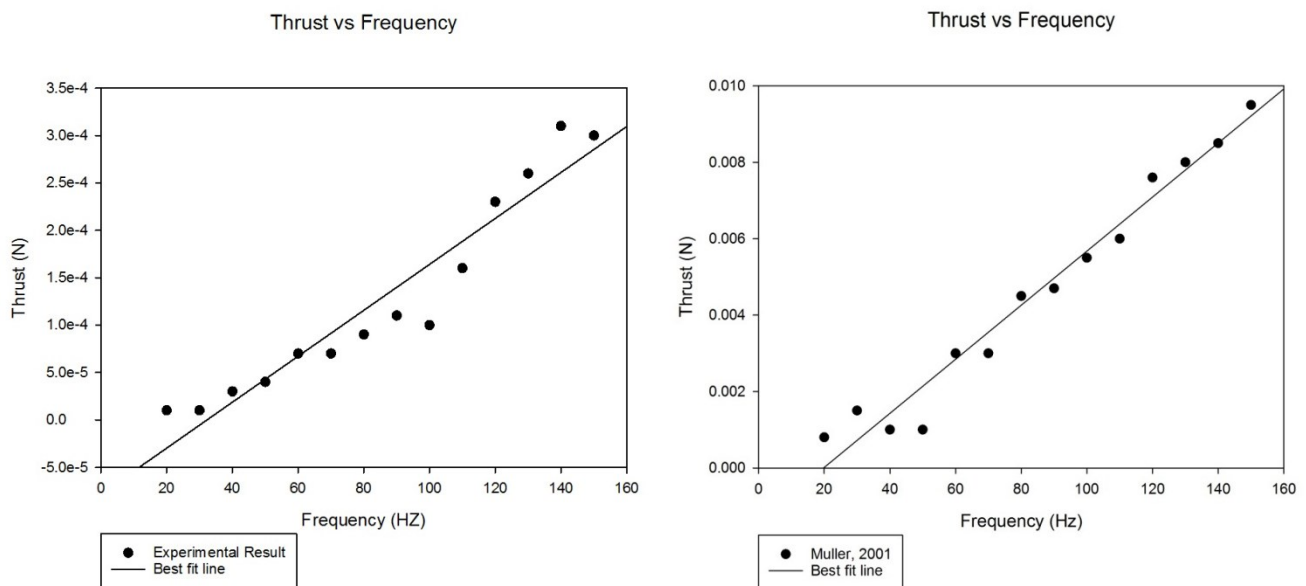


Figure 12. Experimental result (left) & experiment by Muller (right)

From Fig. 11 (left), by increasing the actuation frequency using function generator, the reading of weight increases gradually. The weight increment indicates the increasing thrust. The pulse generated by synthetic jet produces higher thrust at higher frequency. This is because the vortex rings produced are close to each other; hence increase the entrainment effect [5].

Experimental data have a lowest thrust of 0.01mN at 20Hz and highest thrust of 0.31mN at 140 Hz. At 10Hz, no reading was recorded in the analytical balance, means that the fluid ejected is not able to circulate and produce a pulse. This may come from

suction effect on the flow structure whereby synthetic jet flow with L/D less than 1 cannot attain circulation and no vortex ring produced [12].

Results from preliminary work (right) has higher value of thrust generated. The thrust ranges from 0.8mN to 9.5mN at frequency between 20Hz to 150Hz. The current experiment shows a positive result as it agrees with the previous experiment data in term of increasing pattern. However, the thrust generated from current experiment is lower compared to preliminary study because the geometry was scaled down but maintained the ratio of the diameter of the orifice and the cavity.

The actuation power was reduced because of size reduction from original synthetic jet model geometry. This sacrifice is made to increase the compactness of the thruster so that it is suitable to be deployed with a micro - air vehicle.

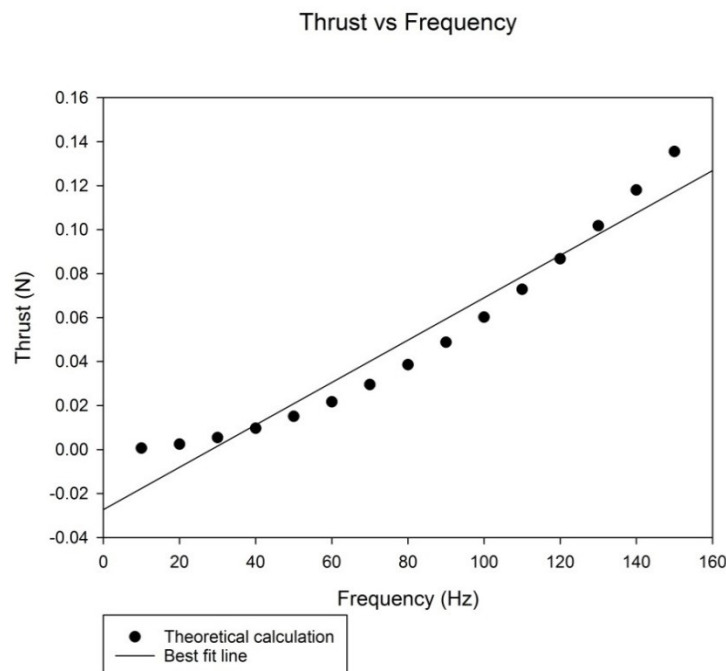


Figure 13. Theoretical calculation of synthetic jet thrust

The theoretical result seems to increase exponentially as shown in Fig. 12. The highest thrust recorded from theory is 0.13N at an actuation frequency of 150Hz. Note that, there is no research has ever produced a scheme of theoretical calculation results; make it unreliable to be compared with experimental work. Some factors may contribute to this incident.

The calculation considered each actuation will produce one complete circulation of ejected fluid and form a successive vortex ring. In reality, the actuation frequency of 10Hz will not produce an exact 10 circulations of ejected fluid. It must be lower because the interaction among parameters such as amplitude, dimension configuration and also interference of external flow.

This vehicle is expected to carry out surveillance-watching task in the supermarket. The drag was calculated with varying values of velocity. A graph was plotted and presented below. It showed the drag increasing exponentially correspond to the speed.

The maximum thrust generated from synthetic jet prototype was plotted as a horizontal line to show the limit of propelling capacity.

The graph indicates that the blimp's velocity must not exceed 0.23m/s because the thruster cannot overcome the drag force. The total weight of the synthetic jet prototype is less than 50g. This will benefit the vehicle in term of mass restriction in which other pertaining component such as extra batteries and more complex electronics circuit can be fitted into the propulsion system. To make it move faster, a combination of synthetic jet thrusters would be applicable.

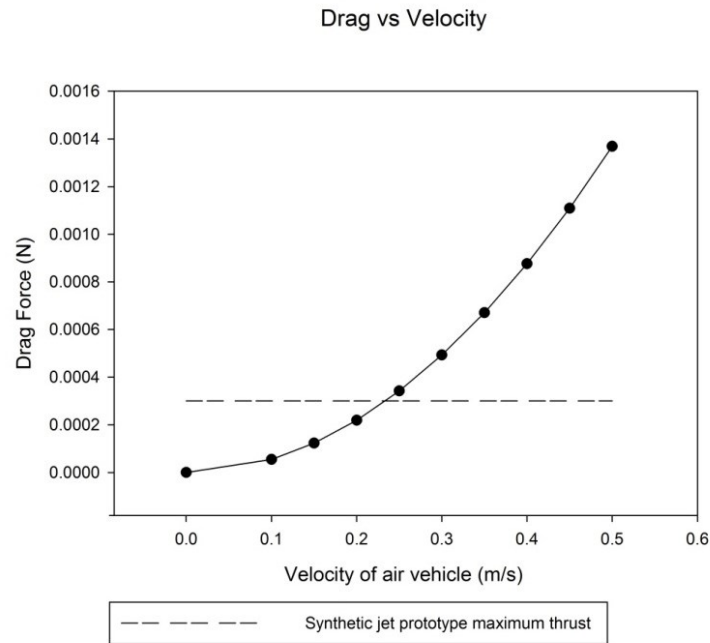


Figure 14. Drag vs velocity graph

4. Conclusion

The thrust performance of a synthetic jet thruster has been analyzed and it is found to be a feasible alternative for micro-air vehicle in term of propelling in horizontal direction. It still needs support from the blimp filled with helium gas to lift up the entire vehicle plus the synthetic jet thruster. The experimental results showed maximum thrust production of 0.31mN, which overcome the drag force of the blimp below 0.23m/s. This vehicle can be improved by constructing a smaller actuator (1/4 of present model) and provide higher actuation power so it can travel faster, and at the same time reduce the total weight.

Acknowledgement

The authors want to express their gratitude and appreciation to Taylor's University School of Engineering for funding this project to enable its successful completion. Additionally, we would also like to acknowledge Mr. Sunny and Mr. Alif for helping authors throughout the construction and experimentation of our synthetic jet prototype.

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Effect of Evaporator Heater Power Input and Condenser Water Flow Rate on the Performance of a Refrigerator – Developing Empirical Models

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Abstract

Refrigerators are heat pumps that transfer heat from a volume of space as to reduce the temperature compared to the ambient temperature of its location. Refrigerators are also the one of the notorious contributors to high monthly electricity bill. This paper presents first a comparison between theoretical and experimental determination of the coefficient of performance (COP) of a vapor compression refrigeration cycle. Secondly, derivation of empirical models based on experimental results that would allow refrigerator designers to check on the significance of each investigated parameter on the COP value. There were three models created. Model 1 took both evaporator heater power input (EHPI) and condenser water flow rate (CWFR) in to consideration and produced the most accurate at 97.2%. Model 2 and Model 3 just took into account EHPI and CWFR respectively and produced accuracies of 94.3% and 3.12% respectively. Therefore, Model 1 was found to be as the best predictor of COP. The results produced by the final model were within the uncertainty range of -9.49% and 2.55% compared to the experimental results. This was with in the acceptable range of $\pm 10\%$. The overall error could be minimized by including other important parameter in to the model and also by further limiting the heat transfer to the surrounding.

Keywords: Coefficient of Performance, Refrigeration, Efficiency, Vapor Compression Cycle, Empirical model.

1. INTRODUCTION

1.1. Background

Household refrigerators are machines or devices that are normally used for preserving food by reducing the temperature of its storage compartments. There are a few types of refrigeration cycles that are suitable to achieve this function. However, vapor compression refrigeration cycles (VCRC) are the most widely used cycle for household refrigerators due to its high versatility. On the other hand, refrigerators are also notorious for their high energy consumption alongside air conditioning systems. Amongst the many reasons for high energy consumption, around the clock operation and the complex irreversibility of the individual mechanical and electrical components are the major two contributing factors. Therefore, optimization of the performance of a refrigerator has become a necessity.

During the past few decades, ejector-vapor compression cycles (EVCC) has been probed significantly in efforts to optimize the COP of basic VCRC. Zhu & Jiang [1] using working fluid R22, Yan et al. [2] using working fluid R134a and Ersoy & Bilir Sag [3] using various different types of working fluids was able to achieve as COP improvements as high as 9.1%, 14.5% and 21.0% respectively. Molés et al. [4] argued that the COP of hybrid cycles operated with low Global Warming Potential (GWP) refrigerants, such as R1234yf and R1234ze(E), instead of more conventional ones, such as R134a, improved up to 15% and 20% while the COP of the basic VCC reduced by 4% to 8%. Still, this study also indicated that replacement of conventional refrigerants may increase the complexity of the practical system and ultimately the cost.

In general, although such integrated EVCCs require a similar amount of operating cost, it contains almost twice the amount of components as a basic VCRC. This increase in the number of components may require more energy and also would be subjected to more losses, despite the overall improvement in performance. Thus, it is believed that the amount of improvement achieved by this hybridization is relatively low. Moreover, Sarkar [5] indicated that, besides promising improvements more research was required to make an impact in large scale usage.

Li et al. and Wang et al. [6,7] argued another type of hybridized cycle, which uses an organic Rankine cycle (ORC) to power up the basic VCC, that improved the overall COP by 0.47 and 0.6. Both studies agreed that an additional recuperator at the ORC side of the system would further increase the overall COP. But, once again it was conclusive that the degree of improvement achieved with severe modification was unsatisfyingly low. Further modification that may need to rise the COP slightly more. This would result in further increase in cost of operation and maintenance.

Besides complex physical modification, refrigeration cycles may also be optimized grounded on mathematical or analytical modeling according to theoretical or experimental data. Model based optimizations are cheap and ideal methods to predict the effect of design parameters on the COP of the refrigeration system during the preliminary design stage. Studies conducted by Domanski et al., Wainaina et al., Zhao et al., Wallace et al. and Gonçalves et al. [8-12] provided insightful models that were related to optimization of the basic VCRC.

Similarly, Jain et al., Yao et al., Waltrich et al., Li & Alleyne, Getu & Bansal and Navarro-Esbrí et al. [14–19] produced optimization model that may improve the VCRC. Though, these studies varied off from the simplicity and was deviated to modified hybrid system and specific operation condition or parameter.

Yusof & Azizuddin [20] performed experimentation and identified how the different parameters of the refrigerators behaved over time. Although, a relationship between these parameters and the COP were not displayed, the combination the selective techniques utilized within these studies would provide a platform. These studies lacked the simple and direct correlation of the COP with other basic operational parameters.

In order to design a refrigerator system with optimal performance, predetermining the correlation of individual design parameters to the COP seems somewhat crucial. Similarly, to understand the significance of the design parameters in an existing system may also provide time and cost saving assistance. Therefore, optimization of the simple VCRC could provide priceless and insightful information which could be used during the preliminary design stage of household refrigerator systems. With such optimized models, a VCRC refrigeration systems could be design to have optimal efficiency with low initial cost and almost negligible amount of testing.

Hence, the aim of this paper is to develop empirical models that correlates the effects of operational parameters such as the evaporator input and water flow rate with the coefficient of performance of the refrigerator, and ultimately fabricating a design table that could be utilized as a quick, cheap and yet reliably accurate tool during the preliminary design stage.

1.2. Coefficient of Performance

Overall Coefficient of Performance (COP) is the ratio between the rate of heat, Q_e , absorbed at the evaporator and the net work done, W_{in} , by the compressor as shown in the Eq. (1) below. It one of the most commonly used measure of performance efficiency.

$$COP_R = \frac{Q_e}{W_{in}} = \frac{Q_e}{Q_c - Q_e} = \frac{h_1 - h_4}{h_2 - h_1} \quad (1)$$

The performance of refrigerator systems could be improved to perform exceptionally better by modifying and altering its elements. However, such modifications and experimentations are usually costly as they may require state of the art components and research. Carnot cycle or ideal VCRC provide crucial information about the full potential. But, it would also indisputably overestimate the COP of a real life refrigeration systems due to the high irreversibility. A comparison between the fundamental theories of the ideal and actual VCRC would help recognize the losses in real operations.

2. METHODOLOGY

2.1. Refrigerant Cycle

Vapor compression refrigeration cycles (VCRC) are known to be one of the most commonly used and versatile refrigeration cycle. VCRC are suitable for almost all applications in a wide range of cooling capacities from just a few watts to a few megawatts. As seen in Fig. 1, a basic vapor compression cycle consists of a compressor, condenser, expansion device, evaporator and a working fluid; a refrigerant.

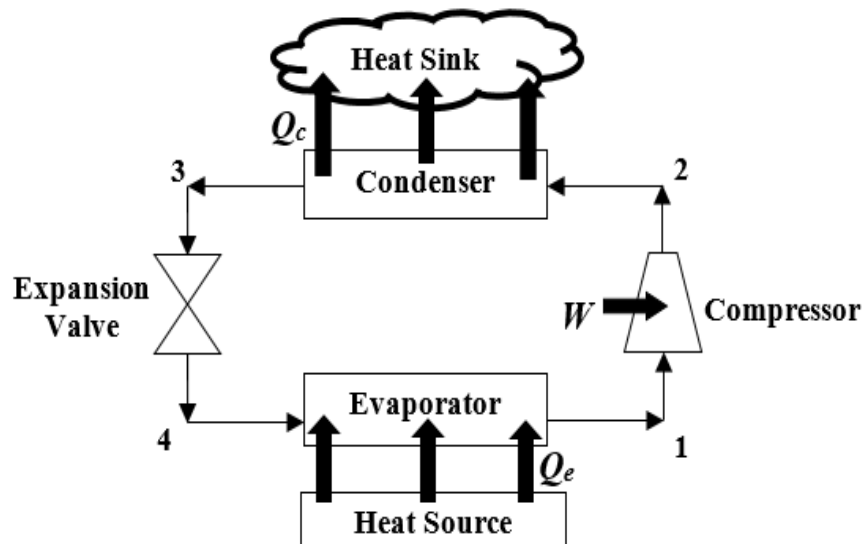


Figure 1. Simple Vapor Compression Refrigeration Cycle

From state 1 to state 2, the superheated refrigerant undergoes compression which its temperature and pressure are increased significantly. During this compression stage, it is necessary that the refrigerant is completely in vapor form because the presence of liquid may damage the compressor. From state 2 to state 3, the superheated vapor travels through the condenser where the heat energy within the refrigerant is transferred to the surrounding or a sink, across a conductive tubing. Due to this quick release of heat, the refrigerant liquefies or condenses into a saturated liquid. However, the pressure drop from state 2 to state 3 is negligible. Hence, across the expansion valve from state 3 to state 4, the pressure is dropped drastically. But due to unavoidable heat absorption, the refrigerant exits the expansion valve in the form of a liquid-vapor mixture with higher percentage of liquid. The liquid-vapor mixture at state 4 then absorbs heat from a heat source across conductive tubing to become superheated vapor at state 1.

2.2. Parameter Selection, Experimental Setup and Assumptions

The experiments for this particular study were conducted using R713 Refrigeration Laboratory Unit by P.A. Hilton Ltd, as seen in Fig. 2. This rig was specifically designed to study the performance of the refrigeration cycle by solely controlling the evaporator heater power input (EHPI), $\dot{Q}_{EVAP}$, and the condenser water flow rate (CWFR), $\dot{m}_{COND}$. Due to this limitation of the available resources, flexibility

of the machine and the time span, EHPI and CWFR were chosen as the independent variable for this study, while COP is the dependent variable. Similarly, a study conducted by Al-Rashed overlooked the effect of evaporator on the COP and found out that it was not likely to optimized both the COP and evaporator performance simultaneously [21]. However, it was also noted the effect of the evaporator performance influenced the overall COP of the refrigeration cycle.

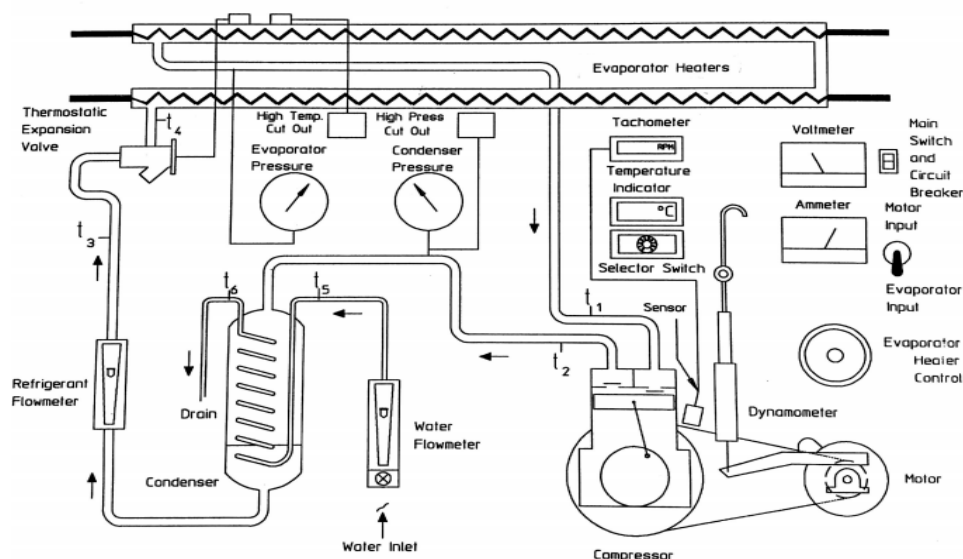


Figure 2. R713 Refrigeration Laboratory unit – Experiment Rig [22]

It was noted by Yusof & Azizuddin, that the COP of a household refrigerator may be effected even with a minor change such as opening the door or wind velocity [20]. Although overall machine control was limited, R713 experiment rig favorably provided more focused and total control over the heat flow in to the evaporator and out of the condenser compared as to what it could be controlled by common household refrigerator. Therefore, if not for the R713 experiment rig, it would require careful control and monitoring over the surrounding to achieve isolative test conditions. Hence, R713 experimental rig was ideal for experimentations as this study also was solely fixated on producing an optimized empirical model of the refrigeration cycle based on the significance of the aforementioned parameters.

In the case of R713 refrigeration unit, the heat sources were two separate electrical heating elements that was controlled by a common dial gauge controller. The heat sink was flowing water which was controlled by a valve in the flowmeter. State 5 and 6 indicated the water inlet and outlet conditions respectively.

The machined was strictly restricted to only use 1,1,1,2-Tetrafluoroethane, or more famously known as HFC134a or R134a. Despite of the inflexibility, according to Qureshi & Zubair, R134a contained multiple favorable properties for small to medium scale applications [23]. R134a is very widely used in the air conditioning and refrigeration industry due to its low Ozone Depletion Potential (OPD) and Global Warming Potential (GWP). Such quick changes in state of the refrigerant is possible due to physical properties such as low boiling temperature at atmospheric conditions.

As previously mentioned, refrigeration cycle is a complex cycle to be looked in to as a whole in a short period of time. Therefore, in order to isolate the behavior of the

EHPI and the CWFR and, the cycle was simplified and the following assumptions were made:

- Atmospheric temperature, pressure and humidity was set as 27 °C, 100kPa and 75% respectively.
- The system runs in steady state.
- Kinetic and potential energy as well as friction losses are considered to be negligible.
- Evaporator, Expansion valve, Condenser and Compressor are considered adiabatic.
- The expansion valve process is isenthalpic (constant enthalpy).
- The working fluid at the evaporator outlet is completely saturated vapor.
- The working fluid at the condenser outlet is completely saturated liquid.
- Pressure drop across the evaporator and condenser are negligible.
- All heat exchange processes were through Copper tubing or constant thermal coefficient of the medium.

Experiments were conducted for 20 g/s, 30 g/s, 40 g/s and 50 g/s CWFR, from the possible minimum to maximum evaporator heater voltage input in increments of 10V. The system automatically sets the EHPI. The minimum and maximum EHPI value was determined by first observing the lowest evaporator heater voltage input that resulted the least positive evaporator pressure and the highest evaporator heater voltage input that cause automatic cut-off of the machine respectively. Each run was given 5 to 10 minute to stabilize and display a consistent reading for each measure.

2.3. Multiple Linear Regression analysis (MLR)

In this study the data was manipulated using IBM SPSS Statistic 20, a special software for statistical analysis [24]. As a simple, yet well-established statistical analysis method, MLR analysis was used to explore the relationship between the multiple independent and one dependent variables and ultimately producing the empirical models.

As previously mentioned, independent variable were EHPI and CWFR while COP was dependent variable for this particular study. The outcome of the study was to be a mathematical model in the form of a linear equation as shown in Eq. 2, Eq. 3 and Eq. 4 below. Additionally, C_1 , C_2 and C_3 would be coefficients for the mathematical COP models 1 2 and 3.

$$COP_1 = C_1(\dot{Q}_{EVAP}) + C_2(\dot{m}_{COND}) + C_3 \quad (2)$$

$$COP_2 = C_1(\dot{Q}_{EVAP}) + C_3 \quad (3)$$

$$COP_3 = C_2(\dot{m}_{COND}) + C_3 \quad (4)$$

3. RESULTS AND DISCUSSIONS

In order to evaluate the COP, the experimental data was analyzed with respect to maximum evaporator and condenser pressures. The COP for each run was calculated using the thermodynamic property tables for the refrigerant R134a. Complete data was tabulated and the optimized formula for VCRC was produced through MLR analysis.

3.1. Evaporator Heater Power Input

Evaporator in a refrigeration cycle is the element at which the working fluid is vaporized by absorbing heat energy. EHPI in this study was the heat source to the refrigeration cycle. Although the heater power was incremented in Volts, the overall input for the calculations were in terms rate of heat produced in watts (W).

A linear behavior between the EHPI and the evaporator pressure was observed, as seen in Fig. 3. It was noted that the average gradient at which the pressure at the evaporator end increased was by 0.287 kPa/W. This was because, as the EHPI increased, the refrigerant molecules were subjected to more energy. Therefore, the molecules undergoes more random and vigorous movements. As a result, the state of the refrigerant was ideally changed from a mixture to a vapor increasing the fluid pressure.

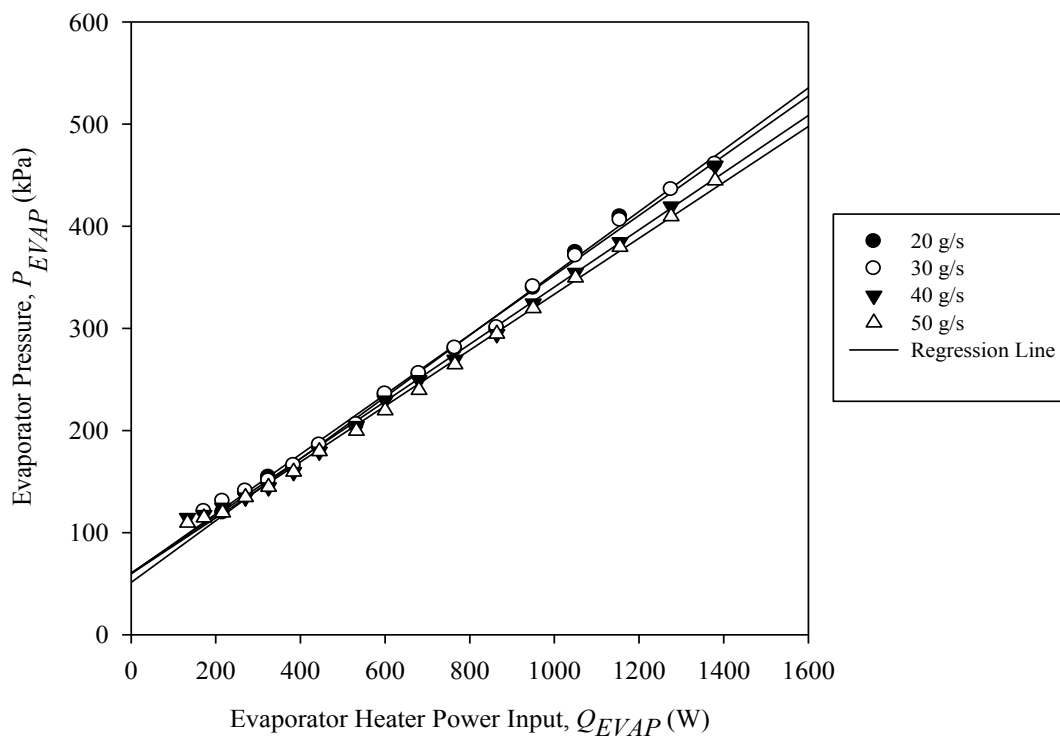


Figure 3. Effects of Evaporator heater power input on the Evaporator Pressure

On the other hand, the manner at which the data was packed along the, almost overlapping, best-fit-lines also indicated the effectual ability of the system to adjust its refrigerant flow rate based on the heat energy transferred in to the refrigerant per unit time, irrespective of condenser flow rate.

For all CWFR, the COP of the refrigeration cycle increased somewhat linearly as the EHPI was increased, as seen in Fig 4. It was observed that the gradients of the regression lines were 0.0015 W^{-1} , 0.0017 W^{-1} , 0.0019 W^{-1} and 0.0021 W^{-1} for CWFRs, 20g/s, 30g/s, 40g/s and 50g/s respectively. This was due to the increasing difference in the temperature gradient between the heat source and the refrigerant at the evaporator end, as the EHPI increased. Moreover, with less reliable data at the most extreme high and lower EHPI and lower CWFR, the rate of COP increase was poorer.

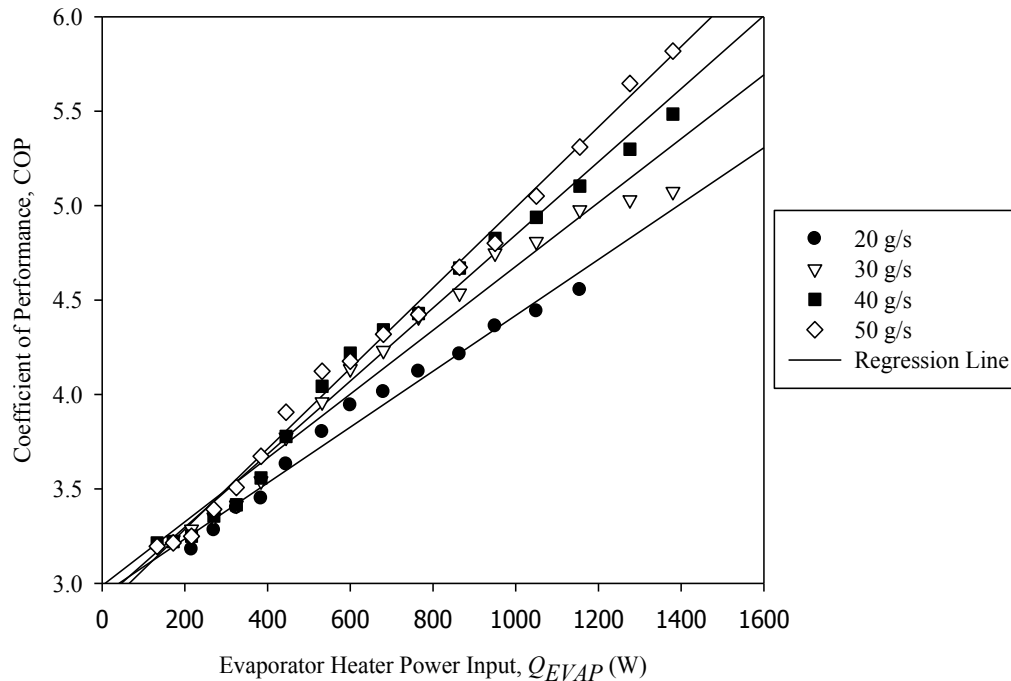


Figure 4. Effects of Evaporator heater power input on the Coefficient of Performance

Below 500W of EHPI, it was observed that the COP values were randomly clustered for all CWFR. This was majorly because of the overall low rate of heat transferred to the refrigerant cycle. Though, as the EHPI passed 500W, the rate of heat transfer was more significant and distribution, or spreading, of data was observed. Nevertheless, the overall COP of the refrigerator cycle will partly depend on the CWFR as well as EHPI.

3.2. Condenser Water Flow Rate

Condenser in a refrigeration cycle is the component at which the compressed working fluid is turned into a saturated liquid through heat extraction. Hence, CWFR in this study was the rate at which the mass of the heat sink flow extracting heat energy across the condenser. Water flow rate was measured in grams per second (g/s).

Similar to the comportment at the evaporator end, the CWFR behaved linearly with condenser pressure, as observed in Fig. 5. However, unlike the evaporator end, the gradient at which the pressure changed was negative with increasing CWFR. It was also noticed that the negative gradient of the slopes increased as the CWFR increased. Additionally, it was distinguished that the range between the highest and lowest pressure also reduced with increasing water flow rate. This was because the rate of heat transfer from the refrigerant to the water rose as the water flow rate

increased. Thus, the refrigerant molecules are subjected to less energy and tends to behave more stably. This stability converted the superheated refrigerant to a saturated liquid dropping the pressure across the condenser.

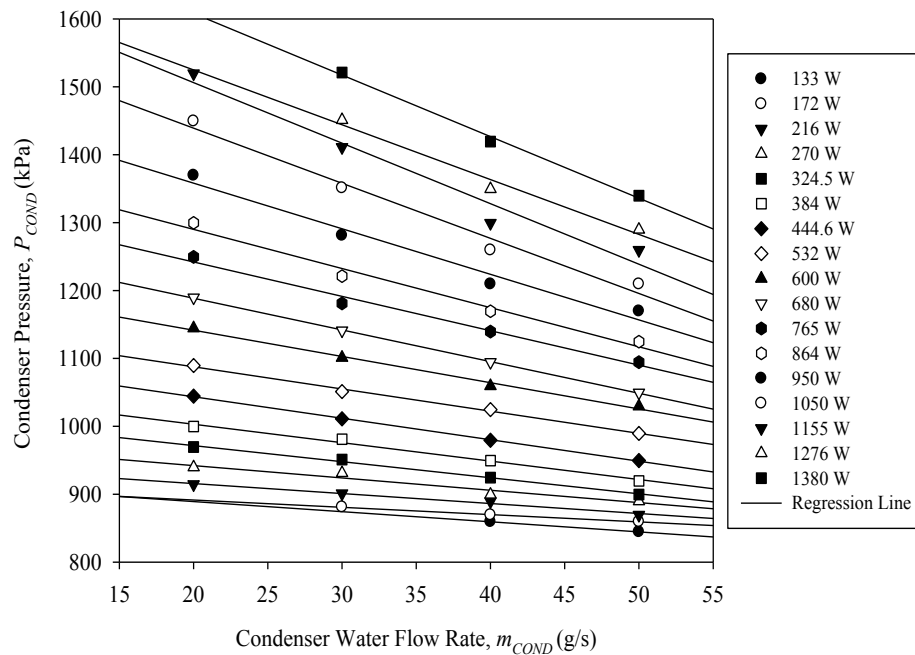


Figure 5. Effects of Condenser Water Flow Rate on the Condenser Pressure

CWFR also had a positive effect on the COP of the overall system as seen in Fig. 6. However, the largest range of COP was achieved for 50 g/s due to the greater heat transfer capability compared to the remaining CWFR fixtures. Likewise, the smallest range of the COP was obtained for 20 g/s due to lower rate of heat transfer.

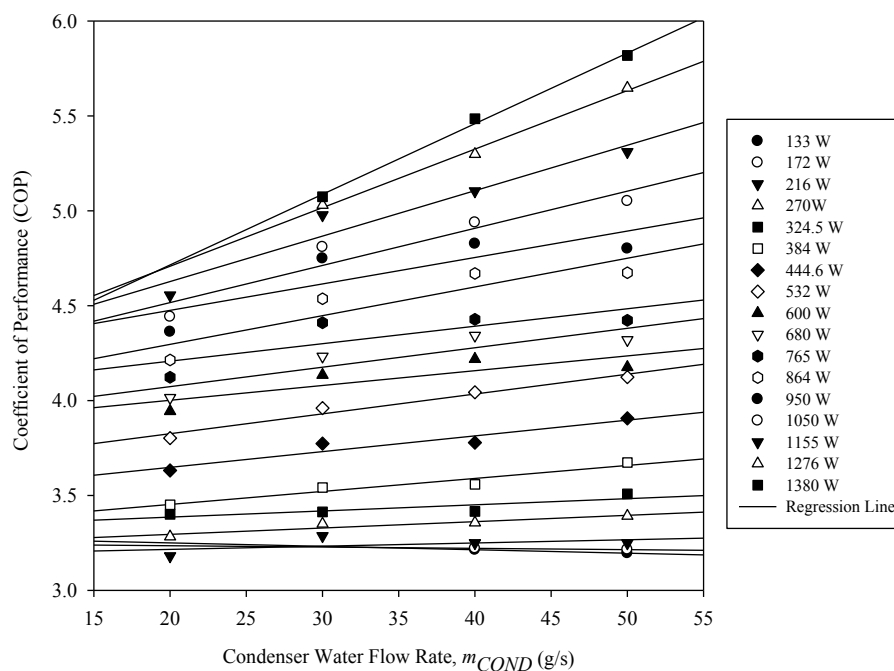


Figure 6. Effects of Condenser Water Flow Rate on the Coefficient of Performance

Moreover, the gradient of COP was observed to be greater for constant high EHPI. Yet again, the obtainability of data for low CWFR conditions at the extreme EHPI was limited. Hence, the gradient of the regression lines when EHPI was 133 W and 172 W were negative. Besides the low heat transfer rates, fluctuations in condenser water inlet temperature accumulated to the randomness of data. As a relatively low amount heat is absorbed by the refrigerant at the evaporator end, the amount of heat to be expelled into the condenser water was also relatively low.

3.3. Regression Analysis

Based on the experimental results, it was conclusive that an increase in both EHPI and CWFR had a positive correlations to the COP. Similarly, as the increase in EHPI positively affected the evaporator pressure and the increase in CWFR negatively affected the condenser pressure. Therefore, the higher the pressure difference between the evaporator and the condenser, the higher the COP of the system was believed to be.

The expected outcome of the study was mathematical models in the form of a linear equations that could predict the COP based on predetermined independent variable Hence MLR analysis was used. However, numerical regression calculation generally time consuming if it were to be done manually. Therefore, IBM SPSS statistics 20 software was utilized to generate the results. Hence, the COP data obtained was input to the software with respect to the EHPI and CWFR.

According to the descriptive statistical result of the MLR analysis shown in Table 1, it was found that the mean COP of the system was 4.14 with a standard deviation of 0.72. Similarly, both EHPI and CWFR had mean values of 661.75W and 36.03 g/s respective while the standard deviations were 370.65 W and 11 g/s respectively. Therefore, the average COP of this refrigeration unit may vary between 3.42 and 4.86. The average EHPI and the CWFR that would achieve the average COP were 661.75 W and 36.03 g/s respectively. Moreover, the average evaporator heater power input may vary between 291.1 W and 1032.4 W, while the condenser water flow rate may vary between 25.03 g/s and 47.03 g/s.

Table 1 Descriptive Statistics

Variables	Mean	Standard Deviations
COP	4.14	0.72
$\dot{Q}_{\text{EVAP}}$ (W)	661.75	370.65
$\dot{m}_{\text{COND}}$ (g/s)	36.03	11.00

Furthermore, the Table 2 shows the percentage of variability in the dependent variables that was taken into account by all of the independent variables combined. As total of three model were generated, Model 1 considered both EHPI and CWFR as independent variable, while Model 2 and Model 3 only considered EHPI and CWFR respectively.

Table 2 Model Summary

Models	R-square	Adjusted R-square
1	0.972	0.971
2	0.943	0.942
3	0.0312	0.0153

R-square, or coefficient of multiple determination in multiple regression, is the statistical measure of accuracy of the data fitted into regression lines. Therefore, the closer the value of R-square was to one, the more accurate the data would be. Based on Table 2, Model 1 produced the highest accuracy with 97.2%. Model 2 was 94.3% accurate while Model 3 was the least accurate with just 3.12%.

However, as the amount of data are relatively small, the R-square values would be an over estimation. Thus, the regression software also generated adjusted R-square. Still, Model 1 produced the highest accuracy with 97.1%. Likewise, Model 2 was 94.2% accurate while Model 3 was again the least accurate with just 1.5%. The difference in the R-square and adjusted R-square was small due to the almost negligible effect of the least significant independent variable, CWFR.

Nevertheless, as the R-square and adjusted R-square values for Model 2 and Model 3 were compared, it was conclusive that the EHPI contributed more significantly to the overall COP than CWFR. But, it was also decisive that taking both dependent variables into consideration produced the most significant model, as in Model 1.

Moreover, it was necessary to evaluate each of the independent variables in order to identify which variable in the model contributed most to the COP. Hence, a 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. This was so that a standalone constant was not required, unlike the unstandardized coefficient as seen in Table 3.

Table 3 Unstandardized and Standardized Beta Coefficients

		Unstandardized Coefficients	Standardized coefficient
Models		B	β
1	Constant	2.505	0.000
	$\dot{Q}_{\text{EVAP}}$	0.002	0.970
	$\dot{m}_{\text{COND}}$	0.011	0.169
2	Constant	2.895	0.000
	$\dot{Q}_{\text{EVAP}}$	0.002	0.971
3	Constant	3.725	0.000
	$\dot{m}_{\text{COND}}$	0.011	0.175

Elimination of zero β level in standardized coefficients would reduce the accuracy of the model. Therefore, ideally, the unstandardized coefficients would be the more relevant set of coefficients for the model, provided that both the independent variables

were known. Also, with the findings related to the behavior of R-square and adjusted R-square for all the models, the most appropriate model was Model 1. Therefore, replacing the coefficients C_1 , C_2 and C_3 in Eq. (2), Model 1 would be presented as:

$$COP_1 = 0.002(\dot{Q}_{EVAP}) + 0.011(\dot{m}_{COND}) + 2.502 \quad (2.1)$$

Up on comparison, it was observed that there were uncertainties between the experimental and the regression model COPs. As seen in Table 4, higher deviations from the experimental values were resulted in lower CWFR applications compared to the higher CWFR. The highest deviation was -9.49% when the EHPI was the highest for the lowest CWFR. In overall system performance, the error ranged from -9.49% to 2.55%. However, the model was also able to achieve results with as accurate as -0.02% uncertainty. Nevertheless, the result uncertainties were within the expected range of $\pm 10\%$. The error could be minimized even further by including more effective, yet varying, parameter such as refrigerant flow rate and also by further limiting the losses.

Table 4 Error Analysis

Evaporator Heater Power Input	Condenser Water Flow rate			
	20 g/s	30 g/s	40 g/s	50 g/s
133	-	-	0.18	-3.69
172	-	1.55	-1.97	-5.34
216	0.86	0.68	-3.69	-6.75
270	0.63	-0.67	-3.61	-5.58
324.5	0.88	-1.95	-4.87	-5.22
384	-1.14	-1.63	-4.10	-3.85
444.6	0.56	1.39	-1.39	-0.89
532	0.43	1.64	0.92	0.17
600	0.56	2.55	1.85	-1.79
680	-1.66	0.96	0.93	-2.10
765	-3.05	1.10	-0.98	-3.47
864	-5.31	-0.52	-0.02	-2.23
950	-5.62	0.35	-0.33	-3.06
1050	-7.89	-2.50	-2.06	-1.96
1155	-9.49	-3.21	-2.83	-0.97
1276	-	-6.60	-3.56	0.77
1380	-	-9.26	-3.81	0.11

Also, according to Table 4, it was noticed that the majority of the uncertainties lied at the negative side. This may have been due to the high heat loss to the surrounding during the operation.

4. Conclusion

In conclusion, it was found that both the EHPI and CWFR had a positive effect on the COP of the overall system. Among the three mathematical models created, Model 1, taking both EHPI and CWFR in to consideration, produced the highest accuracy in data distribution about the MLR line with 97.2%. Likewise, Model 2, considering just EHPI, was 94.3% accurate while Model 3, considering just CWFR,

was again the least accurate with just 3.12%. Therefore, upon choosing Model 1 as the best predictor of COP, unstandardized coefficients were assigned to the variables. Hence, the final COP predictor model was $COP_1 = 0.002(\dot{Q}_{EVAP}) + 0.011(\dot{m}_{COND}) + 2.502$. The results produced by the final model had minimum and maximum uncertainty of -9.49% and 2.55% respectively. The overall uncertainty could be minimized by incorporating other significant parameter such as refrigerant flow rate and also by further limiting the heat losses to the surrounding.

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An Engineering Approach to Reduce Noise Level in a Public Area

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Abstract

This paper covers the research currently being performed to expand the field of restaurant acoustics with the case in focus being a restaurant named Temptations in Taylor's University Malaysia. Research on this topic was initiated by another student in 2013 and the goal of this project is to expand on what has been done, to analyse the restaurant in an alternative manner than the previous research and to implement a strategy to mitigate the noise and reduce it to a level which is more acceptable. Initially, a thorough and comprehensive research on the project background has been performed which encompassed a literature review which covered the basics of sound as this is not an area which is familiar to the project team nor is it in the scope of learning in the Mechanical Engineering Degree Programme at Taylor's University. A numerical study using the Acoustics Extension in ANSYS 15.0 Workbench, represents the next phase of the project. Singular and multiple excitations were represented in the software to study how the sound is behaving and to determine if the model can be used credibly to perform the analysis. The validation and verification was done by comparing the results from the numerical analysis with that of the experimental one whereby the absorption coefficient as well as the theoretical and actual reverberation times of the restaurant were calculated. From the results, it can be seen that the numerical model is credible and the behaviour of the sound correlates with that of the literature review and the experimental analysis. It is also verified that there is significant basis for this research to be carried out as the target location does require sound attenuation based on the reverberation times calculated and the manner in which the sound propagates in the target location from analysing the numerical results. It was initially intended that the research team should formulate and propose a cost effective, efficient and ideal strategy to attenuate the noise level in the restaurant based on research done on potential solutions. However due to significant time constraints, largely due to issues in using a new application of the software for which there are extremely limited materials on and which was unavailable for half the duration of the research, a solution was not able to be completed.

Keywords: Restaurant Acoustics – Numerical – Experimental – Noise – Attenuation

1.0 Introduction

1.1 Research Background

The importance of sound in our lives is something that cannot be overstated. From the simple act of communicating with one another, to experiencing the audible feast that is music, our sense of hearing has an intrinsic role in our lives and it gives us a whole new dimension of experience. However, there is an aspect of sound which brings much distress and chagrin to us and that is the phenomenon called noise. Noise can be either good or bad, depending on circumstances, but in general, noise is defined as an undesirable or disagreeable sound [1]. We encounter noise in many forms, from construction works, the sound of traffic, impacts of objects being dropped, even a loud conversation can be classified as noise as it is something that is undesirable. Sometimes, the presence of noise cannot be avoided and for a long time, this is how the problem was faced, with tolerance. However, with the advancements in science and technology we are now able to combat noise, provided we have a substantial understanding of it.

Acoustics is an area of science that has a wide assortment of applications which all revolve around the study, understanding, measurement, manipulation and control of sound. Architectural acoustics represents ‘the study of the generation, propagation and transmission of sound in rooms, dwellings and other buildings’ [2]. Architectural acoustics come into play in building design to ensure that its inhabitants are able to fully maximise, utilise and appreciate its functionality. Take for instance, a restaurant which serves to provide a place for diners to enjoy a meal in. To be able to fully appreciate the functionality of a restaurant, the diners must feel that the ambience of the restaurant is welcoming, comfortable and hospitable. However, one of the most significant issues that most diners will attest to, as confirmed by a study done by ZAGAT in 2013 across the United States of America is that noise levels in restaurants are too high thus disrupting conversations and providing an unsatisfactory atmosphere. Noise in restaurants usually arise from the sound of the occupants conversing with one another and sounds from the kitchen both coupled with the lack of sufficient noise treatment.

Architectural acoustics may have been implemented since the age of the Roman Empire, with their amphitheatres designed in such a way so as to provide exceptional clarity and fluency required, but restaurant design in terms of acoustics is a relatively new field of study as suggested by the minimal amount of literature available which directly relates to it and one which can be delved into and developed exponentially. This project aims to expand the field of restaurant acoustics with the case in focus being a restaurant named Temptations in Taylor’s University Lakeside Campus, Malaysia. Research on this topic was initiated by another student in 2013 and the goal of this project is to expand on what has been done and to implement a strategy to mitigate the noise and reduce it to a level which is more acceptable.

1.2 Objectives

This project will be spread out over the course of two semesters as part of two correlated modules in the Engineering Degree which are Final Year Project 1 & 2. For the first module, the scope of the works will be the ‘conceive and design’ aspects whilst the final semester will focus on the ‘implement and operate’ areas. The objective of this study is summarized as follows:

- i. To utilize numerical software analysis to aid in the experimental evaluation and examination of the acoustics at the target location, Temptations Restaurant at Taylor's University
- ii. To formulate and propose an efficient, cost effective and ideal strategy to attenuate the noise level in the restaurant

1.3 Scope

The scope that this project aims to cover focuses on two main areas of study which are the experimental and numerical fields of research. To supplement the research being carried out, a thorough and comprehensive study of architectural acoustics and sound will first be performed, so as to enhance the integrity of the work being performed.

The thesis which was produced by Mohd Afiq (2013) [3] was used as a main reference and the literature review found in this document is done to fill in the gaps which were not covered by him. Definitions and explanations of the fundamental elements of acoustics such as wavelength, frequency, pitch, etc. will not be provided here and instead, can be referred to that document. The focus of the literature review of this research will be to breach the gaps that were not covered by Mohd Afiq and to delve further into Architectural Acoustics.

Numerical analysis of the target location will be performed utilizing an Acoustics Extension under ANSYS 15.0 Workbench which incorporates creating a basic three-dimensional model of the target location and analysing it using the software and will be covered in further detail in the Research Methodology Section. A numerical analysis has been chosen as the basis and the first step over an analytical and experimental one due to the fact that it is much easier to perform the optimisation using a software in which the components, items, layout, etc. of the restaurant can be altered much more easily and readily. The numerical study will be supported by experimental works which will be covered by the data acquisition process whereby the restaurant will be studied and data from it such as noise levels, reverberation time, sound absorption and distribution, etc. amongst others will be collected in order to identify the source of the problem. A combination of a numerical and experimental study will allow for a validation and verification of the results obtained and comparisons to be identified and drawn, all of which will aid in ascertaining a final solution to solve the issue at hand as well as enhancing the credibility and quality of the research being performed [2].

1.4 Research Question

1. How can an engineering approach be utilised to study the behaviour of the acoustics in the Temptations Restaurant in Taylor's University in a manner that is different than what has already been done before
2. How can the noise level of the Temptations Restaurant In Taylor's University be reduced to a more acceptable level.

1.5 Contribution to Body of Knowledge

There is a significant lack of literature available for the field of restaurant acoustics as compared to other architectural structures such as amphitheatres, concert halls, and

places of worship which are the predominant locations for sound treatment. There has however been a significant increase in the interest devoted to this sound attenuation for restaurants, but usually without the appropriate scientific approach [9]. The methods that have been used are usually done based on a general approach taken to all restaurants without the specialisation or individual aspects of each location taken into account or even by implementing techniques from other architectural facets [11]. This research was done in hopes to contribute to this gap in the field of architectural acoustics whereby by expanding the research that has been done so far and by providing an alternative way of analysing the sound in the target location than that has already been carried out. With that, it is hoped to formulate a procedure or template to be used for analysing sound in restaurants from an engineering approach.

2.0 Research Methodology

This project comes under the field of quantitative study, which is divided into two methods of analysis i.e. numerical and experimental. The numerical and experimental analysis will yield results which will be compared and evaluated, from which a solution will be derived based on the evaluation coupled with the knowledge garnered from the research phase.

2.1 Numerical Analysis

For the numerical analysis, the software of being used is ANSYS Workbench 15.0 with the addition of the ACT Acoustics Extension. ANSYS is a widely renowned and powerful simulation software that has been long favoured by the engineering community in applications for computer-aided engineering and design due to its versatility, robustness and ease of use.

In the realm of acoustics, there are three different types of analysis that can be performed which are the modal and harmonic analyses which are in the frequency purview as well as the transient analysis which is in the time domain. For the analysis of a room, the harmonic response analysis was chosen for various reasons. As seen in other works of research, the harmonic response method is favoured over the transient and modal analyses when the application is based for noise propagating in a room [10]. A harmonic analysis is selected when the response of a linear structure to loads which are varying in a sinusoidal (harmonic) manner are acting on it. For the case at hand, the sinusoidal loads represent the noise generated by the diners and the response of the linear structure is taken as the air in the restaurant and the walls of the restaurant itself. A harmonic analysis was also chosen based on the post-processing and the output quantities available that are required to determine the behaviour of the sound propagating in the restaurant. For this case, it is necessary to obtain the acoustic pressure, sound pressure level, the near field parameters as well as the acoustic time-frequency plot. The software also allows for a visual representation of how a single or even multiple sources of excitation interfere with one another, reflect off the walls and propagate throughout the restaurant.

Initially for the first phase of this project, the first step was to perform a complete and thorough study and understanding of the software so that when the actual analysis was being performed, it could be carried out in an efficient manner. The preliminary steps include the building of the model of the restaurant in the Design Modeller. A basic

cuboid shaped room was modelled in the Design Modeller with dimensions akin to that of a simplified version of the Taylor's Temptations Restaurant just for familiarisation purposes.

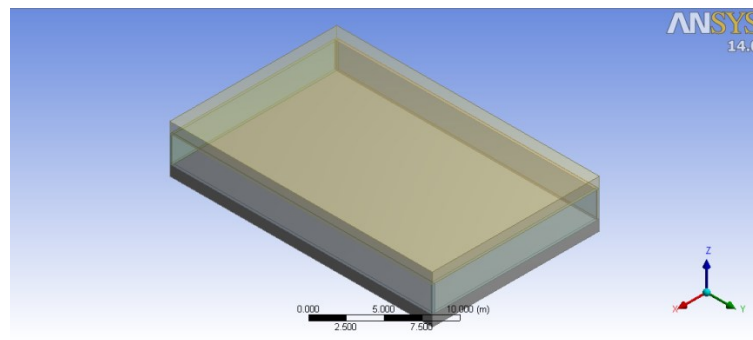


Figure 12 Initial Model

This was followed by the simulation of a more intricate and realistic version of the restaurant. The next stage is the input of the material data in the Engineering Data library which will form the materials used to construct the room. The materials were taken as a close approximation from a visual inspection of the restaurant as well as a review of the most commonly used building materials in the construction industry and materials which are common to the region [7]. The estimates and assumptions made for the numerical analysis were done with as much care and integrity so as to simulate the acoustic behaviour of the sound acting in the Taylor's Temptations Restaurant as accurately as possible. The model is shown below in the Mechanical application with the walls at the fore representing the front of the restaurant made out of glass. The materials for each wall and their corresponding dimensions which were obtained from the measurements taken, as well as the Young's Modulus and the Poisson's Ratios (which require a manual input) are as follows [11]:

Table 7 Wall Dimensions and Properties

Location	Material	Dimensions (m)	Young's Modulus (GPa)	Poisson's Ratio	Thickness (m)
Front Wall 1	Glass	13.67 x 2.45	70	0.23	0.16
Front Wall 2	Glass	21.42 x 2.45			
Front Wall 3	Glass	12.08 x 2.45			
Front Wall 4	Glass	18.82 x 2.45			
Rear Wall 5	Brick & Cement	7.97 x 2.45	30	0.18	
Rear Wall 6	Brick & Cement	3.36 x 2.45			
Rear Wall 7	Brick & Cement	16.46 x 2.45			
Ceiling	Gypsum Plasterboard	-	1.7 - 2.5	0.2 - 0.3	0.05
Floor	Ceramic Tile		41.78	0.14	0.16
Inside	Air	-	0.00011	-	-

For simplification, as with the first model, the restaurant is taken to be made out of 4 parts which are the ceiling, the floor, the front walls made out of glass and the rear walls made out of bricks and cement.

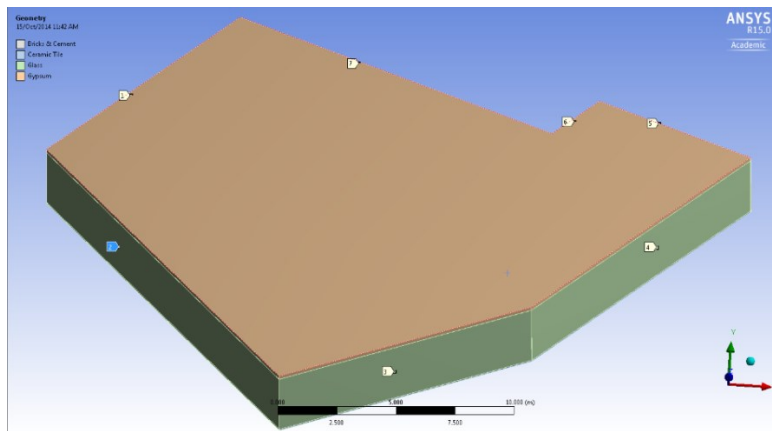


Figure 13 Updated Model

This is followed by the application of the meshing, boundary conditions, fixed supports of the model. For the mesh, there are several different methods and attributes that can be changed and altered before the analysis is performed. The element size can either be left as default or be user defined. The patch conforming method can either be left as independent or set as tetrahedron. As for the relevance centre, it is either set as fine, medium or coarse. These factors will all lead to differences in the nodes and corresponding elements. The result of all this is the accuracy at which the model can be analysed. A finer mesh will lead to a more accurate rendering and analysis of the model [16]. However, this accuracy comes at a cost, which is a slower processing time but it is a necessity in order to enhance the credibility of the work being done. For this particular model, the element size was taken to be as 0.1m, the patch conforming method to be independent and the relevance centre to be fine. These input properties are selected based on standard practices for models of this type as well as through experience in using this software [17].

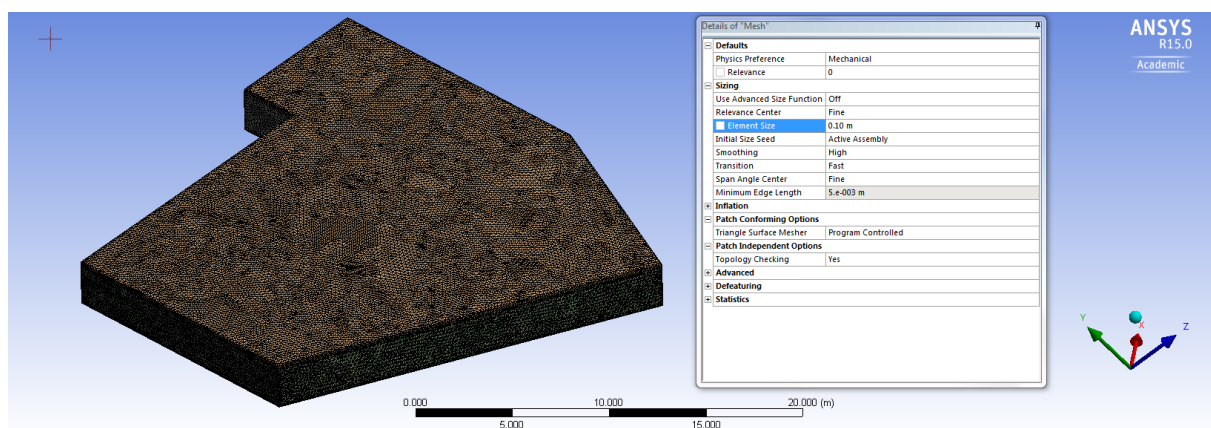


Figure 14 Meshing

The next step is the determination of the boundary conditions for the analysis settings. Firstly, the minimum and maximum of the frequency range is set at 125 and 4000 Hz respectively as this is usually the frequency range of concern when analysing restaurants and the optimum speech frequencies [1]. Next, the declaration of the computational domain (entire geometry of the model) as an ‘acoustic body’ is performed. The mass density and speed of sound in the medium (taken as the values for air) of concern are then keyed in. This is a coupled analysis whereby the study is being done on the interaction of the air in the room with the walls surrounding it as the propagation of sound occurs. Another boundary condition whereby an acoustic pressure of ‘0’ magnitude is applied to the outward faces to ensure that all the sound is contained within the structure to maximise the impact of the sound propagation in the venue which mimics a worst-case scenario of having no sound escape the venue [16]. The Fluid Structure Interface (FSI) whereby the acoustic planes that come into contact with the structural members are also determined and registered into the software. These represent the action of the pressure transfer from the medium to the structure. Next, the fixed supports for the restaurant are selected. Due to the nature of the restaurant’s construction, the fixed supports are selected to be the ceiling, the floor, and all of the back walls leaving all the front walls free as they are made of glass and are not connected to any other structures along their surface.

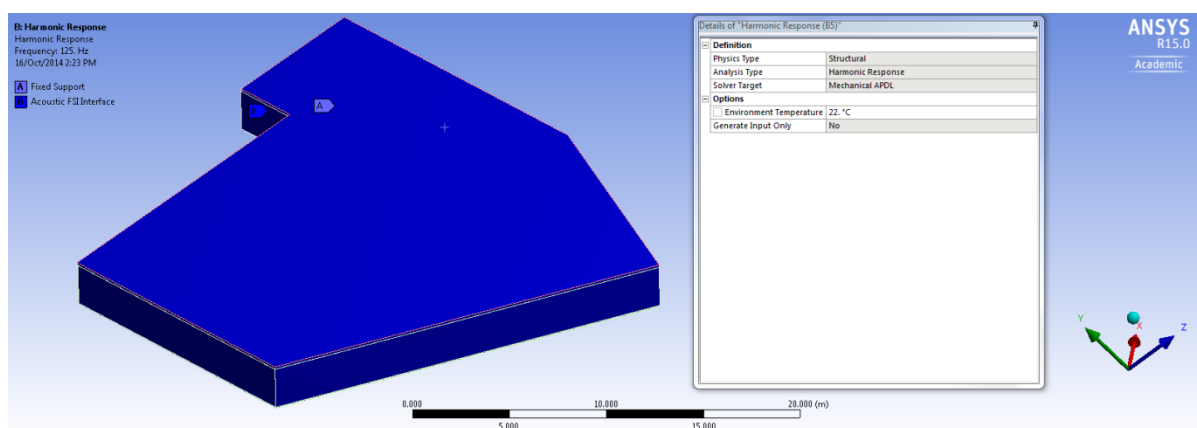


Figure 15 Boundary Conditions

Lastly, the acoustic excitations are defined. There are several types of excitations to choose from but based on research in this field and the application with ANSYS as well as the focus of the source of the noise which from the experimental analysis is confirmed as the patrons of the restaurant, an acoustic incident monopole wave source is selected [16]. A monopole wave is selected as its symmetry will lead to a production of harmonic spherical waves irrespective of the medium of propagation and various sources tend to exhibit behaviour similar to it [17]. The omnidirectional propagation of the monopole wave is very appropriate for simulating the noise being generated by diners in the restaurant. The wave is selected to be radiating from the centre of the room with a phase angle of 90°, and amplitude of 0.025 Pa which is obtained by converting a noise level rating of 62.2 dbA to Pascal’s. The value of the noise level is obtained from measurements taken from the restaurant of the average noise level of the patrons which was found to be 62.2dbA.

An analysis with multiple sources of excitation is then performed with the additional waves being generated at the centre of each of walls of the restaurant. The reasoning

behind the location of the sources of excitation is to have a more uniform and even distribution so as to simulate and to view how much of an effect the geometry of the restaurant has in contributing to the way that the sound waves are travelling in it. This will lend to an appropriate way to select the best possible solution for the location of the sound absorbers. The waves are all selected to have the same properties such as amplitude and phase angle as they are assumed to be of the similar sources which is conversation from the diners. The waves are placed at a height from the floor to simulate the mouth level of a diner who would be seating which is approximately 1.2 meters from the ground.

It was hoped that even more sources of excitations could be simulated in the software but due to time constraints which occurred due to problems with the software itself, this was not able to be completed. All the analysis will thus be done by analysing the single and multiple wave sources.

2.2 Experimental Analysis

Measurements will be taken from the restaurant using instruments such as a measuring tape to obtain the dimensions of the restaurant needed as well as a Sound Level Meter (type 2 ANSI SL4) to obtain the decibel level in the restaurant over the span of several days. This will give an average reading and allow to account for the expected variances such as crowd volume. All the required apparatus will be provided by Taylor's University. Besides that, the source of the noise in the room will be identified from visual inspection. The source is divided into two potential causes which are airborne and structure borne and the elements which contribute to these sources will be identified. From the results obtained through the measurements, the necessary calculations to obtain the actual values for the reverberation times and the absorption coefficient will be done. The following equations will be utilised in the numerical analysis of the restaurant.

The experimental phase involving the calculations and analysis of data will be followed by a numerical analysis done side-by-side once the necessary values have been obtained from the measurements. This is so that the understanding of the actual behaviour of the sound and noise in the room will be enhanced. The results of the numerical and experimental studies which will yield the actual and theoretical values should correlate and proving this will greatly enhance the credibility of the research

1) 2.21 Measurements

Before any analysis could be performed, be it numerical or experimental, the first step taken was to obtain the dimensions of the restaurant. This was done with a measuring tape and was preferred over obtaining the measurements from the Facilities Management Office because over time, there have been amendments and modifications to the restaurant. Although it was significantly time consuming, this allowed for a more precise and current outlook of the target location. The measurement of the restaurant was done in meters and then transferred to a computer to be used in the numerical analysis. The measurements taken were combined and then modelled as 4 entities namely the ceiling, the floor, the rear walls and the front walls.

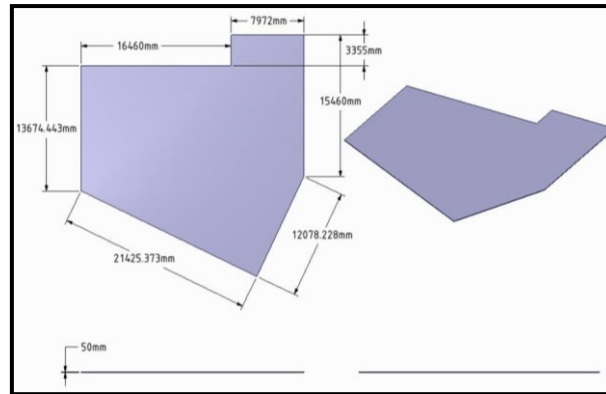


Figure 16 Dimensions of the ceiling

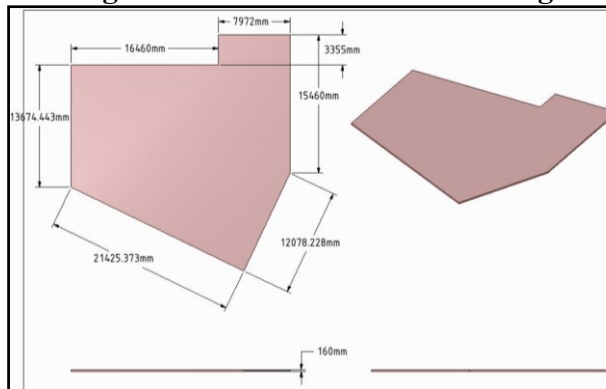


Figure 17 Dimensions of the roof

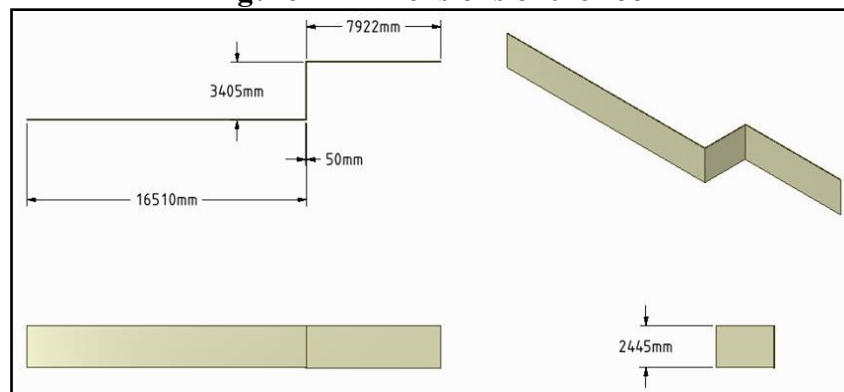


Figure 18 Dimensions of the rear walls

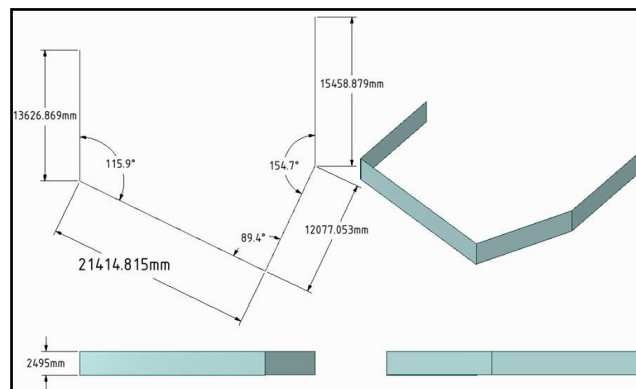


Figure 19 Dimensions of the front walls

2) 2.2.2 Sound Level Meter

A Type 2 ANSI SI.4 sound level meter was used in this study to obtain the decibel level in the venue during the experimental analysis. It is a general purpose sound level meter which is more suited for field use as opposed to the more precise and accurate Type 1 meter which is more appropriate for studying building acoustics but was not chosen due to its lack of availability. The tolerance for the Type 2 meter is ± 1.0 dB, just 0.3 shy of the Type 1 variant. The sound level meter chosen does conform to the standards set by both the International Electro technical Commission (IEC 60651) as well as the American National Standards Institute (ANSI SI.4) for the measurement of sound in buildings [2].

The sound level meter was set with the following functions as per the type of analysis being performed. An A-Weighting was used as the type of frequencies being detected are for general sound level measurements in the band that is detectable by the human ear which is 500 to 8000 Hz. A slow response was chosen as opposed to a fast one as it allows for a 1 second time constant interchange whereas the alternative is of 125 milliseconds. The appropriate decibel range as well as slower fluctuations will allow for the readings to be obtained in an easier manner.

In order to calculate the reverberation time of the restaurant, two different approaches were taken to obtain both the actual and theoretical values.

3) 2.2.3 Potential Noise Sources

Based on a study on architectural acoustics and a visual inspection of the target venue, the sources of noise in the restaurant were divided by their method of generation and propagation be it by an airborne route or through the structure itself. Table 8 displays the findings

Table 8 Potential Sources of Noise

Airborne Noise	Structure-borne Noise
Air-Conditioning (13 units) Fans (4 units) Kitchen (noise from staff) Patrons	Impact Noise (cutlery, footsteps, trolleys, miscellaneous)

4) 2.2.4 Noise Level

It was an objective of this research to identify which of the potential noise sources is the largest contributor towards the inadequate noise level of the restaurant. In order to do so, the sound level meter was used to obtain readings of the decibel levels for each of the potential noise sources identified above. The impact noise was not selected as it is not a constant and occurs much more infrequently compared to the airborne noise and it is not as much of a contributor towards to problem at hand as compared to the airborne noise sources, concurring with literature review on this matter [12]. The readings were taken in a manner of which the source being measured was isolated from other potential sources. As for example, the noise from the fan and air-

conditioning systems were taken when the restaurant was empty and the noise from the patrons and the kitchen was taken when the restaurant was in full service which was identified as the peak operating time during lunch hour. The measurements were taken repeatedly over the duration of five days, the plot of which can be seen in the Figure 20. It can be seen that the noise originating from the fans and air conditioning system are generally very constant. The noise from the kitchen and patrons does change but the variance is minimal, approximately 3 and 4 decibels respectively.

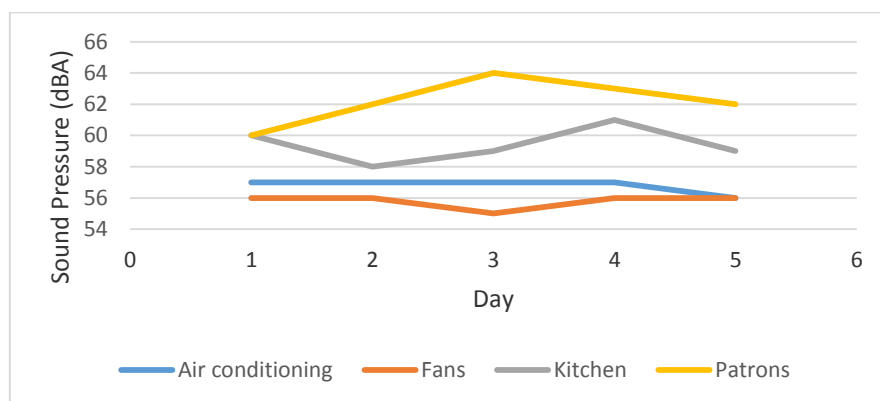


Figure 20 Noise Level from various sources over the course of 5 days

To obtain the actual reverberation time of the room, the Impulsive Noise method was chosen whereby a sound with a large amplitude is utilised to excite all the frequencies in a room [12]. It was conducted in a manner whereby the restaurant was vacated of all occupants (bar the people to conduct the testing) and all forms of noise such as from the air-conditioning, kitchen equipment, fans and ambient music played in the restaurant were eliminated so as to obtain a clearer recording. The furnishings such as the tables, chairs and decorative elements were kept in place as they contribute to the reflection of the sound and also they remain constant whereas the number of patrons varies. An impulsive noise, in this case a balloon was popped in the dead centre of the restaurant and the resultant noise generated was recorded in the audio sampling software Audacity 2.0.6. From there, the waveform recorded is normalized to a level of 60dB as the impulse generated by the balloon is only approximately 20dB. The resultant time of propagation of the sound wave to die down is taken as the reverberation time which coincides with the definition of reverberation time or RT60. The procedure of normalising or extrapolating results is in accordance with BS EN ISO 3328 as it can be difficult to generate an impulse of 60 dB and the results obtained are labelled as RT60 (T20) [14]. The experiment was performed a total of three times to obtain an average value.

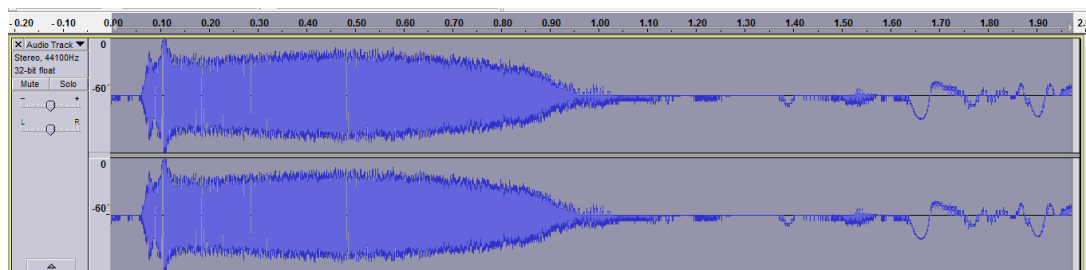


Figure 21 Sound waveform of balloon burst

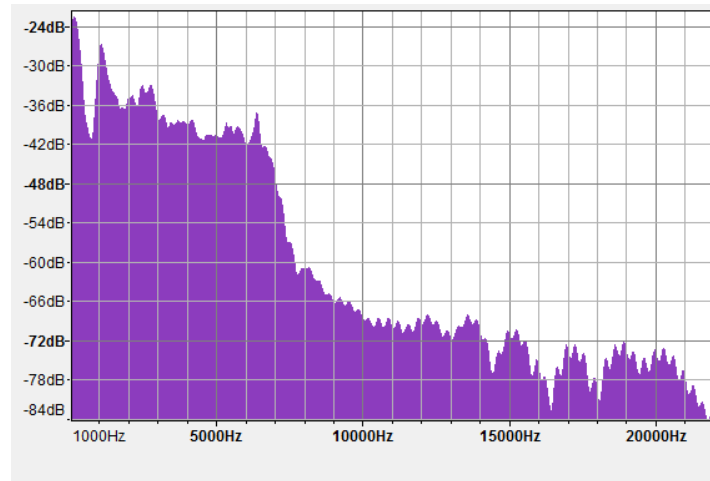


Figure 22 Extrapolated waveform to 60 dBA

The reverberation time obtained by performing the Impulsive Noise method is taken as the actual reverberation time and will be then compared with the theoretical reverberation time obtained using the following formula.

Sabine Formula to calculate reverberation time assuming reverberation decay is continuous [14]

$$t = \frac{0.16 \times V}{A} \quad (1)$$

Where

t = reverberation time (s)

V = volume of the room (m³)

A = total absorption of the room surfaces (m² sabins)

A = Σ (surface area x absorption coefficient)

Whereby sabins is defined as unit sound absorption. It is a product based measure which is particularly suitable for products discontinuity in space and is calculated by

$$\text{Number of Sabins per unit} = \text{total exposed surface area to sound} \times \text{absorption coefficient of that material} \quad (2)$$

$$A = S_1\alpha_1 + S_2\alpha_2 + \dots S_n\alpha_n = \Sigma S_i\alpha_i \quad (3)$$

Where

A = total absorption of the room surfaces (m² sabins)

S_n = area of the actual surface (m²)

α = absorption coefficient of the actual surface

$$\text{Absorption coefficient, } \alpha = \frac{\text{Absorbed sound energy}}{\text{Incident sound energy}} \quad (4)$$

3.0 Results and Discussion

Based on the data obtained from measuring the noise levels from the various sources over the span of five consecutive days, the average for each of the noise sources is then calculated and the results are shown in the Table 9. From it, we can see that the main source and largest contributor of the noise is originating from the patrons conversing in the restaurant. Therefore, assumptions for the source of excitation for the numerical analysis of the restaurant will be modelled based on the speech of the diners.

Table 9 Average decibel level of the potential noise sources

Source of noise	Decibel (dbA)
Air conditioning	56.8
Fans	55.8
Kitchen	59.4
Patrons	62.2

5) 3.1 Theoretical Reverberation Time

In order to obtain the theoretical reverberation time, the Sabine formula detailed previously is utilised. This approach is selected as opposed to the Norris-Eyring and Millington-Sette methods due to the fact that it is the standard practice for live rooms with a relatively low absorption coefficient [12]. The Norris-Eyring method states that there will be a sporadic decay of the sound with the influx of lesser reflections whereas the Millington-Sette formula is a much more tedious and complex formula and is used only when there are various absorption coefficients of the materials [11]. The Sabine equation is used in a case where the sound will decay in a continuous and smooth fashion, leading the sound to behave in a manner which is considered to be 'live' and not 'dead' as can be seen in the target location [6]. For the Sabine equation, the first step is to calculate the surface area and volume of the target location. This is done so by obtaining the values from the modelled restaurant in ANSYS. This represents a much more accurate and precise manner to obtain the values as the model of the restaurant in the software was done with the actual dimensions of the restaurant. This opposes what was done by Mohd. Afiq where the approach taken was to simplify the geometry of the restaurant and perform the calculations manually. The table below depicts the volume of the entire restaurant as well as the resultant surface areas which have been split into 4 components, namely the front walls made out of glass, the rear walls made out of bricks and cement, the ceiling made from gypsum plasterboard and the floor made from ceramic tiles.

Table 10 Measurements of the walls for the restaurant

Location	Material	Area (m ²)	Volume (m ³)
Front Wall 1-4	Glass	308.843	927.116
Rear Wall 5-7	Bricks & Cement	139.953	
Ceiling	Gypsum Plasterboard	946.622	
Floor	Ceramic Tile	956.953	

A tabulation of the absorption coefficients (α) for the respective building materials are shown below at the various frequency ranges that are of concern for this analysis [12]

Table 11 Absorption coefficient for the building materials used

Material	125 Hz	250 Hz	500 Hz	1000 Hz	2000 Hz	4000 Hz
Glass	0.18	0.06	0.04	0.03	0.02	0.02
Bricks & Cement	0.01	0.01	0.02	0.02	0.02	0.03
Gypsum Plasterboard	0.15	0.11	0.04	0.04	0.07	0.08
Ceramic Tile	0.01	0.01	0.01	0.01	0.02	0.02

The surface areas are then multiplied with their respective absorption coefficients for the various frequency ranges to obtain the absorption in metric Sabin, and are then used to obtain the resultant reverberation time as depicted in the table below.

Table 12 Absorption and reverberation time at the various frequencies

Frequency (Hz)	125 Hz	250 Hz	500 Hz	1000 Hz	2000 Hz	4000 Hz
Absorption of the room, A (m² metric Sabin)	208.556	133.624	62.583	59.495	94.371	105.237
Reverberation time, t (s)	0.71	1.11	2.37	2.49	1.57	1.41

From the results garnered, it can be seen that the reverberation time is particularly low when the frequency range is also low, at values of 125 and 250 Hz. For optimum speech frequencies of 500 and 1000 Hz, the reverberation time is at the peak [5]. The calculations performed do however have the limitations of ignoring the furnishings of the restaurant.

6) 3.2 Actual Reverberation Time

These values are then to be compared with the actual reverberation time obtained by performing the Impulsive Noise method reverberation time test. The normalized and extrapolated graphs of the sound wave generated from the balloon burst are shown below. From there, the average of the three reverberation times is obtained to be 1.86 seconds.

From the two sets of experimental results, it can be seen that the reverberation time calculated for the Temptations Restaurant is well above the acceptable and even recommended value for a restaurant which is found to be 1.0 to 1.5 seconds [13]. Therefore the task to find a solution to this issue and the purpose of this research is justified.

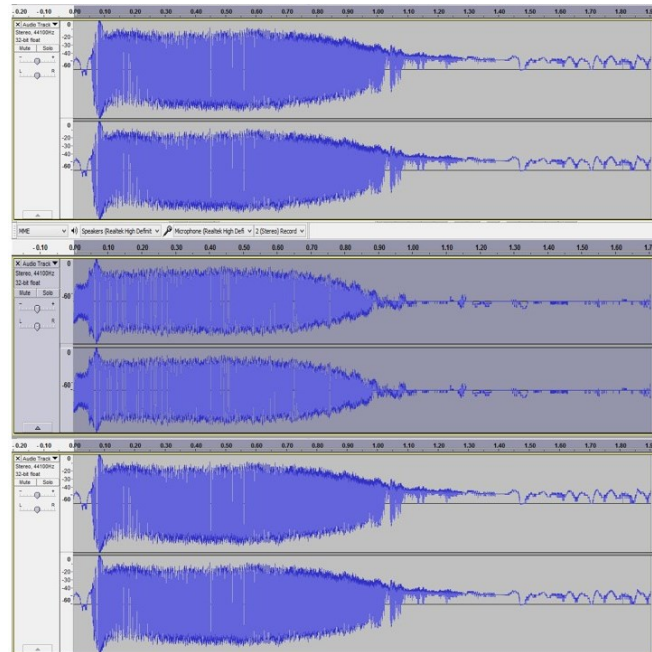


Figure 23 Normalized and extrapolated waveforms of the balloon tests

Table 13 Reverberation times from balloon tests

Test	Reverberation Time (s)
1	1.90
2	1.97
3	1.70

3.3 Numerical Analysis

7) 3.3.1 Single Source

Figure 14 shows the acoustic sound pressure level with the monopole wave as the source of excitation propagates through the restaurant. The maximum value of the SPL is found at the epicentre of the source and the minimum is found at the furthest possible point from the centre of the source which is the expected wave behaviour. However, the maximum value of 57.953 does not tally with the input of the excitation source which is 62.2 dbA (converted to 0.025 Pa) which is due to damping and dispersion of the wave.

Table 14 Results from Numerical Analysis for single source of excitation

Results	Minimum	Maximum
Acoustic Sound Pressure Level (dbA)	33.492	57.953
Acoustic Pressure (Pa)	-0.00350	0.00358

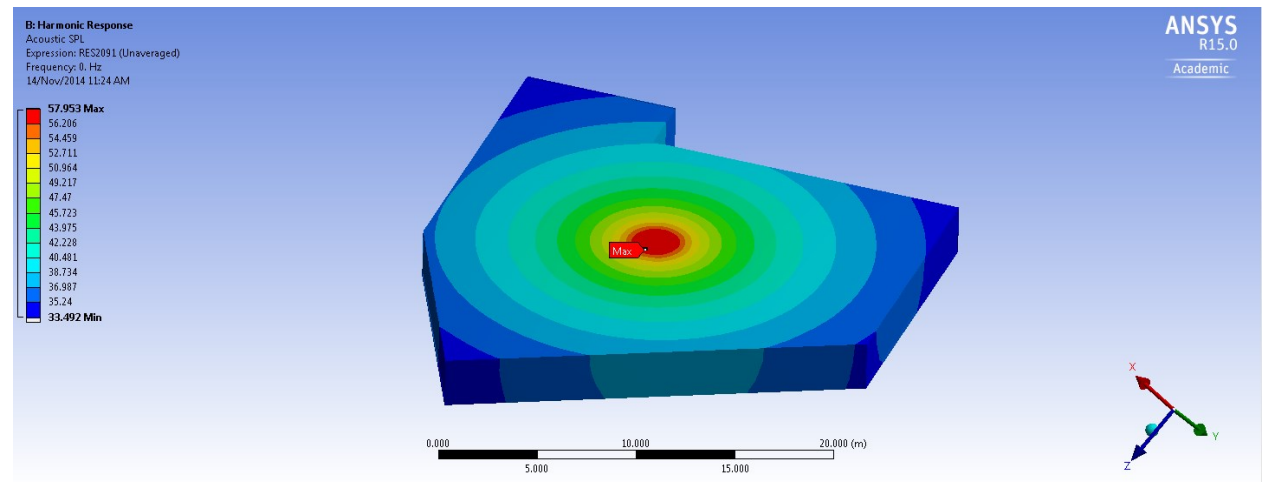


Figure 24 Acoustic Sound Pressure Level for single source of excitation

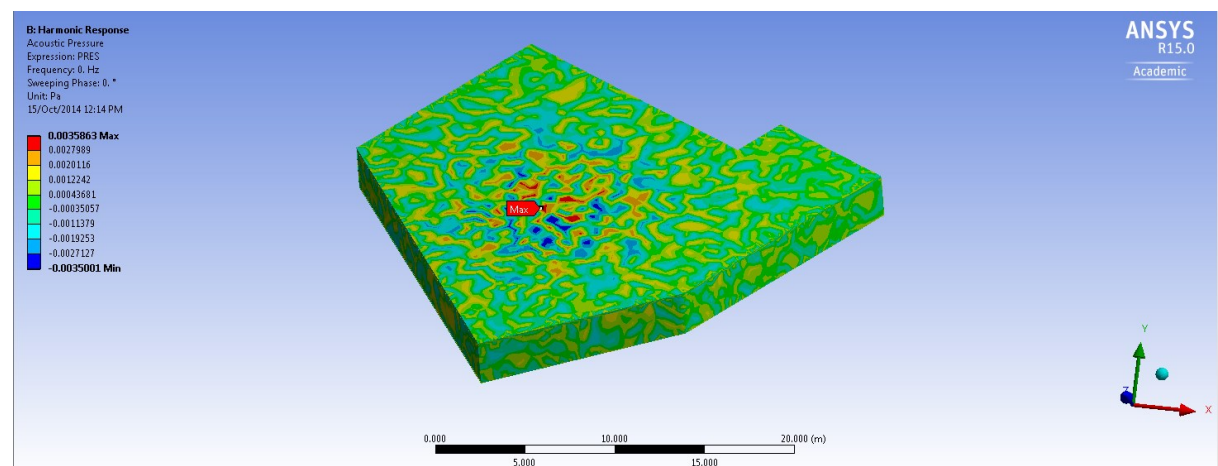


Figure 25 Acoustic Pressure for single source of excitation

The propagation of the acoustic pressure is depicted in the figure above. The acoustic pressure for this particular analysis is the degree of freedom for the acoustic problem resolution and thus it can be seen that there is a decrease in the degree of freedom where there are regions of high pressure. It shows that the pressure is scattered around the room with the concentration being at the centre where the excitation is placed. The maximum value of 0.00358 tallies with the literature on this subject as after dispersion, there is bound to be a drop in the pressure of the source [10]. However, the negative value for the minimum acoustic pressure attained is not one that can be justified and that is taken to be as an error for the reasons stated above in the discussion of the acoustic pressure. From the analysis of the propagation wave in terms of the acoustic sound pressure level and the acoustic pressure, it can be seen that even with a singular source, the sound is dispersing throughout the entire restaurant with large areas of significant levels of sound pressure level and acoustic pressure.

8) 3.3.2 Multiple Source

Table 15 Results from Numerical Analysis for multiple source of excitation

Results	Minimum	Maximum

Acoustic Sound Pressure Level (dbA)	3.4121	60.921
Acoustic Pressure (Pa)	-0.023307	0.021699

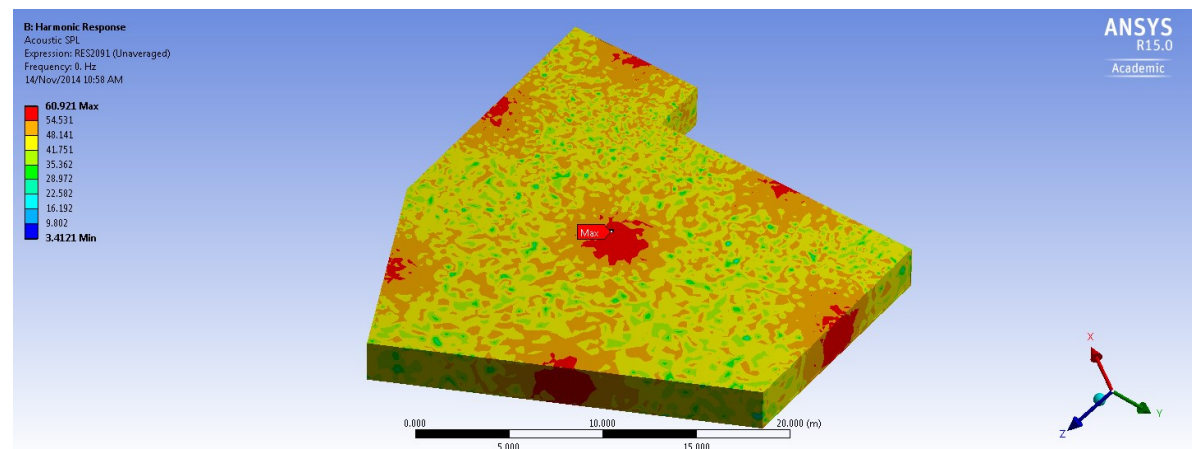


Figure 26 Acoustic Sound Pressure Level for multiple sources of excitation

The figure above shows the acoustic sound pressure level with multiple monopole waves as the sources of excitation propagating through the restaurant. As with the single source of excitation, the maximum value of the SPL is found at the epicentre of the source and the minimum is found at the furthest possible point from the centre of the source which is the expected wave behaviour. The maximum value of the sound pressure level has risen now to 60.921 dbA.

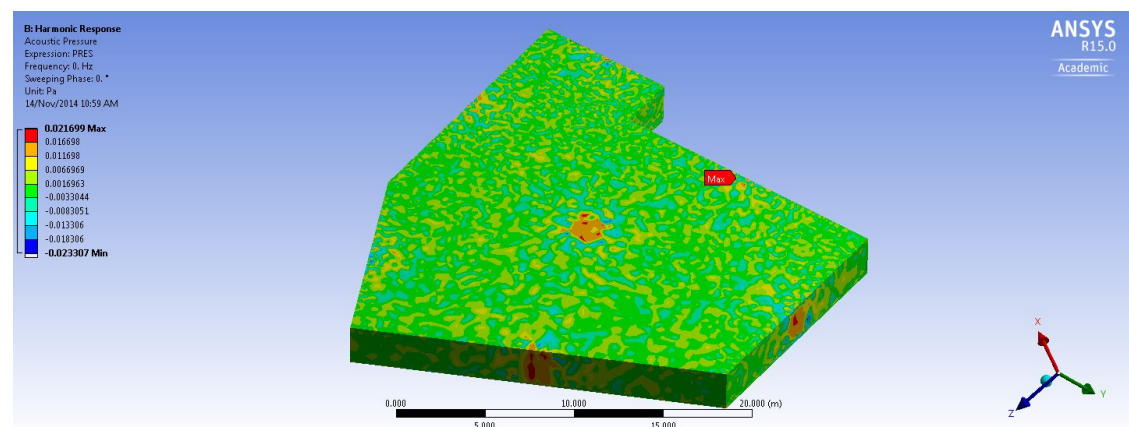


Figure 27 Acoustic Pressure for multiple sources of excitation

For the acoustic pressure there is also an increase to 0.0216 Pa as compared to the single source of excitation. There is a decrease in the degree of freedom towards the centre of the restaurant as well as where the sources of excitations are placed.

All of the figures shown above depict the maximum values of the sound pressure level and the acoustic pressure which occur between 1.5 to 2 seconds after the excitation begins. This tallies with the experimental analysis performed to obtain the reverberation time, thus showing the critical values are occurring during that period of reverberation of the sound wave. This also validates that the model is accurate in simulating how sound normally propagates in a room and thus provides verification of

the numerical simulation [16]. If we compare the propagation of the single wave and multiple wave excitation, we can see the difference of how multiple sources of excitation interact with one another and cause interference. The resultant interference of the multiple wave sources leads to higher values for the acoustic pressure and acoustic sound pressure level, as can be seen by the coloration of the figures whereby there are increased tones or yellow, orange and red for the excitation by multiple sources.

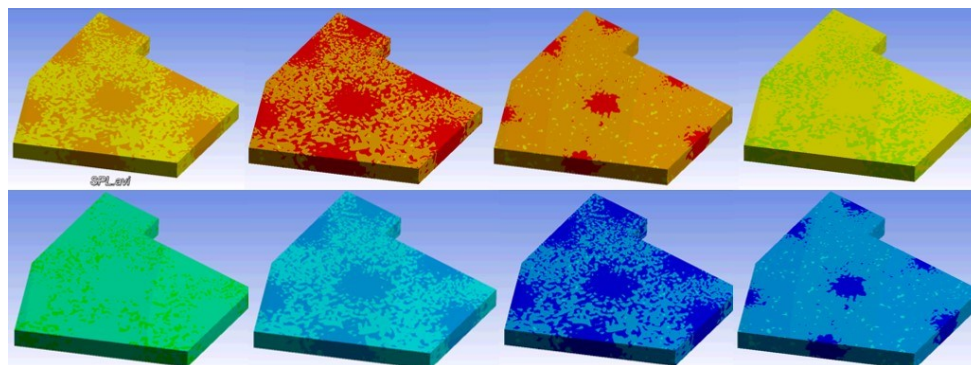


Figure 28 Entire propagation of acoustic Sound Pressure Level for multiple sources of excitation

By looking at the entire propagation for the excitation with multiple sources, the interference of the waves after the excitation begins and as the wave disperses it can be seen clearly whereby around the sources of excitation, there are regions of high acoustic sound pressure levels throughout the duration of propagation of the wave [7]. This lends to add credibility to the numerical analysis being performed as the wave behaviour that is depicted tallies with the theory on the matter.

4.0 Conclusion and Future Work

To review the success of this project, one must not only look at the tangible progress that has been made in terms of results and data, but instead, the progress of the project is reviewed in terms of the knowledge that has been gained and the resultant work performed based on that knowledge, all given the sheer difficulty of the task at hand. It was known from the start that this is a field that the researcher had no significant technical background in as sound and noise is not covered at all in the in the scope of learning in the Mechanical Engineering Degree Programme at Taylor's University. However, the sheer difficulty in undertaking a research topic for which one has no foundation in was clearly underestimated, along with the duration it would take to perform seemingly unassuming tasks such as a study of the basics of sound or familiarisation with the software being used in the numerical analysis. This, along with an overestimation of the allotted time led to delays in the predicted progress for the project. It was assumed that the numerical study could have already been started by the end of the first semester, however due to the fact that the ANSYS Acoustics Extension was not available in the university until the second semester and given the fact that it is a very new component of the software and thus, there are very limited materials on it, significant delays were experienced. The research team had to perform most of the analysis by trial and error as opposed to following a standard procedure or template for which to use the software to perform analysis in a room, let alone a restaurant. The numerical study that was performed only contained a maximum of

seven sources of excitation whereas in an ideal scenario, each table or even each patron of the restaurant would be modelled as in individual source of excitation. The numerical study that was performed was validated by the experimental results obtained which showed a high reverberation time for the restaurant. The method of obtaining the reverberation time was a significant advancement on the method performed by the previous researcher as the restaurant dimensions were not simplified and instead were done so much more precisely. Given more time and with a greater understanding of the software, it is a certainty that more significant progress could have been made to perform a more extensive and complete numerical analysis and thus, possibly leading to a solution to the noise attenuation problem.

In terms of the literature review for this research, one must really look at the thesis produced by Mohd Afiq (2013) [4] as this research is based on the work that he has done. The basics of sound and noise were covered thoroughly by him and therefore were not to be included in this text but instead, taken as research material on a personal level to allow for an understanding in this field to be built. The objective here was to expand the effort that has been done by him and use his work as a foundation. The focus was on covering the areas not touched on in that text as well as a study on potential solutions for noise attenuation in restaurants from current journals. It should be noted, that based on the research performed in this project that restaurant acoustics is an area of study for which there is inadequate material available from journal papers which explains their limited appearance as reference material in this text.

It can be readily concluded that the work being performed for this project over the duration of this project has been successful, despite the delays and progression made. It can be affirmed that the necessary building blocks and foundation has been laid for a successful continuation of this project which will hopefully yield an optimal solution to the noise attenuation problem for the Taylor's Temptations Restaurant.

In terms of future work, recommendations on how to alleviate the shortcomings and limitations from the effort that has been done can be made regarding better time management and less focus and emphasis on research from journal papers. Besides this, it is also recommended that more emphasis be placed on the experimental side of the project, as well as ensuring that the necessary tools such as the software upgrade is readily available from an earlier stage.

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Development of an Integrated Approach to Tube Assembly FE Model Correlation

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Abstract

Resonance occurs during transportation of an outdoor air-conditioning unit. Structural failure due to vibration was found on the copper tube assembly located within the interior of an air-conditioning unit. Modal study is required to prevent copper tube failures due to vibration during transportation and shipping. Finite element (FE) modal analysis has been implemented to replace the traditional design cycle, which is costly and time consuming. However, the reliability of FEA results greatly corresponds to the accuracy of FE model and also the boundary conditions. Hence, modal validation is needed to validate the accuracy of FE model with experimental data. The purpose of this research is to identify an integrated approach to validate the FE model of copper tube assembly. Finite element modal analysis of copper tube assembly is conducted using NX Nastran software. Pre-processing which includes meshing of copper tube and boundary condition setting were also implemented in the FE model of copper tube assembly. The modal result is obtained using the Lanczos mode extraction method. Test-analysis model (TAM) is created to represent the actual test structure. Impact hammer test is conducted based on TAM and measured frequency response function (FRF) is transferred to Bruel and Kjaer PULSE REFLEX software for modal parameter extraction. Extracted natural frequency and mode shape is compared with the FE model through modal correlation. Results show good agreement between the mode shape of FE model and mode shape based on experiment. On the other hand, natural frequency predicted by FE model is slightly lower compare to experiment. The maximum percentage differences is about 5% between natural frequency of FE model and experiment. This difference in natural frequency is within the allowable range. Hence, validated FE model of copper tube assembly was ready for design optimization and the calculated dynamic properties of the copper tube assembly were representative of the actual structure.

Keywords: Modal study, finite element modal analysis, Impact hammer test, Model correlation.

1. Introduction

In Panasonic Appliances Air Conditioning R&D Malaysia, there are exists risks of copper tube failures due to transportation and shipping. Copper tube is an important part in the outdoor air-conditioning unit to complete the refrigerant circuit through connection with other components. Failure of copper tube may cause leakage of refrigerant to the environment. The possible reason for this issue may arise from the exposure of vibrations during transportation. Resonance happens when the vibration frequency of the system coincides with the natural frequency of the copper tube assembly [1]. With the occurrence of resonance, a structure will tend to vibrate at its maximum amplitude, undergo high deformation which ultimately cause catastrophic structural failure. To avoid resonance, the researcher has employed mitigation techniques such as the traditional design cycle and the modern Finite Element Analysis (FEA) to determine the dynamic properties of the structure. Traditional design cycle is one of the common utilized traditional problem-solving methods [1]. However, this design cycle requires not only an immense amount of cost, but also requires a long period of time in order to reach a satisfactory level. Hence, FEA was introduced as an alternative solution to improve the traditional design cycle. Various finite element modal studies were conducted in civil infrastructure health monitoring fields [2, 3]. For an example, Wei *et al.* [4] have created a FE model for cable-stayed bridge using ANSYS modeling and simulation software to study the dynamic properties of the structure. On the other hand, Salam *et al.* [5] have studied the prospects of using FE modal analysis to help with bridge examinations in order to identify locations of critical high stress zone and validates the results with experimental data obtained from waveform analysis. With the advancement of finite element modal analysis, a rather detailed study of natural frequency and mode shape on a complex structure can be obtained easily and therefore able to minimize the costs and resources spent on traditional design cycle. However, the reliability of FEA results greatly relates to the accuracy of an FE model and also the boundary conditions set [6]. Hence, the validation of an FE model with experimental data is a crucial step in order for an accurate FE model to be produced.

For automobile and aerospace industries, modal analysis practices using FE method have been conducted since the past decades [7, 8]. The dynamic study of the structure have become a common practice for companies in these industries before taking any action to optimize the design of the structure. However, in terms of the air-conditioning industry, this practice is considered as a new research development in the field of vibration. The pioneer researchers who started modal study in the air-conditioning industry are Yusuhiro *et al.* [9] who made use of modal study to develop a set of manual for air-conditioning piping design. Later on, Ling *et al.* [10] invented an alternative to predict vibration response of air-conditioning unit through digital simulation technique. The use of modal analysis on air-conditioning units began after Chuan *et al.* [11] introduced a boundary condition used to test pipe lining systems of air-conditioning units during operation. Up to date, Lim *et al.* [12] have developed a methodology to correlate FE models with experiments through model correlation. As compared to the automobile industry, the development of modal analysis in air-conditioning industry is still observed to be gradually increasing.

Research and development of modal analysis in air-conditioning units so far focus only on single component studies. Lack of modal study is conducted based on assembly structure. Hence, the main objective of this research is to develop an integrated approach to validate the FE model of copper tube assembly with less than 10% error compare to experiment data. Validated FE model of copper tube assembly can be used for design optimization to avoid structural failure due to vibration.

2. Methodology

2.1 Finite Element Modal Analysis

2.1.1 Meshing

An outdoor air-conditioning unit's multi-bent deoxidized copper tube assembly is used for this research. Fig 1 shows the 3D model of the copper assembly tube and its location in the outdoor air-conditioning unit. The dimension of copper tube assembly suggests the length and width of the tube is large compared to the thickness of the tube. Hence, a 2D element (shell element) of copper tube is created rather than a 3D element [13]. Research has been conducted to compare the accuracy of 2D and 3D element to predict the natural frequency of multi-bent copper phosphorus tube [12]. Results show that 2D element yield better prediction of natural frequency compares with 3D element. This result was supported by Allemang *et al* [14] claim that 3D element yield higher natural frequency due to poor bending behavior compare to 2D element.

Before conducting FE modal analysis, the 2D shell element of the copper tube assembly is meshed with CQUAD 4 (quadrilateral) element of 1 mm size. Each node of the CQUAD 4 element consists of 6 DOFs. A total number of 37731 CQUAD 4element is created. The selection meshing element type and meshing size were proven as the optimum condition by Lim *et al* in the research about multi-bent deoxidized copper phosphorus tube [12]. The material assigned to the FE model of copper tube assembly is C10100 copper material available in material library of NX Nastran. The young's modulus for C10100 is 114 GPa.

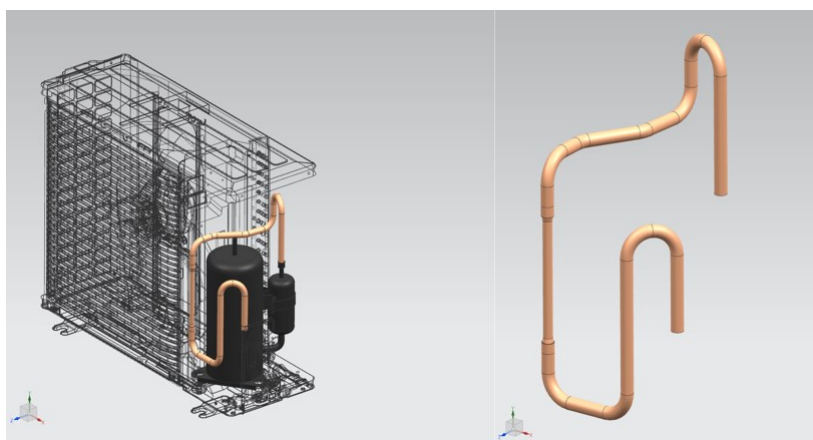


Figure 1. FE model of outdoor air-conditioning unit and magnified view of copper tube assembly understudy in PAPARAMY 1.

2.1.2 Copper Tube Assembly

In air-conditioning industry, copper tube is jointed together through brazing technique. Brazing is different from the welding process as it does not involve melting of base material [15]. Heat is applied to the copper tube at a temperature of 690 °C - 790 °C to melt the filler material. The filler material use in PAPARADMY 1 is phosphor copper alloy. Melted filler metal will fill up the gap between copper tube for the entire length and circumference. The melted filler material allows to solidify once the gap is completely filled with filler material. Once two copper tubes are connected, it is assumed that the assembly region will have no relative motion. In NX Nastran, this condition can be modelled using surface to surface gluing method to link the two copper tubes together. This method creates a gluing effect as the association between two surfaces to prevent any relative motion between two connected surfaces of different mesh sizes [16]. This method allows accurate displacement and load transfer, resulting an accurate strain and stress condition at the interface. Fig 2 shows the FE model of copper tube assembly using surface to surface gluing method.

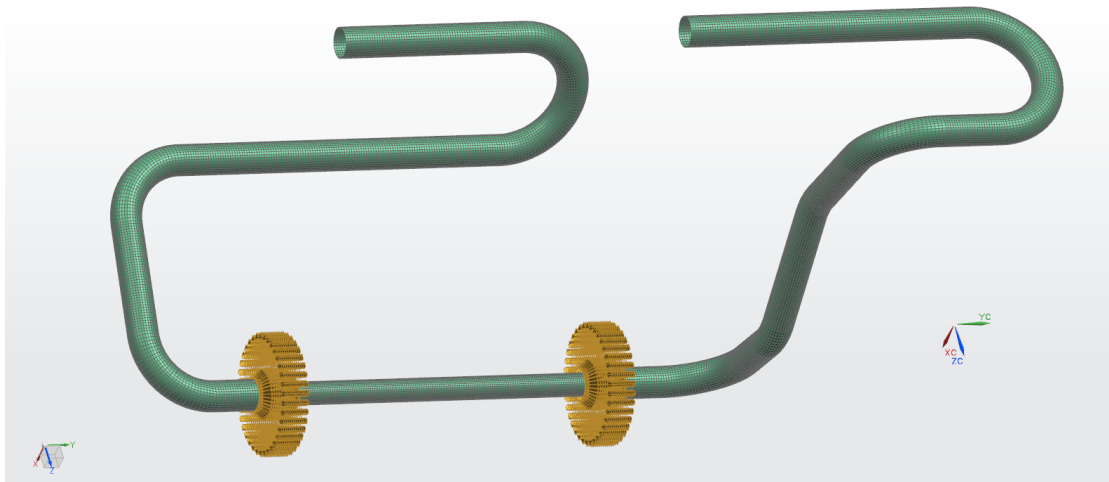


Figure 2. FE model of copper tube assembly using surface-surface gluing method.

2.1.3 Constraint

The interested frequency range for this study is between 3 HZ to 300 Hz. This interested frequency range is compliant with ISO 13355 Packing—Complete, filled transport packages and unit loads [17]. For finite element modal analysis, free boundary condition is approximate, meaning the structure the structure is freely suspended in space without any attachments to ground [18]. Hence, no external force and fixed boundary condition were applied. Also, it was assumed that copper tube assembly is linear throughout the experiment. Thus, the properties of copper tube assembly do not change with time [19].

2.2 Experimental Modal Analysis (EMA)

Modal analysis is the study of the natural frequency and mode shape of a designed structure which is subject to vibration. Knowing these dynamic properties of

the structure help preventing catastrophic failure of the structure due to resonance. Impact hammer test is one of the most common use experiments to perform modal analysis of structure. The procedure of EMA requires; pre-test planning, impact hammer test and parameter estimation.

2.2.1 Pre-Test Planning

Pre-test planning is the first and foremost prerequisite for the experimental modal analysis. Pre-test planning is conducted to reduce the DOF of FE model to a suitable set of DOF which can be used for the experiment. The reduced DOF model is known as the test-analysis model (TAM) which is used to represent the actual model of copper tube assembly in the experiment. Pre-test planning mainly include the selection of sensor location and excitation location. The selections of sensor and excitation points are vital as it strongly affects the results of the model correlation. Pre-test planning of copper tube assembly is performed using NX Nastran software with a total of 24 measurement points were selected to capture all desire mode within interested frequency range. Fig 3 shows the TAM for copper tube assembly together with the corresponding measurement node number. The numbers appear in Fig 3 indicate the node number for the measurement point use for the experiment.

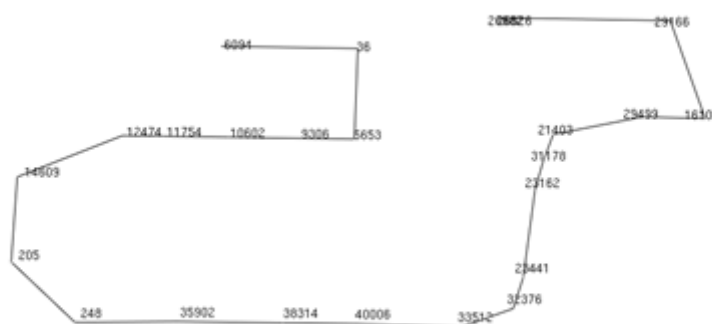


Figure 3. Test-analysis model for copper tube assembly.

2.2.2 Impact hammer test

Impact hammer test is one of the commonly used methods for modal analysis of structures [13]. Bruel and Kjaer instrumentation series, namely; miniature impact hammer type 8204, 0.65 milligram uniaxial accelerometer type 4517 and FFT analyzer with 12 channel input module type 3053-B-120 was utilized in this experiment. Fig 4 (b) shows Bruel and Kjaer FFT analyzer use in this experiment. Bruel and Kjaer MTC Hammer was used as the measurement software and all accelerometers is calibrated with Bruel and Kjaer calibration exciter type 4294 at 1 kHz before attached to the copper tube assembly. The calibration error for the accelerometer is within the range of 3%. A free boundary conditions are hardly modeled in actual tests. Hence, elastic cord is used to approximate free-free boundary

condition of copper tube assembly. Other configurations, including the sampling frequency of 1023 Hz over a frequency span of 400 Hz, frequency resolution of 1 Hz, linear averaging and transient weighting is applied for analyses.

Fig 4 (a) shows the setup of the experiment for copper tube assembly with 10 uniaxial accelerometer attached to the structure. The copper tube assembly is excited with impact hammer over 5 times to obtain an average response for every single measurement point. The experiment considers the 10 sensors and 24 measurement points were included and the response of the structure is measured by the uniaxial accelerometer attached to the structure. The responses measured by the accelerometer are then processed by Fast Fourier Transform (FFT) analyzer to convert the data into the frequency response function (FRF). The FRF of copper tube assembly displays the information about the natural frequency and mode shape of the structure. The measured FRF of copper tube assembly is transferred to Bruel and Kjaer PULSE REFLEX software to extract the dynamic properties of the structure through the parameter estimation process.

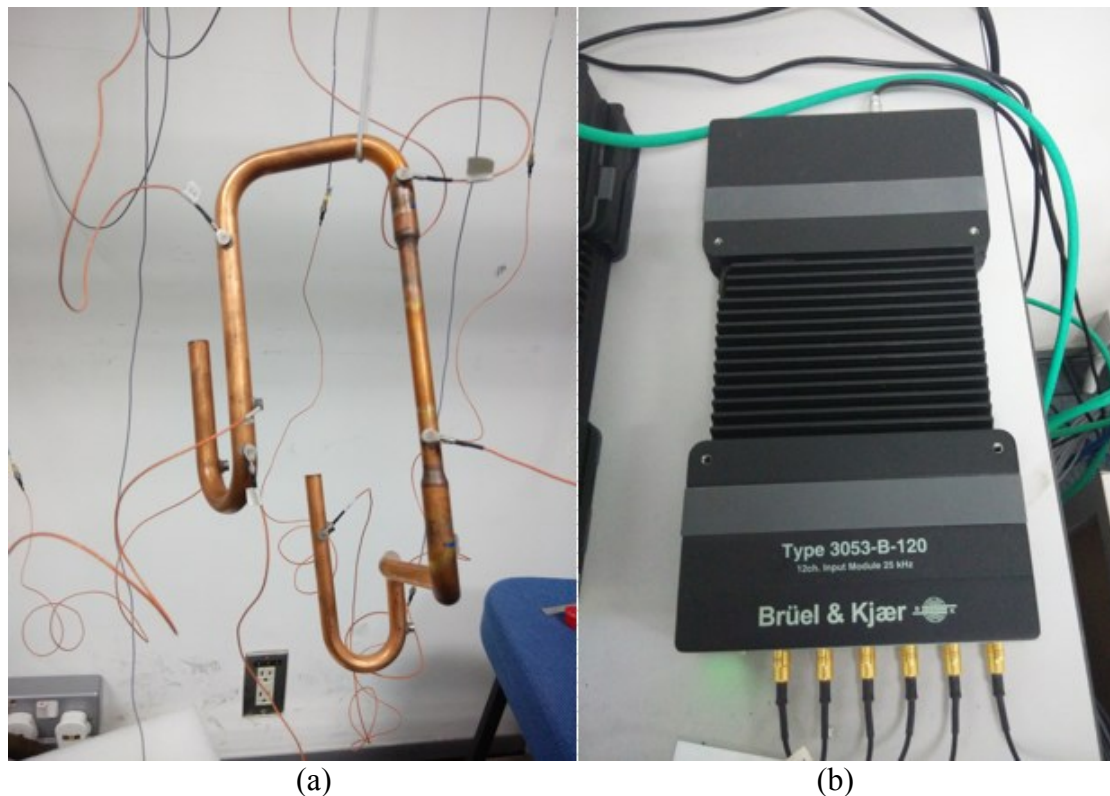


Figure 4. Experimental setup of copper tube assembly (a) and Bruel and Kjaer FFT analyzer (b).

2.2.3 Model Correlation

Modal Assurance Criteria (MAC) is a validation process to compare the natural frequency and mode shape obtained through experiment and FE model. The degree of similarities and dissimilarities of the mode shape between experiment and FE model can be evaluated based on MAC plot value of 0 to 1. An ideal example of a correlation outcome will have a diagonal element of more than 0.9 and an off-

diagonal element of 0.1 or less. For a mode shape obtained from experiment (ψ_{EXP}) and mode shape from FEA (ψ_{FEA}), the MAC value can be obtained using Eq. (1) [14].

$$MAC = \frac{|\psi_{EXP}^T \psi_{FEA}|}{(\psi_{EXP}^T \psi_{EXP})(\psi_{FEA}^T \psi_{FEA})} \quad (1)$$

3. Results and observation

3.1 Finite Element Modal Analysis

Finite element modal analysis is conducted using NX Nastran SEMODES 103 solution. The natural frequency and mode shape of the copper tube assembly is extracted using Lanczos method. Within the frequency range of 3 Hz to 300 Hz, a total of 7 natural frequencies and its respective mode shapes were predicted. Fig 5 shows the mode shape of the copper tube assembly for mode 1, 4 and 6. As shown in Fig 5 (a), (b), (c), mode 1, 4 and 6 are bending modes at different natural frequencies. The natural frequency of each corresponding mode is shown in Table 1.

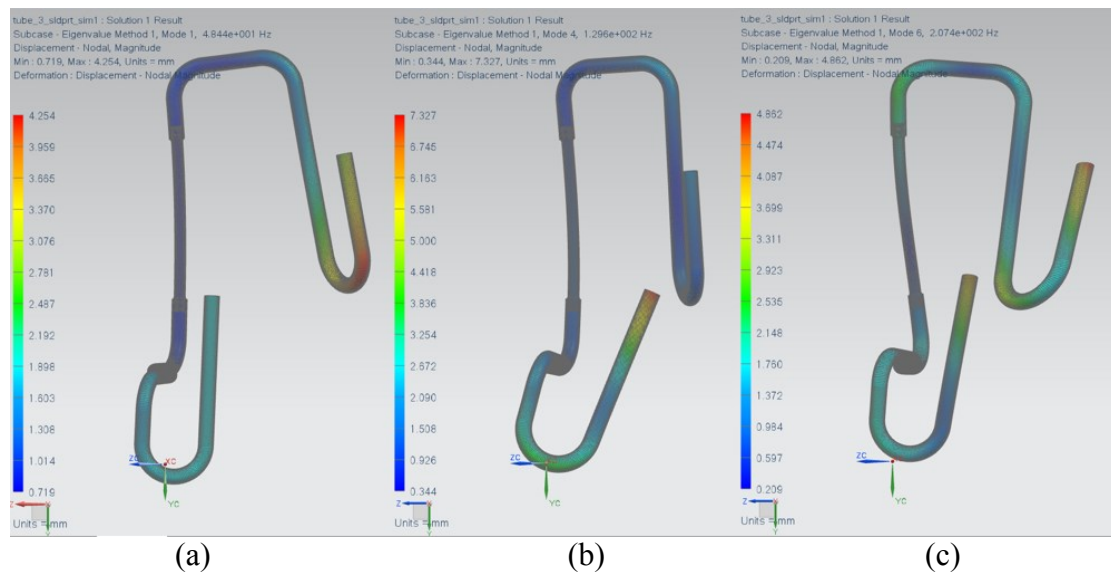


Figure 5. Mode shape of copper tube assembly for mode 1 (a), 4 (b) and 6 (c).

3.2 Experimental Modal Analysis (EMA)

Impact hammer test was conducted on copper tube assembly. 10 uniaxial sensors were utilized and a total of 24 measurement points, including sensor point were excited using impact hammer. Impact hammer is used to excite each measurement point with an average of 4 hit per measurement point. Hence, Fig 6 shows an example of FRF output obtained from one of the measurement points. The peak of the FRF indicates the natural frequency of the copper tube assembly. On the other hand, the mode shape of the structure can be obtained from phase relation between the frequency response at different measurement point and the amplitude of FRF. This FRF is transferred to Bruel and Kjaer PULSE REFLEX software to extract

the value for natural frequency and corresponding mode shape of the copper tube assembly.

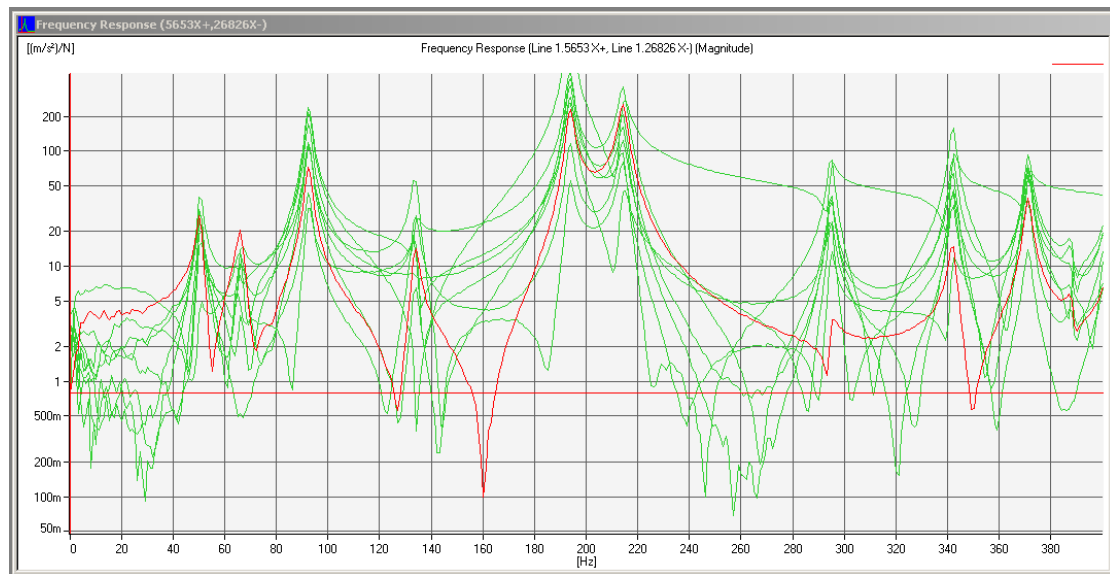


Figure 6. Frequency response function (FRF) of copper tube assembly.

3.3 Comparison between FE Model and Experiment

Accuracy of FE model requires validation with experimental data. Accuracy of FE model were asses through natural frequency obtained from both FE result and experimental modal analysis. Table 1 compares the natural frequency of the copper tube assembly obtained from the FEM with natural frequency extracted from the experimental modal analysis.

Table 1. Comparison between natural frequency of FE model and experiment.

Mode	Natural frequency		Freq. % Difference
	FEA	EMA	
1	48.44	50.28	-3.65
2	62.43	65.86	-5.21
3	88.63	92.30	-3.97
4	129.56	133.68	-3.08
5	189.15	193.62	-2.31
6	207.36	214.18	-3.19
7	281.55	294.65	-4.45

Model correlation is performed to compare the mode shape predicted by FEM with actual mode shape extracted from the experiment. The coordinate system of the TAM was aligned with the FE model of copper tube assembly. The comparison between FE modal model and experimental mode shape can be evaluated based on the MAC plot show in Table 2. Fig 7 shows the graphical comparison between the mode shape of FEM with experiment for mode 1.

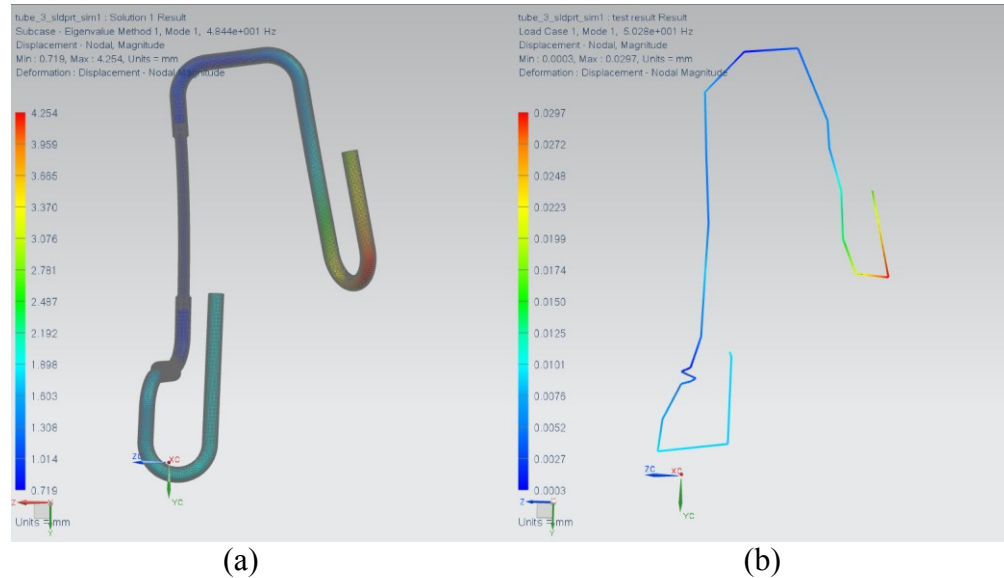


Figure 7. Mode shape comparison between mode 1 of FE model (a) and experiment (b).

Table 2. MAC plot of FE model against experiment.

	EMA 1	EMA 2	EMA 3	EMA 4	EMA 5	EMA 6	EMA 7
FEA 1	0.94	0.00	0.00	0.01	0.00	0.02	0.01
FEA 2	0.18	0.85	0.08	0.05	0.01	0.00	0.02
FEA 3	0.00	0.09	0.95	0.01	0.00	0.04	0.06
FEA 4	0.01	0.03	0.01	0.91	0.00	0.02	0.01
FEA 5	0.00	0.02	0.00	0.05	0.96	0.02	0.00
FEA 6	0.01	0.01	0.05	0.01	0.00	0.87	0.01
FEA 7	0.00	0.01	0.02	0.00	0.00	0.02	0.96

4. Discussion

As shown in MAC plot, the diagonal of the plot show fairly acceptable MAC value of more than 0.8. The results indicate that all FEM mode shapes within the interested frequency range is well correlated with relations to the EMA outcome under the accuracy of more than 80%. Hence, it is justified that the configuration applied to FE model allow accurate prediction on the mode shape of the structure with an accuracy of more than 80% compared to experiment. As for the off-diagonal values, overall MAC plot shows value of less than 1. This indicates individual mode can be distinguished clearly without any similarity with other individual mode. However, the slightly high MAC value of 1.78 was found between FEM mode 2 and experiment mode 1 showing a difference in 20%. A good correlation of FEM with EMA should have an off-diagonal MAC value of less than 0.1. The results of the poor

correlation between FEM mode 2 and experiment mode 1 can be due insufficient of sensor use to distinguish FEM mode 2 and experiment mode 1.

Although mode shape shows a positive outcome between FE model and experiment, natural frequency predicted by FE model is slightly lower compare to the actual natural frequency of copper tube. The largest difference in natural frequency was found in mode 2, relatively a difference of 5%. The discrepancy may possibly be due to two factors where; the density of FE model is slightly higher as compared to actual copper tube and the increasing stiffness due to brazing which affect the natural frequency of copper tube. Since the relationship between natural frequency and mass of the structure is inversely proportional, thus increase in density result in lower natural frequency. However, this difference is still within the acceptable range [20].

A good modal correlation does not come with ease. Several trail experiment have been conducted before obtaining good correlation plot shows in Table 2. Parameter including, measuring point used to experiment, sufficient of measured degree of freedom, number of accelerometer and hanging position may affect the precision of the experimental result and thus affect the mac plot [21]. In order to deal with this issue, MAC plot of FE model against initial TAM model need to be assessed before conducting the experiment. This mac plot allows theoretical prediction of the correlation between FE models with TAM model represent the actual copper tube assembly. Experiment can only be conducted when this theoretical prediction suggests good correlation between FE model and TAM.

5. Conclusions

Modal study is essentially important to avoid risk of copper tube failures due to transportation and shipping. FE modal analysis is conducted using NX Nastran sol 103 software to identify the dynamic properties of the copper tube assembly. An experimental modal analysis is conducted to validate the result of FE model. Model correlation is conducted to identify the similarity and dissimilarity of the mode shape for FE model and experiment. The correlation result shows good correlation between FE model and experiment. The similarity of mode shape between FE model and experiment is more than 80%. The off-diagonal in mac plot shows value of less than 0.1 indicating that the individual mode were clearly differentiated from each other.

The natural frequency of both FE model and experiment were also compared to identify the percentage difference. Results show that natural frequency predicted from FE model was slightly lower as compare with experiment. The largest difference in natural frequency was found in mode 2, relatively a difference of 5%. The discrepancy may possibly be due to two factors where; the density of FE model is slightly higher as compared to actual copper tube and the increasing stiffness due to brazing which affect the natural frequency of copper tube. However, this discrepancy is still within the desired level. Hence, this validated FE model with the mentioned configuration could be used in design optimization with great confidence that the calculated dynamic properties of the copper tube assembly were representative of the actual structure.

Acknowledgment

This project was carried out with full support of equipment from Panasonic appliances Air-Conditioning R & D (M) Sdn. Bhd. (PAPARADMY 1), Malaysia. Special thanks are extended to PAPARADMY 1 Deputy Director Mr. Low Seng Chok for the approval and procurement of Copper assembly tubes for testing. Also, the author would like to acknowledge Mr. Cheng Chee Mun, General Manager of the Cost Management Department (CMD) for authorising the use of B&K test equipment and Siemens PLM Software.

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Evaluation of maximum temperature of Rayleigh Plesset Noltingk Neppiras and Poritsky (RPNNP) equation

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Abstract

The main objective behind this research is to understand the concept of microbubble cavitation. Cavitation occurs when ultrasound with a frequency of 20 kHz or more is directed to the fluid which contains microorganisms. During cavitation, a phenomenon called acoustic cavitation will occur and this phenomenon refers to the collapsing of a cavitation bubble. Furthermore, this phenomenon can be modelled numerically with the help of the Rayleigh-Plesset equation. Further study of the Rayleigh-Plesset (RP) equation can show that it is a nonlinear ODE model which take into consideration of the radius of the bubble surrounding the liquid. With the help of other researchers, Noltingk, Neppiras and Poritsky took into consideration the surface tension as well as the fluid viscosity during the bubble cavitation and added their findings into the RP equation thus forming the Rayleigh-Plesset Noltingk, Neppiras and Poritsky (RPNNP) equation. With the understanding of physics terms such as the placement of pressure on the inner and outer layer of the bubble, derivatives of the resonant frequency equation could be obtained and later on model using the MATLAB R2013a software that is found in Taylor's University Lakeside computer labs. The findings of this is that when the RPNNP equation is taking into consideration and compared with the RP equation. The resonant frequency produced from the RPNNP equation shows that it is greater than the ones from the RP equation. This is due to the input of the surface tension and fluid viscosity factors.

Keywords: Rayleigh-Plesset Noltingk, Neppiras and Poritsky equation , resonant frequency, cavitation bubble,

1. Introduction

1.1 Research Background

Microbubbles are normally used in the analytical usage for ultrasound. The microbubbles are formed through the phenomenon called cavitation. Ultrasonic treatments have the characteristics of a wave for example a pressure wave which consists of an ultrasound with a frequency of 20 kHz or more. A normal ultrasound configuration can hold a frequency of 20 kHz to about 100 kHz. In high powered ultrasound with lower frequency (20 Hz to 100 kHz) is referred to as 'power ultrasound' is capable of causing cavitation which causes inactivation in microorganisms (Piyasena, Mohareb, & McKellar, 2003). acoustic cavitation refers to the collapsing of the a cavitation bubble will cause liquid jet to burst towards the centre of the bubble that is collapsing (Chandrapala, Oliver, Kentish, & Ashokkumar, 2012). Cavitation refers to the shear stress caued by viscous dissipative eddies which arises from ultrasound disruption from the shock waves produced from bubbles from the ultrasound imploding. Shear forces which creates eddies that are larger than the microorganism are more likely to be moved rather than disrupt whereas eddies which are smaller than the microorganism are more capable of generating a disruptive shear stresses. The basics of the mathematical models for cavitation used to analyse the cavitation phenomenon that occurs during cavitation is tthe Rayleigh-Plesset (RP) equation. This equation came about when Lord Rayleigh who studies the cavitation of microbubbles and thus came up with the ODE model which then becomes the Rayleigh-Plesset equation (Stride & Sa, n.d.). Continuing the study of Rayleigh-Plesset is the works of Noltingk and Neppiras and Poritsky who in turn modified the original Rayleigh-Plesset equation to form the Rayleigh-Plesset, Noltingk, Neppiras and Poritsky (RPNNP) equation which took into consideration the surface tension and fluid viscosity to the model.

1.2 Project Scope

In the research of bubble cavitation, an important equation is created by Lord Rayleigh during the 19th century. The RPNNP equation is a nonlinear ODE models which takes into account the radius change with regards to the time. In the early stages development of this equation, surface tension as well as fluid viscosity is not included in the equation but later on was added into the equation by the contributions of Noltingk and Neppiras and Poritsky and thus the equation was named to be the RPNNP equation. The project scope that is set for this research is to obtain the derivative from the RP equation and its evolution to the RPNNP equation. Another thing that is taken into consideration is the effects of resonant frequency with regards to its change in bubble radius.

1.3 Project Objectives

The objectives of this research is to derive the RPNNP equation from its original equation which it's the Rayleigh-Plesset (RP) equation. Following that objective is to determine the derivative of the resonant frequency equation and input the equation into the MATLAB R2013a software and obtaining the graph of resonant frequency with respect to initial bubble radius. Lastly is to obtain the maximum

temperature equations from the derivative of the RPNNP equation and evaluation of these values.

2. Research Methodology

2.1 RP equation

The Rayleigh-Plesset equation is a second order nonlinear ODE to take into account the radius of the bubbles which moves around in the liquid. The RP equation shows the bubbles in an incompressible fluid of a constant density ρ (Stride & Sa, n.d.). In the first stages of derivation, the assumption made that the pressure that is further apart from the bubble is classified as p_∞ as the fluid pressure that is present in the fluid. Next is the consideration of the sound fields that are driven in the area further apart from the fluid making

$$p_\infty = p_o + P(t) \quad 1.1$$

Where in this equation p_o is a constant.

The ODE model that is prepared by Lord Rayleigh with accordance to the $R(t)$ radius is shown below:

$$\ddot{R}R + \frac{3}{2}\dot{R}^2 = \frac{p_L(t) - p_\infty}{\rho} \quad 1.2$$

p_L is the pressure of the liquid that can be found on the surface of the bubble.

When the gas bubble that is considered is spherical in an incompressible liquid, the fluid velocity of $u(r,t)$ is an inverse square law in accordance to range r being the assumption of an incompressible fluid which gives the equation

$$u(r,t) = \frac{R^2(t)}{r^2(t)} \dot{R}(t) \quad 1.3$$

Where the $R(t)$ is the radius and $\dot{R}(t)$ is the bubble wall velocity. As time goes by, the change in the bubble radius causes work to be done from a pressure that is exerted from the centre of the bubble if there is no bubble present. During the phase when the pressure highly exceed the bubble radius, it will equals the liquid pressure which is further from the bubble from the previous assumption $p_\infty = p_o + P(t)$ which includes the component $P(t)$ (Stride & Sa, n.d.). The differences that can be seen from the pressure and the pressure done on the bubble wall p_L gives a similar kinetic energy to the liquid and can be balanced and expressed as below:

$$\int_{R_o}^R (p_L - p_\infty) 4\pi R^2 dR = 2\pi\rho_0 R^3 \dot{R}^2 \quad 1.4$$

By differentiating equation 1.2 with respect the R and taking note equation 1.5

$$\frac{\partial \dot{R}^2}{\partial R} = \frac{1}{R} \frac{\partial \dot{R}^2}{\partial t} = 2\ddot{R} \quad 1.5$$

Which gives,

$$p_L(t) - p_\infty = p_o \left(R\ddot{R} + \frac{3\dot{R}^2}{2} \right) + O(\dot{R}/c) \quad 1.6$$

From equation 1.6, the last hand side is the differences of the work done at the bubble walk at the outer pressure that is further away from the bubble. The right side is the energy that is given out when it is separated from the liquid. From equation 1.1, when this condition applies and substituted into equation 1.6 it gives the Rayleigh-Plesset equation:

$$R\ddot{R} + \frac{3\dot{R}^2}{2} = (p_L(t) - p_o - P(t)) + O(\dot{R}/c) \quad 1.7$$

Or writing as:

$$R\ddot{R} + \frac{3\dot{R}^2}{2} = \frac{p_o \left(\frac{R_o}{R} \right)^{3\gamma} - p_o - P(t)}{\rho} \quad 1.8$$

2.2 RPNP equation

With the help of Noltingk and Neppiras and Poritsky which included the effects of fluid viscosity, μ , and also surface tension σ to the original RP equation and is called the Rayleigh-Plesset Nolthingk and Neppiras and Porisky equation (RPNP) which is shown below:

$$R\ddot{R} + \frac{3\dot{R}^2}{2} = \frac{1}{\rho} \left(\left(p_o + \frac{2\sigma}{R_o} \right) \left(\frac{R_o}{R} \right)^{3\gamma} - p_o - P(t) - \frac{4\mu}{R} \dot{R} - \frac{2\sigma}{R} \right) \quad 2.0$$

Equation 2.0 shows that the RPNP equation includes the surface tension as well as the fluid viscosity on the right hand side of the equation. The viscosity is a factors that affects the liquid pressure along the bubble surface whereas the viscous component of the equation is removed with accordance to the spherical symmetry.

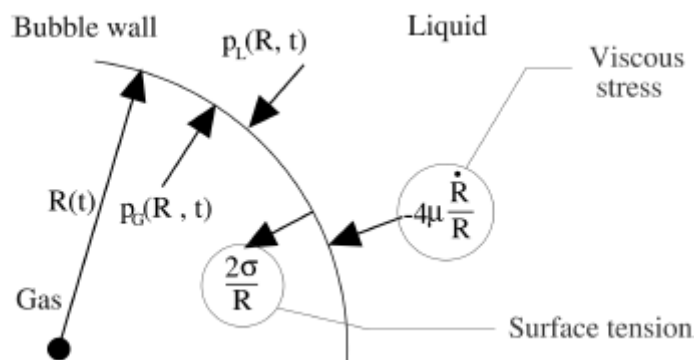


FIGURE 1.1 Forces acting on the bubble surface (1)

By applying the boundary conditions that assumes that the bubble was initially in equilibrium where $\dot{R} = 0$ and if we assume that the pressure at time $0 = 0$ $P(0) = 0$, the inclusion of the boundary conditions makes up the RPNP equation:

$$R\ddot{R} + \frac{3\dot{R}^2}{2} = \frac{1}{\rho} \left(\left(p_0 + \frac{2\sigma}{R_0} \right) \left(\frac{R_0}{R} \right)^{3\gamma} - p_0 - P(t) - \frac{4\mu}{R} \dot{R} - \frac{2\sigma}{R} \right)$$

(Sutherland, 2008)

Linearization of the RP and RPNP equation is done to obtain the oscillatory response along the driving frequency ω . The assumption of the applied pressure $P(t)$ is made to be a low amplitude which causes the radius of the bubble to change to be $R = R_0(1 + x(t))$ where in this case $|x| \ll 1$ and everything is remained in terms of x (first order).

Resonant frequency for Rayleigh-Plesset equation

Following the RP equation from 1.8 when $R = R_0(1 + x(t))$ is substituted into equation 1.8 while ignoring any second order terms of x . It gives:

$$\frac{p_0 \left(\frac{1}{1+x} \right)^{3\gamma} - p_0 - P(t)}{\rho} = R_0^2 \ddot{x} \quad 2.1$$

Next all the pressure terms is further simplify using binomial theorem:

$$p_0 \left(\frac{1}{1+x} \right)^{3\gamma} \approx p_0 (1 - 3\gamma x) \quad 2.2$$

When 2.2 is substituted into 2.1 and dividing both side by R_0^2 it gives:

$$\ddot{x} + \frac{3\gamma p_0 x}{\rho R_0^2} = \frac{-P(t)}{\rho R_0^2} \quad 2.3$$

Equation 2.3 shows that it is a linear oscillator equation with resonant frequency and can be expressed by the following:

$$\omega_0 = \frac{1}{R_0} \sqrt{\frac{3\gamma p_0}{\rho}} \quad 2.4$$

(Wolfrum, 2004)

Equation 2.4 is used to be compared with the RPNP equation of resonant frequency as the resonant frequency for the RPNP equation is shown below:

$$\omega_0^2 = \frac{1}{\rho R_0^2} \left(3\gamma \left(p_0 + \frac{2\sigma}{R} \right) - \frac{2\sigma}{R} \right) \quad 2.5$$

(Wolfrum, 2004)

3. Results & Discussion

Using the parameters that had been set in table 1 or else stated otherwise, the graph of resonant frequency between the RP equation and RPNNP equation is plotted using the MATLAB R2013a software. A series of matrix system with loop which related to the initial bubble size as well as the responding frequency.

Table 1.0: Various values for plotting of resonant frequency (Al-juboori, 2012)

Component	Units	Description
R0	2:10 with step of 1×10^{-3}	Vectors or radius from 2-10mm
P0	101.3 KPa	Pressure Pa
D	1.5×10^{-9}	Shell Thickness
R01	R01=R0	Inner radius
R01	R02=R0+d	Outer radius
σ	7	Surface tension
γ	1000	Fluid density
γ_s	1100	Shell density

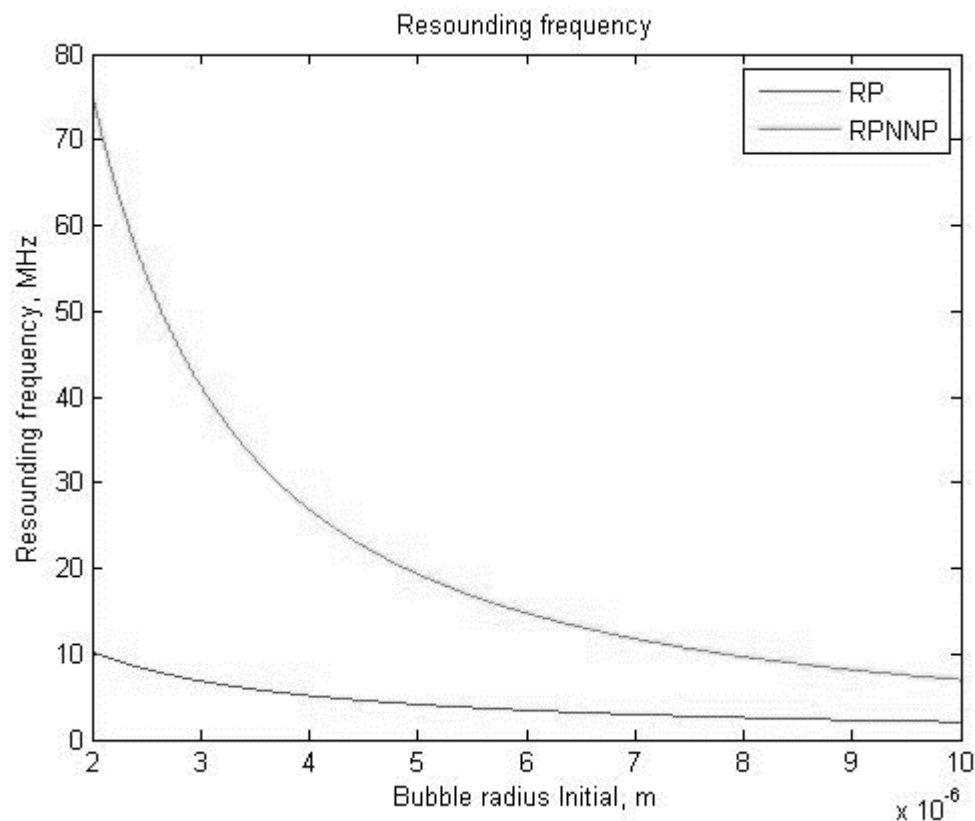


Figure 3.1 Comparison of resounding frequency ω_0 between RP equation and RPNNP equation as a function of the bubble radius which has been set to be initial.

According to figure 3.1, equation 2.4 is used to model the response above where equation 2.5 is used as a comparison. The values that are fitted into the equation can be found in Table 1.0. These parameter were adopted by following the experiments done by (Sutherland, 2008) where the experiments conducted agrees with the findings. As it is shown from Figure 3.1, the response frequency from the RPNNP equation is

higher for when $t=0$ due to the fact of the derivative and adoption of the surface tension as well as the fluid viscosity. Another reason is that for the RPNP equation, it depends more on the R_0 . The derivative can be found from Equation 2.1. Another thing to note is that frequency have a tendency to reaches infinity as it start from 0 for the bubble radius.

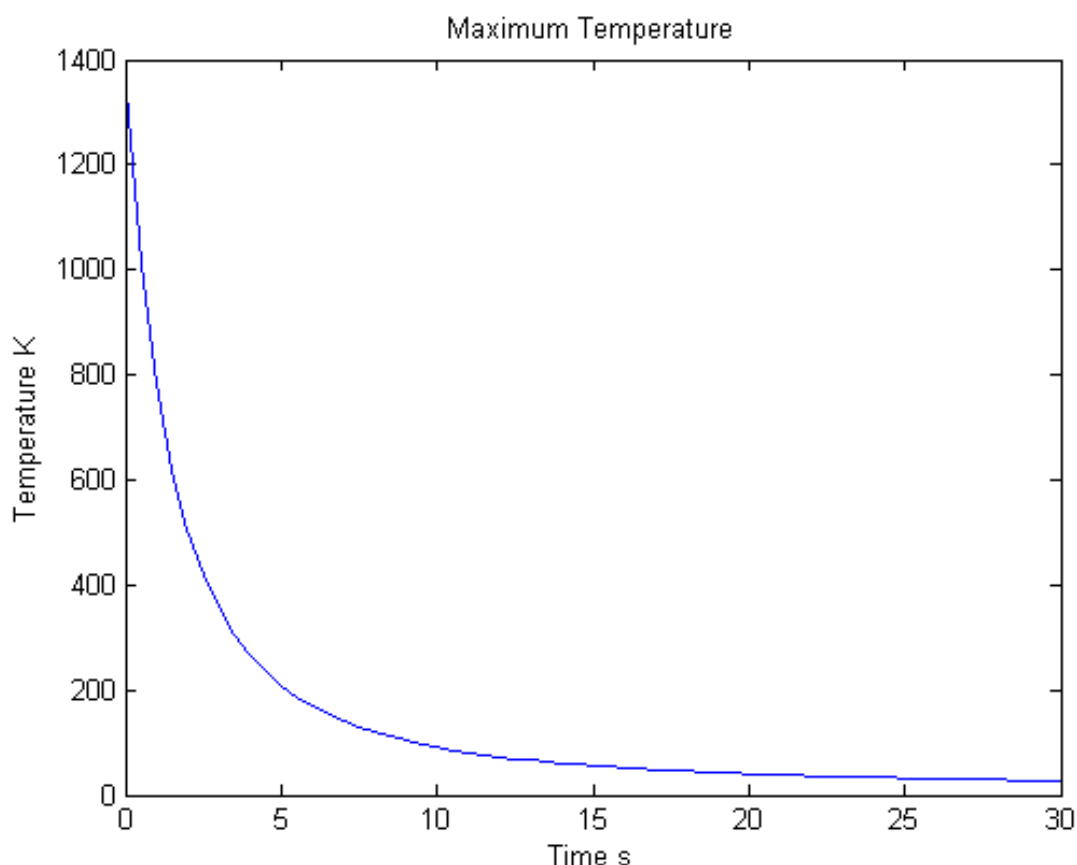


Figure 4.1 Maximum temperature using temperature of bulk solution of 500 K with respect to time

According to figure 3, with the allocated time frame of 30 seconds a study has been conducted to find out the maximum temperature of the cavitation of the bubble when undergoing ultrasound treatment. MATLAB R2013a was used to obtain the graph of the maximum temperature with regards to the time. There are two different parameters that has been changed which is the changing of the temperature of the bulk solution. The temperature of the bulk solution for Figure 3.1 is set to be at 500 K. It is found that the maximum temperature is

1366 K which correlates to the research done by Ashokkumar where the author reported that by identifying the parameters for the equation the maximum temperature has a range of 1000-4600 K. With this result the cavitation process could be done in the future and a thermostat could be placed in along the liquid to measure the temperature of the solution. The maximum temperature of the cavitation process could be determined to ensure that the disruption of the microorganism is best given

the temperature of the solution. This is to ensure that the good bacteria that is needed by humans would be found in the solution and the bad bacteria is discarded from the solution.

Ashokkumar reported that the study of sonochemical and sonoluminescence effects of cavitation by having a research done on the mixture between H_2O/D_2O and found out that the cavitation of the bubble releases a temperature and was solely dependent on the type of parameters use. The final approximate temperature found is falling into the range of 1000-4600 K. The differences can be noted to be due to the difference samples that are collected from various regions of the cavitation process or known as 'hot spot'.

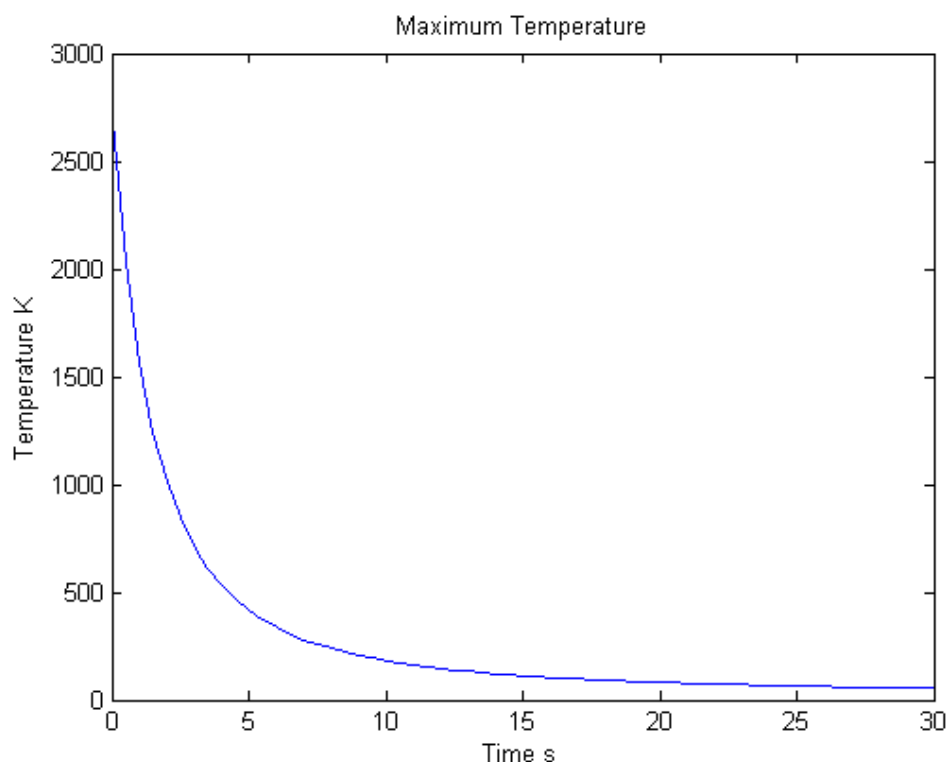


Figure 4.2 Maximum temperature using temperature of bulk solution of 1000 K with respect to time

According to Figure 3.2 the temperature of the bulk solution is set to be at 1000 K and it is found that by increasing the temperature. The maximum temperature that is caused by cavitation is 2733 K. The differences of the maximum temperature during the cavitation process suggest that the temperature of the bulk solution plays a vital role and therefore must be checked before running the experiment.

4. Conclusions & Future Work

In conclusion, the cavitation process will cause implosion of the bubble to occur when exposed to ultrasound waves. When ultrasound is emitted into a liquid medium, the force of the sonic wave will create eddies, these eddies in turn will create bubbles that are form from transient cavitation. Transient cavitation will then causes the implosion of bubble to occur. This is mainly due to the shear that is given out by the ultrasound

wave when it is emitted out towards the liquid medium. A maximum temperature will be achieved to ensure that the good bacteria that is in the liquid medium will stay alive whereas the bad bacteria will be disrupted with the help of the ultrasound wave.

The resonant frequency that is obtain using the parameters that is given shows that the RPNP equation with the added surface tension as well as the fluid viscosity can greatly affect the outcome from the resonant frequency. It is also noted that from the graph the resonant frequency obtained at radius = 0 and has a higher tendency of reaching infinite. The maximum temperature that is recorded from this project is 1366 and 2733 K respectively. Both these values are a respective of the difference in the temperature of the bulk solution which are 500 and 1000 K respectively. It is found that the higher the temperature of the bulk solution the higher the maximum temperature reaches for bubble cavitation.

For future works, the RPNP equation could be derive further to determine the relationship between the effects of temperature and pressure towards the change in bubble cavitation time. Furthermore, the numerical analysis for the effects of the heating condition could be done to ensure that the bubble cavitation processes is accurate and experimental works could be done to test out the thermal damping of the heating process as the RPNP equation does not consist of thermal damping.

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Graphene Oxide Nanofluids Characterization & Electrical Conductivity

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Abstract

Recently GO Nanofluids has become one of the emerging topics discussed in engineering applications due to its favorable characteristics in thermal and electrical conductivity. The substance is a combination of nano-size particles of graphene oxide dispersed in a base fluid, commonly distilled water. Two-step preparation method was used to prepare the nanofluids in this experiment. Graphene oxide nanoparticles were created by using simplified Hummer's method. Oxidized from graphite, the material is proven to have ability to conduct electricity and heat. To determine the characteristics of the graphene oxide nanosheets, FTIR and XRD test were carried out on the sample. The corresponding results showed that the graphite was fully reduced and oxidized to graphene oxide. In order to monitor the stability of the sample photo capturing was carried out. It was conclude that with a pH around 7.8 and ultrasonic time of 70 min produced samples that is stable for at one month. In terms of electrical conductivity enhancement it is showed that sample with 0.03% volume fraction of graphene oxide has the highest electcial conductivity with a value of 161.44 $\mu\text{S}/\text{cm}$. This colloidal suspension is able to conduct electricity is basically due to the formation of dielectric layer and the surface charge of the nanoparticles. In terms of electrical conductivity enhancement of the base fluid, sample with volume faction of 0.03% produced an enhancement value of 106%. The samples did not show any significant enhancement when the temperature is manipulated.

Keywords: Graphene Oxide, Nanofluids, Stability, Electrical Conductivity, Enhancement.

1. Introduction

The combination of nanoparticle with a known fluid produces a colloidal suspension called nanofluids. The nanoparticles dispersed can vary from metals to ceramic particles as well as carbon allotropes and all kinds of metal oxide particle, whereas the general type of fluid used are cooling liquids which can be water, organic liquids or even oil and kerosene [1]. This liquid substance have gained considerable attention in recent years due to its ability to enhance thermal conductivity, heat transfer, and electrical conductivity of the base fluid creating potentials to be used as a coolant and electrodes in many advance equipment such as high powered laser, x-ray, microelectronics and industrial cooling applications. Using nanoparticles not only enhances the characteristics of the base fluid compared with millimeter dispersed particles but it also does not cause any sedimentation and clogging in pipes as the size is extremely small and stable in the base fluid [2].

Nanofluids are widely prepared by two-step preparation method whereby the nanoparticles and the base fluids are created separately from its precursor and afterward mixed together. After dispersion, there are high chances that the nanoparticles will agglomerate and sediment forming a two layered solution due to high van der Waals interaction [3]. To avoid this, secondary treatments such as addition of surfactants or surface modification, pH control of the nanofluids and applying strong forces are common steps taken to make sure a stable and homogeneous solution is formed. Surfactants are chemical compounds, when added to nanofluids it helps reduce the surface tension of the base fluid making better immersion of the particles. Sodium dodecyl sulfate (SDS) and Sodium dodecylbenzenesulfonate (SDBS) are commonly used surfactants. Surface disruption is a surfactant free method whereby the particles are made hydrophilic by introducing functional groups to make it immense in aqueous solution. Another step is by pH control of the nanofluids, by means of acid treatment the zeta potential value of the nanofluids is moved away from the isoelectric point and producing a stable and homogenous suspension. Zeta potential is the measure of electrokinetic potential in mV of nanoparticle surface charge. The further away the zeta potential value from IEP the less agglomeration is formed and vice versa [4]. Use of ultrasonic vibration is to successfully break down the cluster of the particles to produce a homogenous nanofluids. Producing nanofluids that is able to be stable for a very long period of time can be extremely useful for potential application, one such nanofluids is the graphene oxide nanofluids.

Recent breakthrough in nanotechnology is using Graphene Oxide (GO) as a new type of nanofluids in many application areas, one specific to this research is using as electrodes to conduct electricity. Graphene is a 2D sp^2 nanostructure material than can be created from graphite. 2D sp^2 means that the graphene is a two dimensional, one-atom thick bonded to each other by sp^2 bonding. Graphene proved to be an ideal electrode material because of their high specific surface area theoretically calculated to be around $2630\text{ m}^2/\text{g}$ and further more due to their chemical stability and the ability to conduct electricity and heat. It is also noted that the material have high mechanical strength, hence summing all these properties makes the material suitable to be used as an electrode [5]. Though having good characteristic yet the material cannot be stable in water due to its hydrophobic properties and tend to

create a two phase suspension. In the contrary graphene oxide proves to be stable in water for a long period of time because of its hydrophilic nature due to the presence of functional group [6].

The oxidation of the graphene can be done by either using Brodie's method or Hummer's method. In Brodie's method the main process is KClO_3 -fuming HNO_3 whereas Hummer's method involves reacting graphite with a mixture of potassium permanganate (KMnO_4) and concentrated sulfuric acid (H_2SO_4). However both oxidation methods introduces hydroxyl, carboxyl and epoxy functional group on the graphene flakes with a carbon/oxygen atomic ratio ~ 2 [7].

Nanofluids are widely acknowledged for its thermal conductivity properties with less information published about its ability to conduct electricity. Available publications regarding electrical conductivity of nanofluids mentioned that the conductivity of nanofluids are based on the ability of charged particles which are the ions in the suspension to carry the charges (electrons) towards respective electrodes when an electric potential is applied, which is similar to the functionality of aqueous electrolyte solution [8]. Also mentioned in the theory of colloidal and surface chemistry, particles dispersed in a fluid get charged due to the formation of electrical double layer (EDL) around the particle surface. EDL are constitutes of the surface charge of the particles with the ion clouds surrounding it. This formation of EDL mainly depends on the surface charge, size and volume fraction of the particles disbursed in the fluid. Hence, when an electric potential is applied the particles and the EDL will move towards oppositely charged electrode whereby the mobility of particles determines the electrical conductivity of a solution [9].

By producing a stable electrical conductive substance, battery technology can be extremely improved. Currently lithium ion technology are used as rechargeable battery in laptops, smart phones and many other electronic devices. In a lithium ion battery the common material used for the cathode is graphite based material. This is because the material is able to store ions during charging, and discharges. Graphene oxide which has high specific surface area makes it able to store more ions, thus producing a high energy density battery. The performance of battery is also directly connected with the conductivity of the material used as well [10].

The purpose of this study is to examine the characteristics of graphene oxide nanofluids and also study the electrical conductivity by varying volume concentration and temperature of graphene oxide nanofluid. Graphene oxide used in this experiment was dispersed in distilled water as the base fluid with volume fractions from 0.005% to 0.03% and experiments conducted with temperature ranging from 25 to 50°C.

2. Methodology

2.1 Materials

Graphite flakes the precursor was purchased from Sigma Aldrich. The remaining chemicals; sulfuric acid (H_2SO_4 , 98% concentration), phosphoric acid (H_3PO_4 , 98% concentration), potassium permanganate (KMnO_4 , 99.9% purity)

hydrogen peroxide (H_2O_2 , 30% concentration) and hydrochloric acid (HCl , 37% concentration) was purchased from Fisher Scientific.

2.2 Preparation of GO

The preparation of GO was done according to simplified hummer's method and the whole process takes roughly about four days to prepare. Initially 360ml of sulfuric acid (H_2SO_4), and 40ml of phosphoric acid (H_3PO_4) was mixed in a beaker using magnetic stirrer. While stirring 3.0g of graphite flakes was added. After 5min of stirring, potassium permanganate (KMnO_4) was added gradually. Precaution should be taken when adding potassium permanganate as it can be explosive. The solution is left to stir for three days [11].

After three days hydrogen peroxide (H_2O_2) was added to the solution in an ice bath. Ice is used to cool down the reaction as adding hydrogen peroxide can increase the temperature. The solution is left to stir for another 10 minutes. At the last stage, the solution is washed with hydrochloric acid (HCl , 1Mole) for 3 times and finally washed with distilled water until the pH reaches 6 or 7 in a centrifuge (HITACHI, CR21GIII temperature control centrifuge). The main observation that needs to be noted is the colour change of the GO suspension from bright yellow to light brown and finally dark brown. Moreover the suspension will also change from a less viscous solution to a more viscous jelly like material [11].

The GO suspension is then dried in an oven (PROTECH, FAC-50, forced air convection oven) for 24 hours at 50°C to remove water molecules finally producing graphene oxide Nano-sheets.

2.3 Preparation of GO nanofluids

The prepared graphene oxide sheets were later dispersed in deionized water (DI water) to produce the desired GO nanofluids with different volume concentration. Two-step preparation method was used to prepare the samples. After dispersing the nanoparticles, the solution is ultrasonicated using a horn ultrasonic (Sonic Vibra cell) for 70min to produce a stable and homogeneous nanofluid. PH of the samples was maintained at pH7.

2.4 Analysis Method

FTIR and XRD are done to determine the oxidation level, present functional group and the interstitial distance of the structure. XRD (x-ray diffraction) data is taken from EMPYREAN, PANALYTICAL and FTIR spectra (Perkin Elmer-spectrum 100 model).

To determine the stability of GO nanofluids Photo capturing was also carried out using a digital camera. The test have been carried out on fresh nanofluid as well as few days after preparation. The formation of sedimentation and the clarity of the nanofluid were used to determine the stability of the solution.

2.5 Electrical conductivity

The electrical conductivity is measured by a 4-Cell conductivity electrode meter (CYBERSCAN CON 11) with inbuilt automatic temperature compensation (ATC). The instrument reads out both the temperature and the conductivity values simultaneously when fully immersed in the solution. Instrument calibration was done with de-ionised (DI) water, 5 repeated measurements were measured to get a consistent reading [12].

The summation of instrumental error and measurement error gives the total error in the experimental data. In terms of measurement error the error is caused by the deviation from the mean value obtained due to environmental factors, the error is known to be $\pm 1\%$. In terms of the instrumental error, the electrical conductivity and temperature measurement gives an error of $\pm 1\%$ and 0.1°C for the range of 0–1999 S/cm. Therefore the total experimental error produced is less than 2%.

3. Results and Discussion

3.1 FTIR Spectrometer Analysis

Fig 1 shows the FTIR result of GO sheets. By analyzing the graph it can be concluded that oxygen and water containing functional groups are present in the lattice. The peaks at around 3500 to 3200 cm^{-1} are due to hydroxyl functional groups the H bonded OH stretch. A sharp peak at 1734 cm^{-1} can be assigned to the C=O stretching known to be the carboxyl functional group and the 1066 cm^{-1} peak for C-O stretching vibration from the primary alcohol bond. Moreover the peak at 1619 cm^{-1} indicates the retention of the C=C even after the oxidation process. The presence of functional groups helps the graphene sheets to interact with water molecules and disperse well [6] [13].

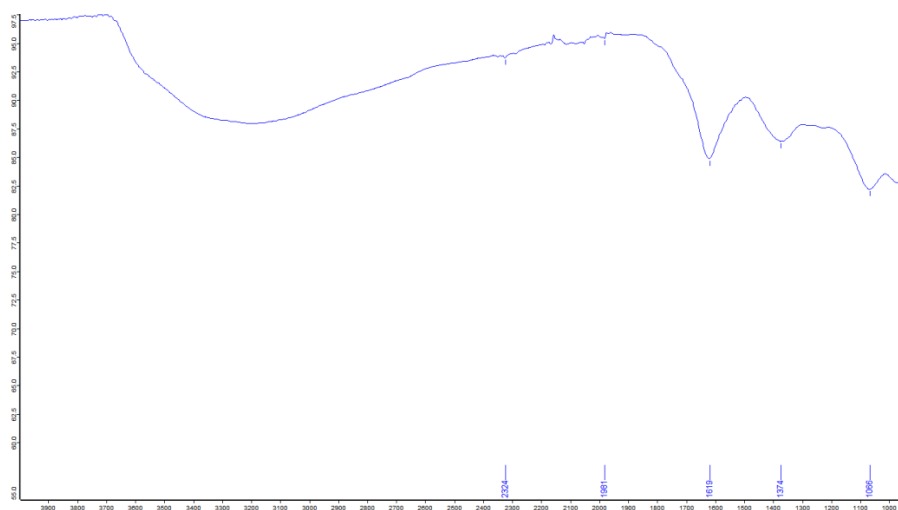


Figure 1 FTIR result of GO

3.2 XRD Pattern

The XRD patterns of the GO is shown in Fig 2. In the XRD pattern of the GO, only one sharp peak around $2\theta = 9.7^\circ$ can be detected, which corresponding to the

(001) plane of graphene oxide, which indicates the presence of functional groups and other structural defects.

Fig 3 shows the XRD pattern of the graphite, the pattern has peak at 26° indicating the (002) plane. Moreover small peaks at 42° , 44° , and 54° indicating a significantly crystalline structure of graphite. By comparing both figures it is evident that the successful reduction of graphite has produced graphene oxide.

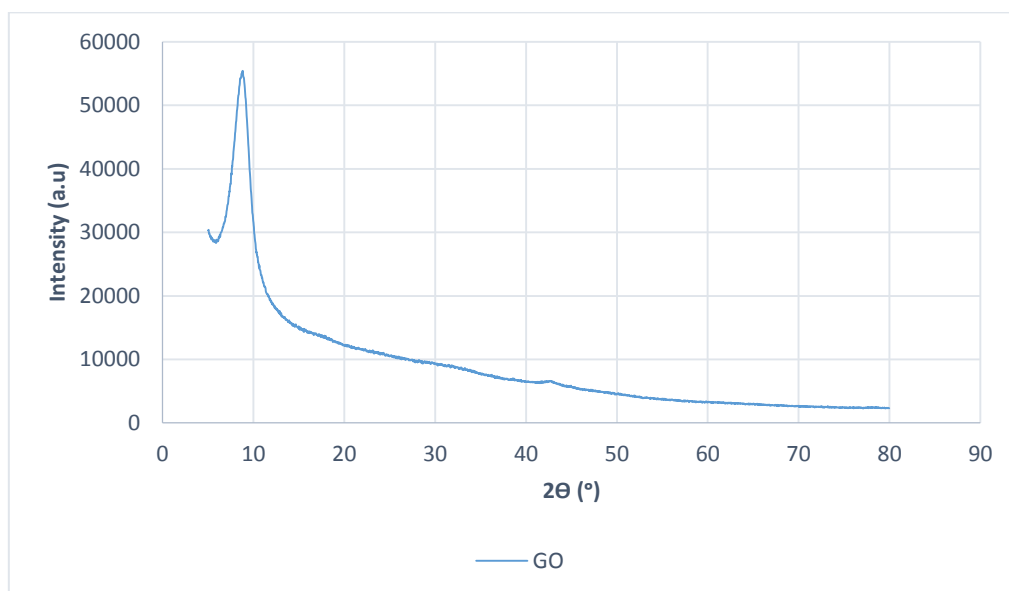


Figure 2: XRD pattern of GO

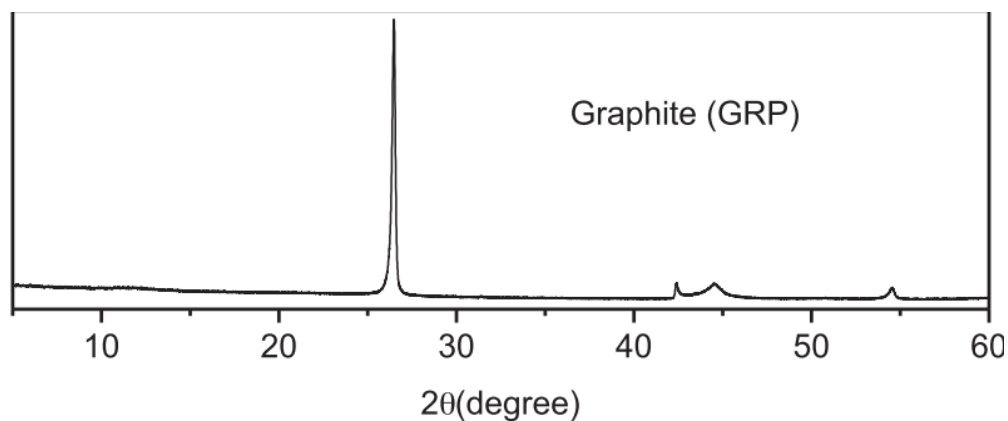


Figure 3: XRD result of graphite [14]

3.3 GO Stability

Stability of nanofluids is related to its zeta potential value and the distance it has from the isoelectric point (IEP). Zeta potential measures the degree of repulsion of similar charged particle dispersed in a solution. It represents the electrostatic value of the particles dispersed, typically having a high zeta potential value more than 30mV or less than -30mv causes electrostatic force to be greater than the attraction force

between the particles, therefore making the nanofluids stable over a period of time. Having a zeta potential value close to IEP causes it to have a low electrostatic value as the IEP point is the point with no net electrical charge hence the attraction force of the particles will be greater causing it to agglomerate and subsequently sediment [8].

One of the key parameter that affects the zeta potential value is the pH of the solution. By changing the pH of the solution its electrostatic charge of the surface will change accordingly. Thus to produce a stable GO nanofluids the pH of the solution was kept around pH 7 from pH 4 by adding drops of Sodium Hydroxide (NaOH) [15].

Besides manipulating the pH of the solution the ultrasonication time also determines the best dispersion of the GO nanofluids. Providing a longer ultrasonication time successfully breaks down the clumps of the GO sheets into fine particles. Table 1 shows the pH value of the samples with the ultrasonic time. Fig 4 – Fig 5 shows the nanofluids produce with corresponding sonication time and Fig 6 – Fig 7 shows the stability of the nanofluids over a period of one week.

Table 1 pH value and Ultrasonic time of samples

Sample number	Initial pH	Final pH	Ultrasonic time (min)	Stability (days)
1	4.6	7.3	67	1
2	4.7	6.9	62	1
11	4.5	7.5	70	1
12	5.2	7.4	71	1
3	4.2	7.0	70	7
4	4.4	7.0	66	$7 < x < 14$
5	5.5	7.1	62	$7 < x < 14$
6	4.4	6.9	66	$7 < x < 14$
8	4.5	7.0	73	$7 < x < 14$
10	5.6	7.5	70	14
9	4.4	7.4	69	$14 < x < 30$
7	4.3	7.0	64	30
13	4.0	7.4	70	> 30
14	4.5	7.8	69	> 30

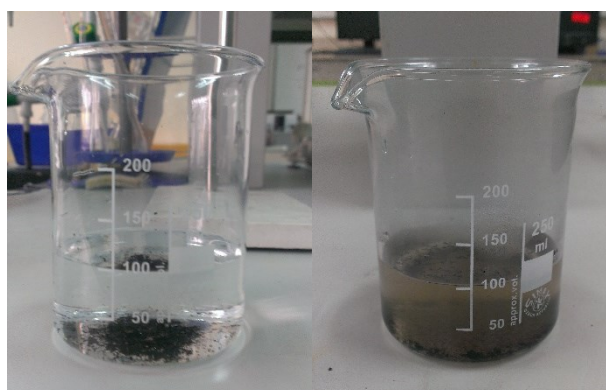


Figure 4: (left) after dispersion, (right) 15min ultrasonication

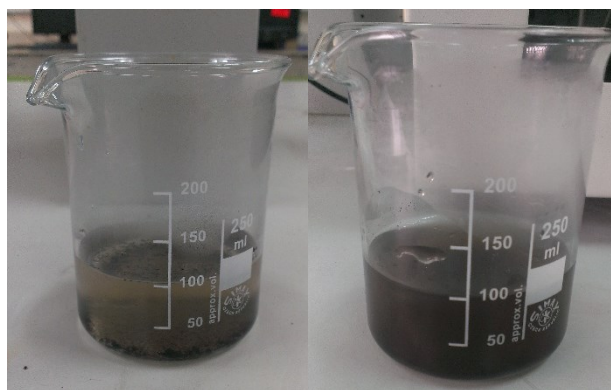


Figure 5: (left) 30min ultrasonication, (right) 70min ultrasonication

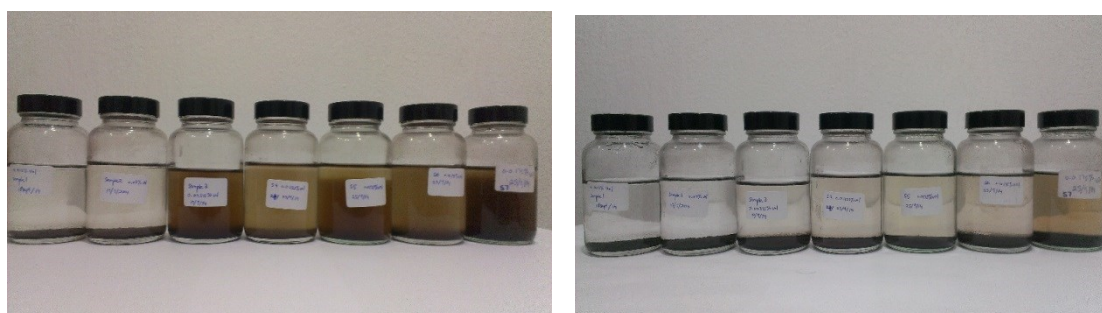


Figure 6: Samples 1-7 (top) 1day after preparation, (bottom) 1 month after preparation.

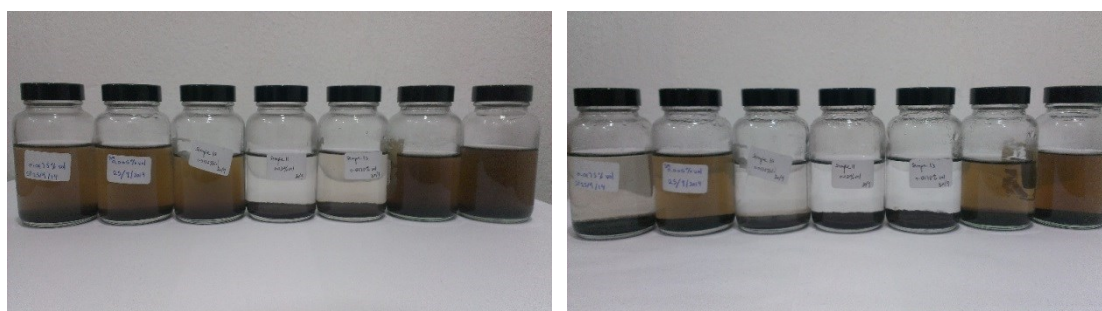


Figure 7: Samples 8 – 14 (top) 1 day after preparation,
(bottom) 1 month after preparation

Based on fig 4 it can be noted that after dispersing the nanosheets in the water, the particles does not homogenize in the liquid as its size is still large. After applying strong forces the particles begin to disburse evenly out in the liquid. As the ultrasonic time increases the clump of particles begin to break down n disperse in the liquid as observed in fig 5.

3.4 Electrical Conductivity of GO Nanofluids

Based on Fig 8, the experimental data indicates that the electrical conductivity of the nanofluids depends on the volume fraction of nanoparticles, when the volume faction increases the conductivity also increases. Whereas for change in temperature there is an increase in electrical conductivity of the suspension but the increase is

insignificant in value. The highest value of electrical conductivity, 161.44 μ S/cm, was recorded for a volume fraction of 0.03 at a temperature of 50°C and the lowest recorded value was 60.94 μ S/cm at room temperature; T=25 °C with volume fraction 0.005.

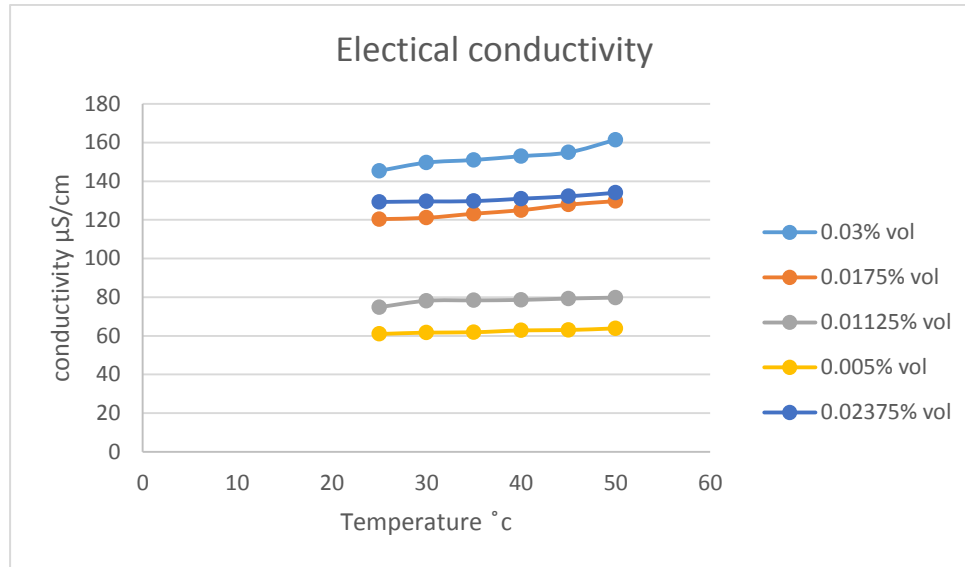


Figure 8: Electrical Conductivity of GO nanofluids with different volume fraction

The percentage increase in electrical conductivity of the base fluid with different volume fraction was calculated using the formula (1), where σ corresponds to the electrical conductivity of the nanofluids and σ_0 correspond to that of the base fluid which is 1.35 μ S/cm. The values are represented in Fig 9

$$k = \frac{\sigma - \sigma_0}{\sigma_0} \times 100\% \quad (1)$$

Fig 9 shows that the rate of enhancement increases with respect to increase in the nanoparticle volume fraction. This shows that the conductivity has a clear dependence on the volume fraction but this variation does not reflect on the temperature in the range of 25 – 50°C. Even as the temperature increases, the enhancement seems to have the similar value to those of lower temperature. A 44% increase in the electrical conductivity was observed for 0.005 volume concentration of GO nanoparticles in water at temperature, T=25 °C. With rise in concentration, a 106% increase in the electrical conductivity was measured for volume fraction 0.03 at the same temperature.

According to the theory of colloidal suspension, electrical conductivity in nanofluids dependence on the formation of dielectric layer on the particle surface and the net electric charge of the particles. Formation of EDL is based upon three factors which are the volume fraction of particles, ionic concentrations in the solution and the physicochemical properties of the particles. When nanoparticles are dispersed in a polar liquid there will be a formation of electric charge on the particle surface. Specific to this experiment, when GO particles are dispersed in the base fluid, electric

charge are formed, this consequently causes ions that are oppositely charged to attract on to GO particle surfaces, which causes the formation of charged diffuse layer around the particle, known to be the electrical double layer [1], [8], [9].

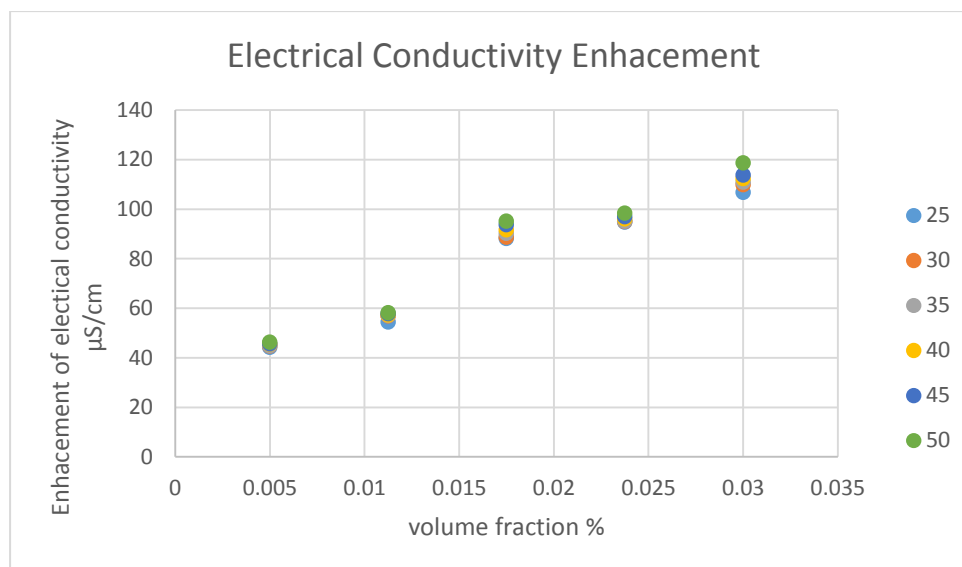


Figure 9: Enhancement of electrical conductivity of GO nanofluids

In situations when the amount of ions in solution is low such as distilled water, there is not sufficient ions to compensate the electric charges of the particle, therefore the net electric charge density becomes higher on the particle surfaces. Subsequently the enhancement of the electrical conductivity of the nanofluid is contributed by the formation of EDI and the net surface charge of the particle. Moreover, having homogeneously dispersed nanoparticles will large surface area, leads to an improvement in electrophoretic mobility [9], Which leads to the increases in electric conductivity of the nanofluid. In conclusion when the particles volume fraction increases, more conducting pathways is formed, which in turn increases the overall electrical conductivity of the solution as witnessed in this experiment [1], [8], [9].

4. Conclusion

Graphene oxide was successfully prepared by simplified hummer's method. After homogenizing by ultrasonic probe (sonic vibra cell) and alkaline (NaOH) treatment, sample number 14 is shown to have good stability with pH 7.8 and ultrasonic time of 70min. GO nanofluids with volume concentration 0f 0.03% and temperature of 50°C is shown to have the highest conductivity value which is 161.44μS/cm. therefore having an enhancement value of 106% GO nanofluids has a potential to be used as an electrode in redox flow batteries,

Reference

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High AOA Aerodynamics of NACA0012 Airfoil at Low Subsonic Speeds – Numerical and experimental

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Abstract

Airfoil can be defined as a wing shaped body, which produces aerodynamic as it moves through fluids. One of the most applicable airfoil in various industries such as aviation, military, wind tunnel and turbo machinery is NACA 0012 due to its symmetrical geometry. This paper investigates the aerodynamic characteristics of NACA 0012 high angle of attack ranging from 0° to 180° at low subsonic speed with Mach number less than 0.1 and Reynolds number less than 5×10^5 . This was done through numerical simulation as well as experiments. The numerical results were obtained by a 2-D simulation using ANSYS FLUENT. A meshing with C-type grid mesh with 120000 cells was applied in the simulation and the $k - \omega$ shear stress transport (SST) turbulence model was utilized. The numerical simulation was performed for 0° , 5° , 10° , 15° and 20° angle of attack. The results obtained from the simulations were validated with a reference data and used to verify the experimental data and methods. The experiments were conducted utilizing subsonic wind tunnel. A test rig was designed and implemented to allow the change of the angle of attack while the wind tunnel operates. The data was obtained using a transducer connected to the test rig structure. The results obtained were then studied critically to understand the aerodynamic characteristics changes at different angle of attack. The results of the study shows that increasing the angle of attack results in lift force increase and hence increase in lift coefficients. The lift increases until the stall angle it starts to decrease with further increments in the angle of attack. Also the drag force acting on the airfoil increases as the angle of attack increase and increment in the drag force results in change of laminar flow to turbulent flow. As the turbulence get higher the flow starts to separate from the airfoil surface due to eddies generated by turbulence.

Keywords: Airfoil, NACA 0012, Subsonic, Aerodynamic, Angle of Attack.

1. Introduction

Airfoil can be defined as a wing shaped body, which produces aerodynamic as it moves through fluids. Airfoils are tested, developed and standardized by the National Advisory Committee of Aeronautics (NACA) which is nowadays known as the National Aeronautics and Space Administration (NASA) research group. These airfoils are assigned as NACA followed by digits according to their specific properties. NACA0012 is of the well-known NACA airfoils that is vastly applied in researches, evaluations as well as practical applications due to its symmetrical shape [1]. The importance of NACA0012 application in various industries such as aviation, military, wind turbine and turbo-machinery has motivated researchers to critically study the aerodynamic characteristics NACA0012 at different boundary conditions. The application of airfoils at post stall angle of attack and low subsonic speed with Mach number less than 0.12 and Reynolds number less than 5×10^5 is increasing due to the recent developments in small wind turbines for commercial purposes, vertical axis wind turbine, aerial vehicles such as unmanned aerial vehicles (UAVs) and micro-air vehicles (MAVs), and also researches on flying birds/insects aerodynamics. Development of the applications of airfoils at low Reynolds number is the result of recent studies conducted by researchers on the aerodynamic characteristics of airfoils at high angle of attack and low subsonic speeds [2, 3]. Aerodynamic characteristics such as lift and drag coefficients are complex factors which are calculated utilizing Eq. (1) and Eq. (2) in which F_L and F_D are obtained through experiments.

$$F_L = \frac{1}{2} V^2 A \rho c_l \quad (1)$$

$$F_D = \frac{1}{2} V^2 A \rho c_d \quad (2)$$

Tousif A. et al. [4] numerically studied the lift and drag coefficient behavior of NACA0012 at 0° to 50° angle of attack and Mach number varying from 0.1 to 1 utilizing the $k-\omega$ shear stress transport (SST) turbulence model. In order to get accurate results, C-type grid topology meshing with 120000 cells were applied. The simulation results were validated by comparing the results obtained from simulations with Abbott and von Doenhoff airfoil experiment data [5] as well as Gregory and O'Reilly data [6] for the drag coefficient and McCroskey experimental data [7] for the lift coefficient. The results show that increasing the angle of attack from 10° to 50° results in increment in drag coefficient and decrement in lift coefficient. Also the study shows that the flow behavior at high angle of attack of 30° , 40° and 50° are extremely unstable and unpredictable..

Douvi C. et al. [8] studied subsonic flow over NACA0012 and the study was conducted through a 2-D analysis of a flow having Reynolds number of 3×10^6 and angle of attack ranging from -12° to 20° to examine the dependence of lift and drag coefficients on angle of attack. The simulation was conducted using ANSYS FLUENT and the meshing type was set to C-type grid topology with 80000 cell number. Turbulence models utilized in the study are $k-\varepsilon$, $k-\omega$ shear stress transport (SST) and Spalart-Allmaras. The results obtained were then validated with Abbott and Von Doenboff data [5] as well as Bacha et al. data [9]. The $k-\omega$ shear stress transport (SST) was found to be the most accurate turbulence model with least variation from the experimental data.

An experimental study was performed by Y. Zhou et al. [3] to measure the mean forces acting on NACA0012 at angle of attack ranging from 0° to 90° and low Reynolds number of 5.3×10^3 and 5.1×10^4 . A closed loop water tunnel consisting airfoil support, torque resisting system and load cell was the apparatus utilized in the experiment. The force measurements were obtained using a load cell at angle of attack varying with 5° increment for $AOA < 20^\circ$ and 10° increment for $20^\circ < AOA < 90^\circ$. The results were then validated with Critzos et al. [10] and Devinant et al. [11] test data for $0^\circ < AOA < 90^\circ$. The study shows that stall angle is considerably dependent on the properties of the fluid. Also, the drag coefficient is linear and relatively small for $AOA < 45^\circ$.

Y. Zhang et al. [12] numerically simulated, analyzed and studied the flow field of NACA0012 at 0° to 180° angle of attack using C-type grid with 360 cells around the airfoil, H-type grid type with 200 cells around airfoil and O-type grid type with 320 cells around airfoil. The Mach number and Reynolds numbers were set to 1.5 and 0.5×10^6 respectively. In order to select the suitable turbulence model, simulation was performed for angle of attack ranging from 10° to 70° utilizing Spalart-Allmaras, standard $k - \varepsilon$ and $k - \omega$ shear stress transport (SST) turbulence models. The simulation results were compared with Critzos et al. [10]. Based on the results comparison and scatter analysis, C-type grid meshing and Spalart-Allmaras turbulence model was found suitable. The simulation results shown a stall angle of 16° while the stall angle based on experimental results is 14° .

Recent studies on aerodynamic characteristics of NACA0012 at pre-stall and post stall angle of attack were conducted numerically while they do not provide experimental data. The simulation results have skepticisms which need to be reduced by conducting experiments. Comparison and analysis of the numerical and experimental data reduces the inaccuracy and errors of the results obtained.

The present paper studies the aerodynamic characteristics of NACA0012 airfoil at low subsonic speed with 0.1 Mach number and Reynolds number less than 5×10^5 . The angle of attack varies from 0° to 180° . NACA0012 was chosen because of its symmetrical geometry and its vast application in various constructions such as helicopters, Boeing Flying Fortress and vertical axis wind turbines. The study was performed utilizing numerical simulations as well as experiments. Experiments were conducted utilizing the subsonic wind tunnel TDA_M630/12AA/7/28 model. The flow speed was set at 30 m/s throughout the study. The results of the experiments were benchmarked with numerical results obtained from 2-D simulations using ANSYS FLUENT. The simulations were performed for 0° to 20° angle of attack and the results of the simulation were used to verify the experimental data and hence experimental method. A C-type grid meshing with 120000 cells was generated to provide sufficient accuracy [4]. The $k - \omega$ shear stress transport (SST) turbulence which is suitable for low Reynolds number was utilized through the numerical simulation [13]. For validation of the results, the numerical simulations data were benchmarked against Douvi C. et al. [8] while experimental data were benchmarked against Abbott and von Doenhoff [5]. The results were then critically analyzed to provide a better understanding of behavior of aerodynamic characteristics of NACA0012 at various angle of attack specifically at post stall angles.

2. Research Methodology

This research methodology for this paper consist of two main sections, numerical and experimental.

2.1 Numerical

2.1.1. Geometry

In order to conduct the numerical simulation, NACA0012 airfoil geometry was created in FLUENT design modeler by importing the coordinates of the airfoil. The coordinates of the NACA0012 airfoil profile were obtained utilizing the NACA airfoil series ordinates formula that is represent in Eq. (3) [14].

$$\pm y_t = \frac{t}{0.2} (0.2969\sqrt{x} - 0.1260x - 0.3516x^2 + 0.2843x^3 - 0.1015x^4) \quad (3)$$

Where x is coordinates along the length of the airfoil, from 0 to c (which stands for chord, or length), y = coordinates above and below the line extending along the length of the airfoil, these are either y_t for thickness coordinates or y_c for camber coordinates, t is maximum airfoil thickness in tenths of chord (i.e. a 12% thick airfoil would be 0.12), m is maximum camber in tenths of the chord and p is position of the maximum camber along the chord in tenths of chord.

2.1.2. Meshing

A fine meshing is one of the requirements to production of correct simulation results with high accuracy. The C-type grid topology is applied through the simulation. The number of cells and growth of the cells are set and controlled utilizing edge sizing and assigning bias factors. Since the flow near the airfoil is more complex, therefore the cells are biased from far field towards the airfoil (Fig. 1) [8]. The geometry mesh characteristics can be seen in (Table 1).

Table 1. Characteristics of Edge Sizing

Linear Surfaces Edge Sizing	
Number of Divisions	150
Behavior	Hard
Bias Type	-----
Bias Factor	400
Curved Surfaces Edge Sizing	
Number of Divisions	250
Behavior	Hard
Bias Factor	No Bias

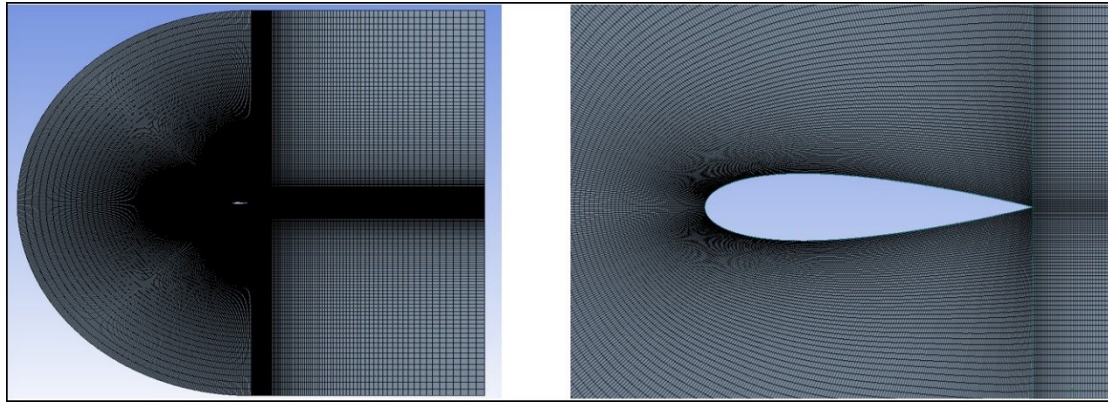


Figure 1 Mesh around NACA 0012 airfoil (left) and detail closed to the airfoil (right)

2.1.2. Numerical Setup

The flow is considered to be incompressible since the Mach number is less than 0.3. Therefore density based solver is applied throughout the simulation. The absolute criteria is set to $1e - 6$ to increase the accuracy of the results obtained. The properties of the fluid are represented in (Table 1).

Table 1. Simulation Assumptions

Fluid Properties		
Fluid	Density ($\frac{kg}{m^3}$)	Viscosity ($\frac{kg}{ms}$)
Air	1.225	1.7894e-05

Literature studies converged that the $k - \omega$ (SST) turbulence model is suitable for this study. Having said that, the model is not applicable for angle of attack higher than 20° . For the simulation solution to converge at higher angle of attacks, Direct Numerical Simulation (DNS) which has high computational costs is applicable. The simulations were conducted for angle of attacks ranging from 0° to 20° in order to validate the data obtained through experiments and hence to validate the experimental method.

2.2 Experimental

2.2.1 Experimental Apparatus

The wind tunnel utilized in the research is an open type wind tunnel model of TDA_M630/12AA/7/28 with 3:4:1 contraction ratio (Fig. 2). The test section of the wind tunnel is rectangular with cross section of $0.303\text{ m} \times 0.303\text{ m}$ and length of 0.885 m . A Gamma DAQ F/T transducer is utilized to obtain force and moment data. The force and moment readings from the transducer sensor is accurately measured and displayed using a PCI DAQ card with model NI PCI-6220 installed on the computer [15]. The flow is created using a fan having a diameter of 0.063 m , 3HP and 4145 V.50 HZ. The speed of the flow was set to 30 m/s which is the highest allowable operational speed for the specified wind tunnel. The velocity distribution in the test section was calibrated using a hotwire prior to the airfoil experiment

conductions. The experiment operational conditions and corresponding factors were measured and assumed to be constant (Table 3).

Table 3. Operational Condition

Fluid	Fluid Properties			
	Speed ($\frac{m}{s}$)	Temperature ($^{\circ}C$)	Density ($\frac{kg}{m^3}$)	Viscosity ($\frac{kg}{ms}$)
Air	30	20°	1.225	1.51e-05



Figure 2. Taylor's University Subsonic wind tunnel

2.2.1 Experimental Setup

A specific test rig mechanism (Fig. 3) has been designed and implemented. the test rig consists of four parts:

- Push rod
- Supporting bars
- Connection rod
- Worm and wheel gear

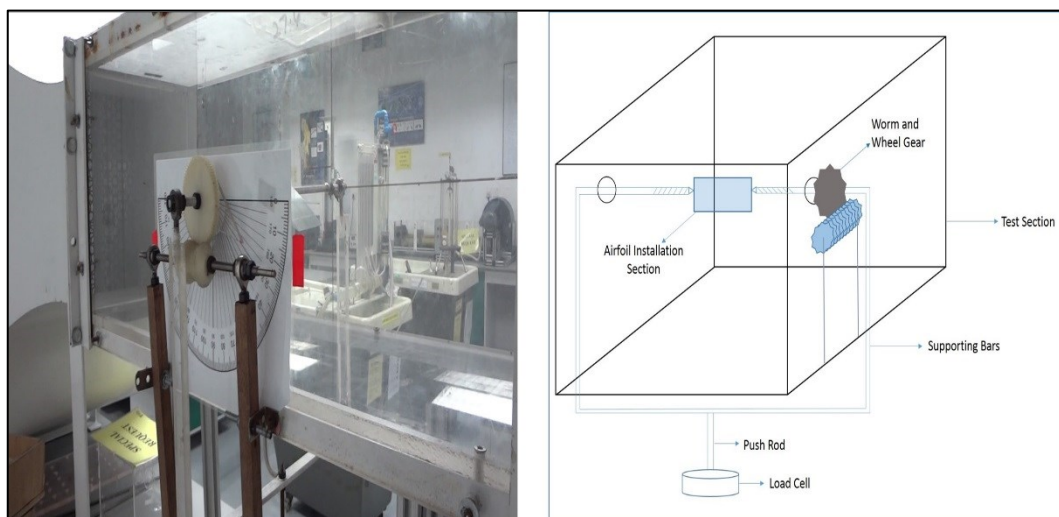


Figure 3. Test Rig Mechanism

The worm and wheel gear is utilized as the angle of attack controlling mechanism for the wind tunnel (Fig. 4). Worm drive gear set consist of two gears,

worm gear as well as wheel gear. The wheel gear is mounted on the connection rod which is connected to the airfoil. The wheel gear is not able to rotate the worm gear due to the wheel gear's teeth orientation, while the worm gear can rotate the wheel gear and hence the angle of attack can be adjusted by rotating the worm gear. The test rig was calibrated using a standard 2N weight to confirm accuracy of force transfer from airfoil to the load cell through test rig structure.

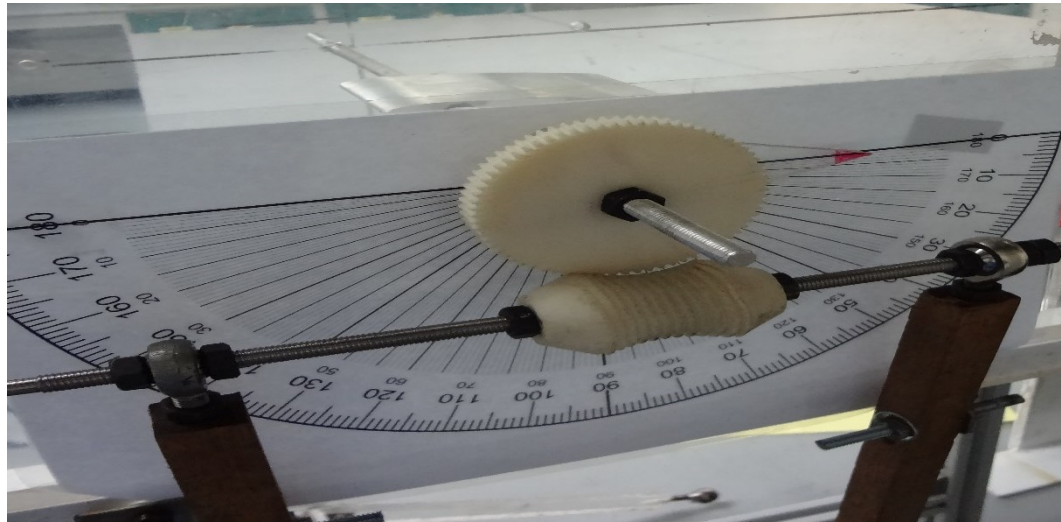


Figure 4. Rotary Mechanism

2.2.1 Experimental Model

The experiments have been conducted on the NACA 0012 prototype which have been created utilizing CNC machine. The prototype has a chord length of 0.1 m and span of 0.09 m. The airfoil has been installed through its aerodynamic center. The aerodynamic center of the airfoil (Fig. 5) has been calculated using the Eq. 4:

$$AC = \frac{c}{4} \quad (4)$$

Where AC is the aerodynamic center from the leading edge and C is the chord length of the airfoil.

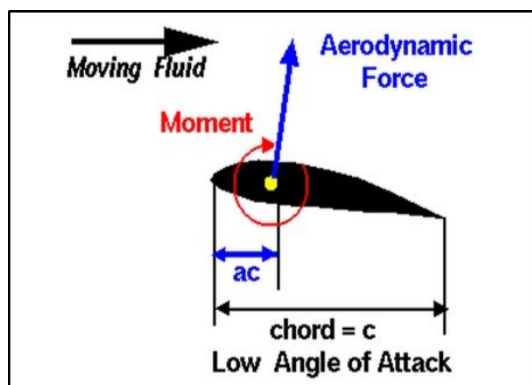


Figure 5. Aerodynamic Centre of Airfoil (Left) and Steel NACA 0012 Airfoil (Right)

3. Results and Discussion

3.1 Numerical Results

The results obtained from ANSYS FLUENT consist of lift coefficient (C_L) as well as drag coefficient (C_D). The velocity of the flow has been set to 35 m/s throughout the simulations. The simulations has been conducted for 0° , 5° , 10° and 15° . Lift and drag coefficients for each angle of attack has been obtained from the simulation and compared with published data.

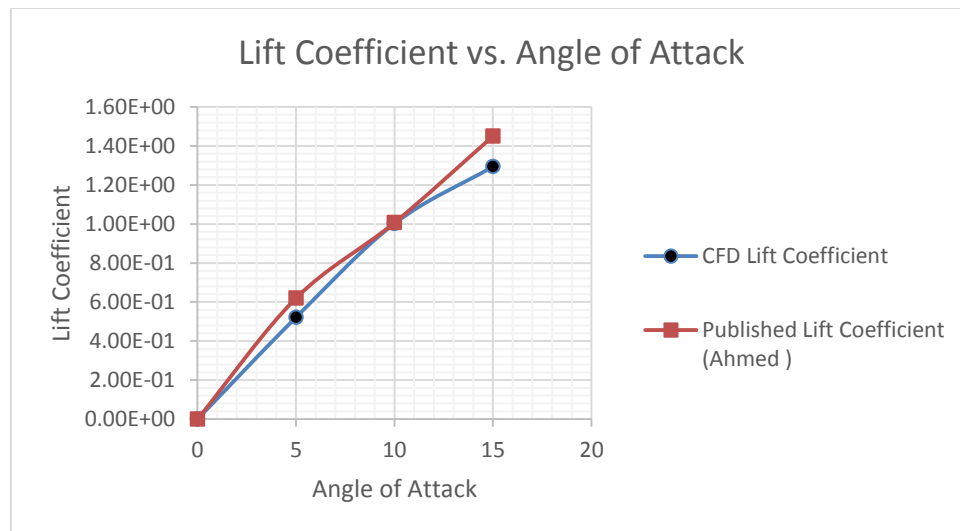


Figure 6. CFD C_L comparison with Published C_L

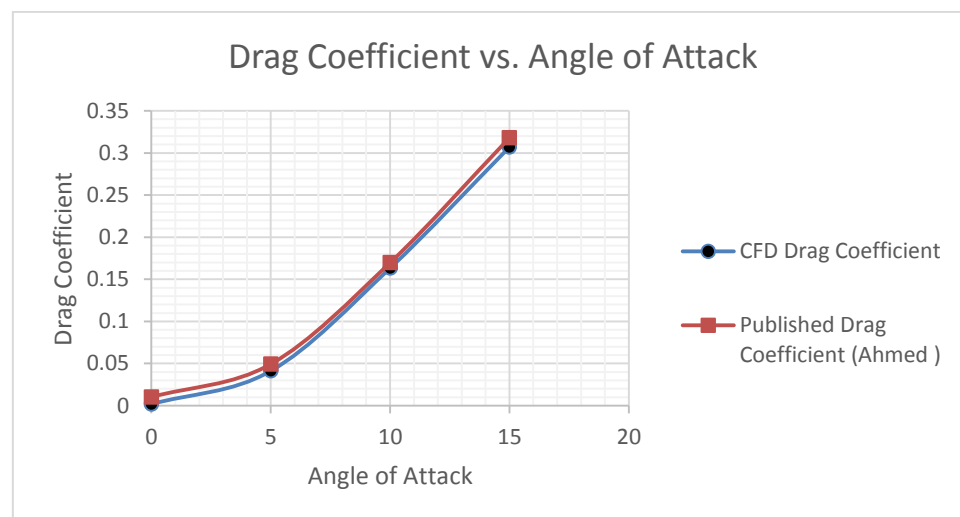


Figure 7. CFD C_D Comparison with Published C_D

The stream flow analysis provides a better understanding of the pressure distribution around the airfoil at different angle of attack (Fig. 8). The flow stream sticks to the airfoil surface at 0° angle of attack. As the angle of attack increases to 5° the stream starts to separate from the airfoil's upper surface, and the separation moves towards the leading edge of airfoil by increasing the angle of attack. Separation of the flow from the airfoil results in the formation of eddies starting from where the flow is

separated towards the trailing edge of airfoil as the flow tends to stick back to the airfoil's surface.

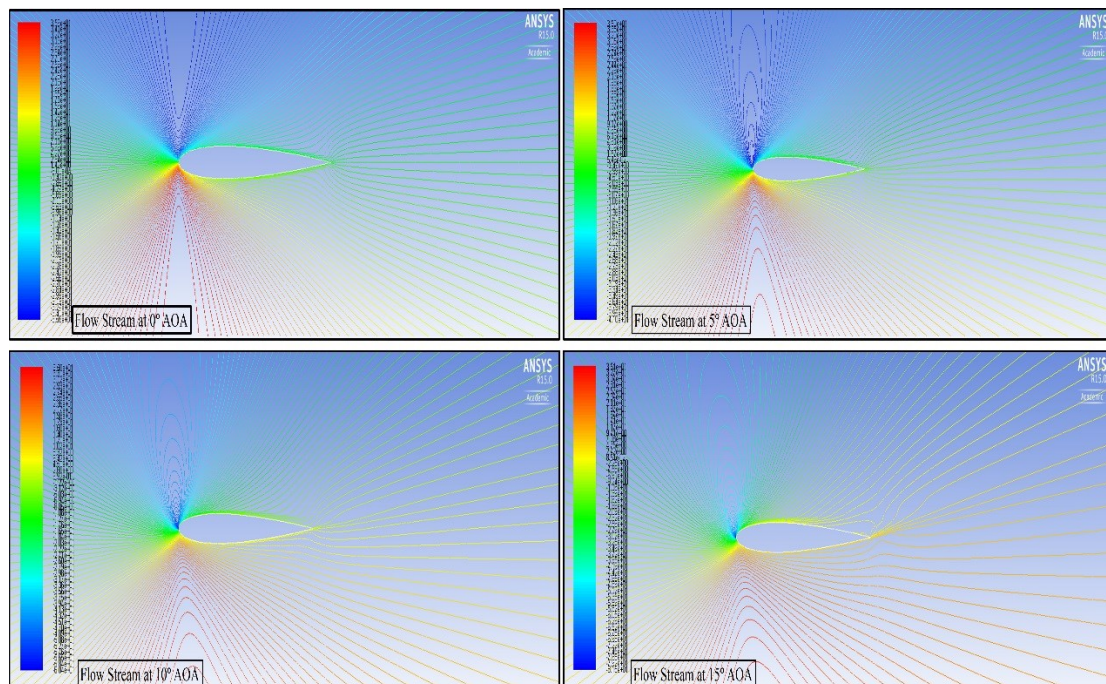


Figure 10. Flow Velocity Stream at 0°, 5°, 10° and 15° Angles of Attack

Formation of eddies causes chaos, therefore the flow loses its laminar characteristics as since the flow path line is not predictable anymore. Increasing the angle of attack results in more separated region from the airfoil surface hence more turbulence (Fig. 11).

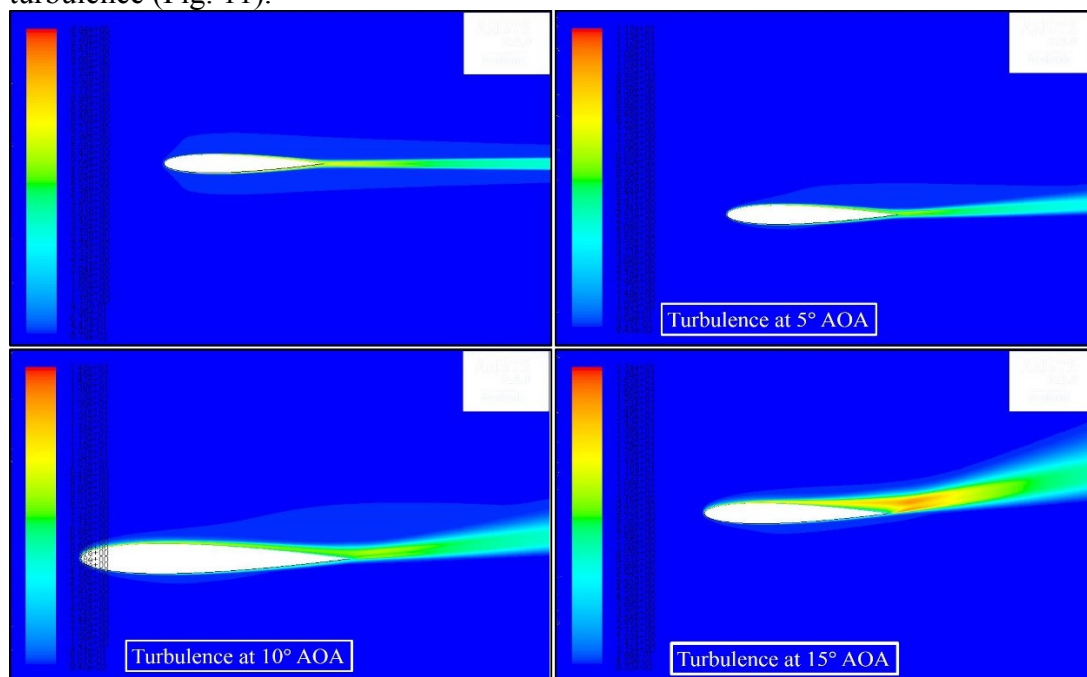


Figure 11. Turbulence at 0°, 5°, 10° and 15° Angle of Attack

Flow stream (Fig. 10) shows that the flow stream is symmetry at 0° angle of attack and the velocity of the upper and lower surface of the airfoil are equal, while

increasing the angle of attack from 0° to 15° results in higher flow velocity on the upper surface compared to lower surface of the airfoil. Based on Bernoulli's principle, air flows at higher speed through regions with lower pressure. Therefore, it can be said that the pressure at the upper surface of the airfoil is less than the lower surface airfoil since the upper surface velocity is higher than the velocity at lower surface (Fig. 12).

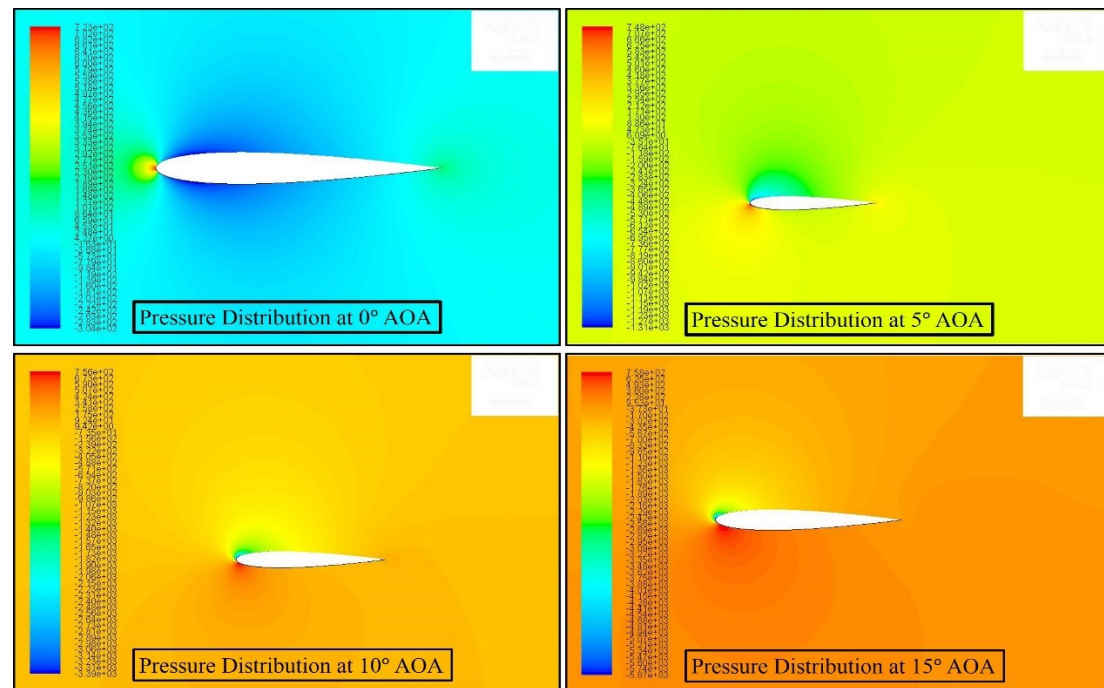


Figure 12. Pressure Distribution at 0° , 5° , 10° and 15° Angles of Attack

The pressure difference between the lower and upper body of the airfoil results in lift force. Increasing the angle of attack from 0° to 15° results in pressure increment on the lower surface of the airfoil which ultimately results in lift force increment as the angle of attack increases.

3.2 Experimental Results

The graph (Fig. 13) clearly shows that the lift coefficient almost linearly increases from 0 to 0.9 as the angle of attack changes from 0° to 16° . While further increment in the angle of attack up to 20° results in drop in lift. This converges that at 16° is the stall angle and the turbulence of the flow has increased and resulted in a lower velocity of over the upper surface and hence higher pressure. Higher pressure on the upper surface causes the decrement in the lift. However, it can be seen that the same but less abrupt path of increment in lift coefficient appears with increment of angle attack from 20° to 42° until it reaches a value of 1.51. It also can be understood that the lift coefficient becomes negative at angle of attack more than 90° and experiences peak values at the 140° and 165° and shows a symmetrical path of changes for the lift coefficient. This symmetry in lift coefficient is caused by the geometry of NACA 0012 where the airfoil has no camber and the flow around the airfoil is directly affected by the angle of attack.

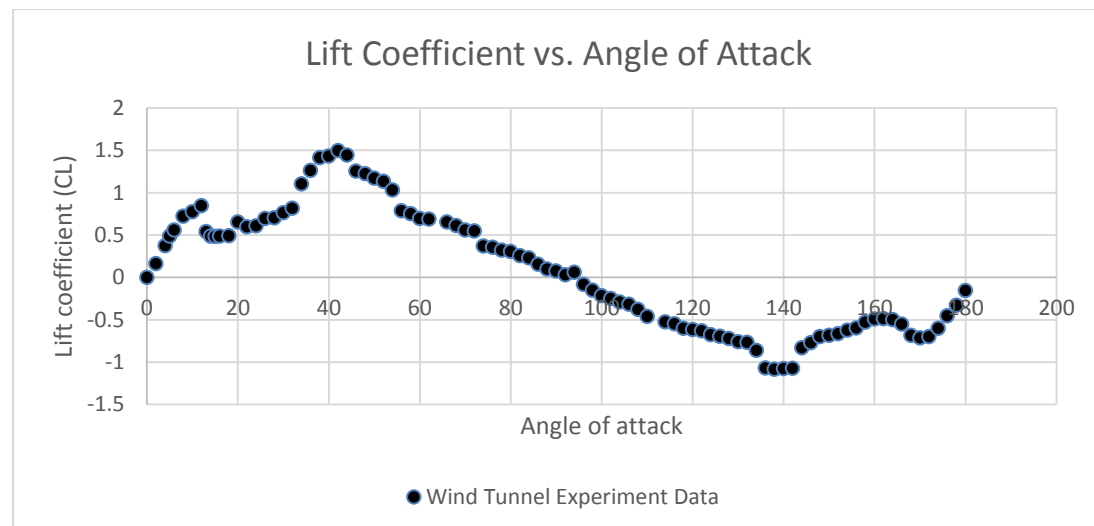


Figure 13. Lift Coefficient at 0° to 180° Angle of Attack

The drag coefficient at low angle of attack below the stall angle are extremely small since the flow (Fig. 14). However, it increases exponentially after the stall and reaches to a maximum value of 2.8 at 90° angle of attack. This great lift coefficient consists of skin drag as well as turbulent drag. The increment in the skin is due to the increase in the perpendicular surface contact with the flow stream which resists the flow stream. While the turbulence drag increases due to the increment in the separation which creates high turbulence due to the formation of eddies. Further increment of angle of attack from 90° to 180° results in decrement in drag coefficient since the flow stream blockage is reduced as well as the flow stream chaos which results in formation of smaller eddies and lower turbulence. Also, it can be seen that the drag coefficient at 0° angle of attack is smaller compared to 180° angle of attack. This can be explained since at 0° angle of attack the flow stream is washed off the trailing edge which is sharp while at 180° angle of attack the flow is washed off from the thick leading edge.

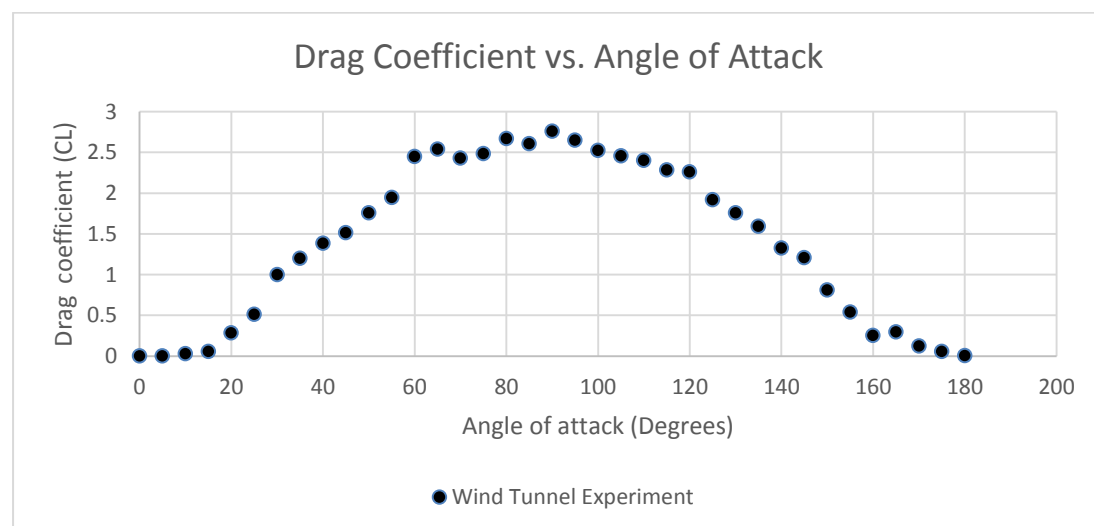


Figure 14. Drag Coefficient at 0° to 180° Angle of Attack

Studying relation between the lift and drag coefficient provides an overview of aerodynamic performance of NACA 0012 (Fig. 15). Drag Coefficient at its lowest for

0° angle of attack and reaches maximum value at 90 degrees, showing the highest amount of drag on the airfoil resulting in lowest lift coefficient. For further increase in the angle of attack, lift coefficient enters its negative characteristic region with reduction in drag coefficient until it returns to zero at 180°.

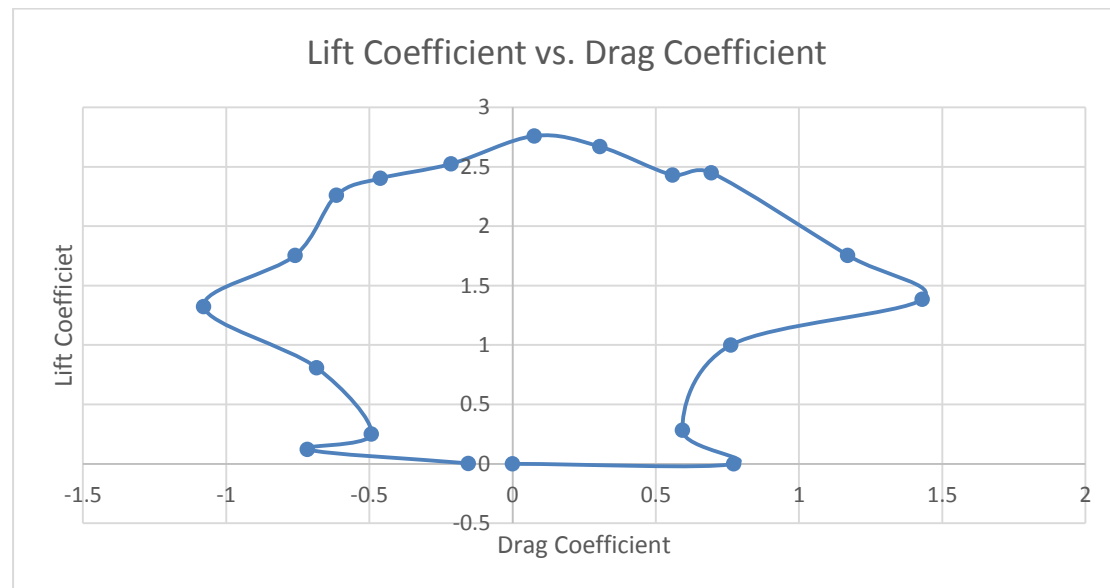


Figure 15. Drag Coefficient Relationship with Lift Coefficient

4. Conclusion

Study and investigate the High angles of attack aerodynamics is a challenging and complicated. In this project an experimental approach is used to determine the effect of high angle of attack on the aerodynamics of the standard NACA 0012 airfoil at low subsonic speed of 35 m/s and Reynolds number of 0.2×10^6 . The main findings of this study are concluded as follows:

- Increasing the angle of attack results in increment The lift coefficient increases until it reaches a value of 0.9 at the stall angle of 16° , then it starts to decrease with further increments in the angle of attack until 20° the lift coefficient reaches a value of 0.7, However the lift coefficient increases again with increment of angle of attack to 40° .
- The drag force acting on the airfoil increases as the angle of attack increase and increment in the drag force results in change of laminar flow to turbulent flow. As the turbulence get higher the flow starts to separate from the airfoil surface due to eddies generated by turbulence.
- Further increment of angle of attack after 90° results in a nearly symmetrical behaviour of lift and drag coefficients with lift coefficient having negative value and drag coefficient reducing to 0.

As the comparison of the results with published data converges, the percentage error of the experiment are to be reduced. The accuracy of the results can be improved by considering the followings:

- Reducing the vibration of the test rig to minimum while the wind tunnel operates. This has to be reduce the misreading of forces by load cell.

- Replacement of the wind tunnel's section wall with a wall which precisely fits the test section.
- Producing the worm and wheel gear with aluminium that is a more rigid material compared to polypropylene. Also the surface finish of the gears should be improve and smoothened to allow the gears to rotate smoother.
- An automatic rotary mechanism to be added to gears to provide a more convenient and accurate solution for the change of the angle of attack. designed to enable the user to change the angle of attack.

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Sintering Study on Commercial Hydroxyapatite

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Abstract

Hydroxyapatite have been actively researched on for its benefits in the medical field due to the material possessing a very similar chemical structure to that of bones. Due to the extensive research it is currently being used to repair small bone defects and certain dental applications. The current direction the research of hydroxyapatite is leading is to create a viable substitute for bone transplant. The current setback of utilising hydroxyapatite as a bone substitute is the weak mechanical properties possessed by the material. Sintering process have long been proven to increase the mechanical properties in bioceramics. Single stage sintering process is used to increase the density and mechanical properties of the hydroxyapatite nanopowder. [1]

The research that is being conducted is the sintering study on commercially available hydroxyapatite powder manufactured by Merck. The densification behaviour and mechanical properties were found to be dependent on the thermal history during the sintering process. To carry out the study, the commercial hydroxyapatite powder was cold isostatically pressed at 10 MPa and pressureless sintered with ramp rate of 10°C/minute at temperature range from 1100 to 1300°C with a holding time of 1hr.

The purpose of this research is to determine the optimal single stage sintering profile of hydroxyapatite which would result in the best mechanical properties. The main challenge in conducting this research is determining the optimal single stage sintering profile that does not compromise the integrity of the sintered hydroxyapatite. Based on the extensive research it can be concluded that the optimal single stage sintering profile will produce a sintered commercial hydroxyapatite with higher mechanical properties.

Keywords: Hydroxyapatite, single stage sintering, mechanical properties

1.0 Introduction

In the past few years there have been a great amount of research on the usage of biomaterials as viable replacements to tissues in medical science. In particular medical research has been giving a lot of attention in the field of bioceramics as possible replacement for bone tissue. Based on the extensive research, bioceramics have been shown to have good biocompatibility with the human body and significantly reduce the chances of the body rejecting an artificial transplant as compared to an actual bone transplant. Bioceramics are a much more viable solution as it has the capability to be mass produced and specifically created to the preferred specification to the recipient needs and a donor that is a biological match is not required for a major transplant which is the current main drawback.

Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) has of late attracted great prospect as a possible bioceramic replacement for bone tissue which can be used in a bone transplant. Hydroxyapatite is at this juncture used for medical applications such as repairing bone defects, dental surgery, and various others. Hydroxyapatite is also used as a base for synthetically built biomaterials as it can be constructed into various shapes and is well known for its high biocompatibility and osteoconductivity. [2]

The medical research community is still showing significant attentions towards hydroxyapatite due to its similar chemical composition to that of bone tissue. The current major drawback of hydroxyapatite is its apparent low mechanical properties within the substance. Research also states how a coating of an apatite layer of hydroxyapatite around a synthetic material has shown to increase the biocompatibility of the material with the host body due to the material's natural promotion towards protein absorption and cell adhesion. [3] At its current state hydroxyapatite has a low fracture toughness which would not be viable to create compatible bone transplant that is able to withstand heavy loads. [4]

The sintering process is technique that utilises heat to heat the desired powder to just under the materials melting point. This would in turn cause the material to form a stronger bond with one another. The stronger bonds are caused due to the diffusion of atoms across the materials boundaries which causes the particles within the material to fuse thus creating the final product. The sintering process significantly changes the density of the sintered material, the grain size within the nanoparticles of the material, and also the size of the final product produced from the process. [5]

Sintering is an essential process in improving the mechanical properties of ceramics. Sintering involves developing the ceramics microstructure to significantly reduce the porosity of the material. [6] Obtaining the optimal sintering profile is a key objective of the study as the sintering profile and mechanism involved would determine the microstructure and properties of the final product. [7]

The sintering process significantly affects the grain size within the material. Grain growth within a material during the sintering process is a major part in creating a product with strong mechanical properties. A final product that possesses a smaller and denser particle with small grain size nanoparticles is highly desirable. This is due to the fact that the densification rate of a material is inversely proportional to the grain size of the final product. [8]

The main purpose of this research is to determine the optimal single stage sintering profile which results in the highest mechanical properties of hydroxyapatite. The reasoning behind this research is to further facilitate the research of producing a viable hydroxyapatite bioceramic for bone transplants.

1.1 Objective

The primary objective of this project can be divided into three main components:

- i) To study and understand various aspects of the project by conducting in depth literature review of journals.
- ii) Conduct an experiment to study the effects of various sintering profiles and the effects on the mechanical properties of hydroxyapatite.
- iii) Determine the optimal sintering profile that results in the best mechanical properties of hydroxyapatite.

The secondary objective of the project is to complete all the modules learning outcomes in order to achieve the requirements for graduation

2.0 Research Methodology

The main aspect of any experimental research is the research methodology. The research methodology allows the researcher to clearly and specifically plan and manage the entire research experimentation requirements in order to achieve the objective set by the researcher within a specific scope and time frame. The main objective behind conducting this research is to further support and advance the research on medical science in order to improve the quality of life of the community at large.

This experimental research is to study and obtain the optimal single stage sintering profile of hydroxyapatite which will result in an increase in mechanical properties. The research methodology of this research can be divided into two major components:

- i) Theoretical studies
- ii) Practical Experiments

2.1 Theoretical Studies

To conduct any significant research experiment of value an equal proportionate of time must be used in order to study the current developments and research that have been recently conducted. The main purpose to conduct literature review and background study is to understand the significant theories, characteristics and principles regarding the research experiment. Literature review is also conducted to ensure that the experiment that is being conducted have not been significantly researched and would add value to the current development in the related field. For this research the background studies includes the current development of hydroxyapatite, the single stage sintering process, and the relationship between sintering process and increased mechanical strength. The focus of the literature topics

are to ensure that the research experiment that is being conducted would produce a hydroxyapatite product with superior mechanical properties.

2.2 Practical Experiments

2.2.1 Hydroxyapatite sample preparation

The hydroxyapatite powders (Merck) obtained are initially weighed on in an electronic digital scale to 1.5 grams for each sample. To conduct this experiment there are two distinct shapes of that is that is required to be made. To create all the samples to be of equal shape and size a precise die is used. Two distinct dies were used to make the circular and rectangular shape samples. After the hydroxyapatite powder weighed at 1.5 grams is inserted into the die it undergoes uniaxial compaction at about 10 MPa. The samples are compacted into two distinct shapes a circular disc and a rectangular bar.

2.2.2 Cold Isostatic Pressing (CIP)

All the samples created both circular and rectangular bar are placed inside rubber latex containers. The air within the rubber latex containers are removed and tightly sealed. The samples then sent to undergo cold isostatically pressed (CIP) at the Standards and Industrial Research Institute of Malaysia (SIRIM). Cold isostatic pressing is essential to ensure that the samples are more consistently compacted from all directions inside an oil medium. The Cold Isostatic Pressing is conducted to ensure the best densification of the sintered sample and also prevents the sample from warping and cracking.

2.2.3 Sintering

For this research a single stage sintering process is conducted. In this experiment the sintering process utilises the conventional pressureless sintering (CPS) method. A rapid-heating furnace with the brand ModulTemp, Australia was used to conduct sintering process. The hydroxyapatite samples will be sintered at various set temperatures. The temperatures set for sintering are at 1100 °C, 1150 °C, 1200 °C, 1250 °C, and 1300 °C at an increment of 10°C per minute and holding for one hour. The samples are placed into the conventional pressureless sintering machine and the conditions are then set in the control panel. After the entire sintering process is completed the sample is removed.

2.2.4 Grinding and Polishing

Before the samples were subjected to the various mechanical testing, the disc shaped samples were carefully polished and grinded. A RaxVision Metapol-2 grinder/polisher machine was utilised to perform this task.

At the grinding stage the sintered sample was grinded with a silicon carbide paper with a roughness value of 800 grit and then continued with a silicon carbide paper with a roughness value of 1200 grit.

At the polishing stage the sample was polished first with a 3 micron polishing cloth and then with a 1 micron polishing cloth with diamond paste is applied. The polishing is continuously until a very reflective surface is achieved.

2.2.5 Properties and Structural Analysis

2.2.5.1 X-Ray Diffraction (XRD)

X-Ray Diffraction is used to track the phases and behaviour of the Hydroxyapatite nanostructures in the experiment. The specimen is placed within an X-Ray Diffraction machine and the structure of the sintered hydroxyapatite along with its characteristics is determined.

The hydroxyapatite sample that was sintered is placed into the X-Ray Diffraction machine one at a time. The machine then releases an output graph based on the composition and structure of the sintered hydroxyapatite. The steps are repeated for the entire batch of sintered samples.

The concept of X-Ray Diffraction (XRD) is based on Bragg's law which proves correlation between the incidence angle a crystal reflects x-ray beams to the periodic atomic structure of the crystals postulated.

2.2.5.2 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is used to analyse and observe the morphology and crystalline structure of the sintered hydroxyapatite. The grain size of the sintered hydroxyapatite is observed and based on the grain size the morphology, crystalline structure, and mechanical properties of the sintered sample can be deduced.

The hydroxyapatite sample that was sintered is placed into the Scanning Electron Microscope one at a time. Before the samples are placed into the Scanning Electron Microscope they are coated with palladium which acts as a conducting layer to deter charging from occurring within the microscope. A focused beam of electrons then scans the sintered sample. An image of the scanned sintered sample is then displayed with a scale and the picture of the scanned image is then saved. The steps are repeated for the entire batch of sintered samples.

2.2.5.3 Young's Modulus

Young's modulus is the value of the gradient of graph between the stress and strain of the material. The Young's modulus is used to determine the resistance of the material to elastic deformation under a load. To obtain the Young's modulus for this experiment the sonic resonance technique is utilised to analyse the resonant frequency of the specimen. The testing instrument (GrindoSonic: MK5 "Industrial", Belgium) which is used to determine the resonant frequency of the sintered hydroxyapatite bar by utilising a transducer to monitor and analyse the vibrational harmonics. The Young's modulus is then calculated utilising the formula stated below:

$$E = 0.9465 \left(\frac{m F_f^2}{b} \right) \left(\frac{L}{t} \right)^3 T_1$$

For this research the Young's Modulus test will be performed to determine the resistivity of hydroxyapatite to elastic deformation.

2.2.5.4 Bulk Density

Bulk Density test is the mass of particles of a material divided by the total volume occupied by the material. The bulk density test shows the ability of a material to function as a support. The water immersion method is used to perform the bulk density test on the specimen of sintered hydroxyapatite.

First, the entire prepared sample before sintering is weighed in air (W) and the weights are recorded down. Then, the thickness (t_1) and diameter (d_1) of each prepared sample before sintering are recorded down. After the sintering process is completed the thickness (t_2) and diameter (d_2) of each sample are recorded down. Then, the weight of the entire sintered sample in air (W_a) is weighed and recorded down. Next, the sintered samples are then weighed while immersed in water (W_w) and recorded down. After, the weight of the sintered sample immersed in water is weighed in air (W_{a+w}) and recorded down to determine the porosity of the sample. The bulk density formula used is as stated below:

$$\rho = \frac{W_a}{W_a - W_w} \rho_w$$

For this research a bulk density test will be performed to determine the structural support integrity of the material Hydroxyapatite.

2.2.5.5 Vickers's Hardness

The Vickers's Hardness will be determined by using the Vickers's indentation test. The Vickers's indentation test will utilise a microindentation device to create an indentation with a set load and duration. The indentation left by the test is then measured using a microscope to determine the diameter of the indentation. The diameter is then placed into the Vickers's hardness formula and the Vickers's hardness, H_v is determined. The formula for Vickers's hardness is as stated below:

$$H_v = \frac{1.854 * F}{(d)^2}$$

After the sample is prepared it is then placed in a micro indenter machine. The micro indenter machine is used to apply a load for a set amount of time and the indentation present on the sample as a result is used to calculate the hardness. The load being applied to the sintered sample by the micro indenter machine is set at 10N for a duration of 5 seconds. Once the load application is complete the diameter of the indentation and the hardness is recorded down. The steps are then repeated twice on

the same sample totalling a number of three indentation per sample. The steps are then repeated for the rest of the sintered samples.

Through this test the Vickers's Hardness, H_v is obtained for the fracture toughness test.

2.2.5.6 Fracture toughness

Fracture toughness by definition is the strength of a material with a crack to resist further fracture. It is essentially used to determine the resistance of a material to fracture when a crack is present. The Niihara (1985) fracture toughness equation is as shown below:

$$K_{IC} = 0.203 \left(\frac{c}{a} \right)^{-1.5} (H_v) (a)^{0.5}$$

After the sintered sample has undergone the micro indentation test to determine the hardness, H_v the samples are then viewed under a digital microscope to observe the crack that propagate in all four corners of the indentation. A picture is then taken of each corner of the indentation. Utilising the scale present in the picture a software is used to measure the length of the crack in micrometres (μm). The lengths are then placed into the formula and fracture toughness, K_{IC} is determined.

For this research the fracture toughness test will be used to determine the fracture toughness of the material hydroxyapatite. Using the data from this experiment we can determine if we have found the optimal single stage sintering profile.

3.0 Results and Discussion

3.1 X-Ray Diffraction

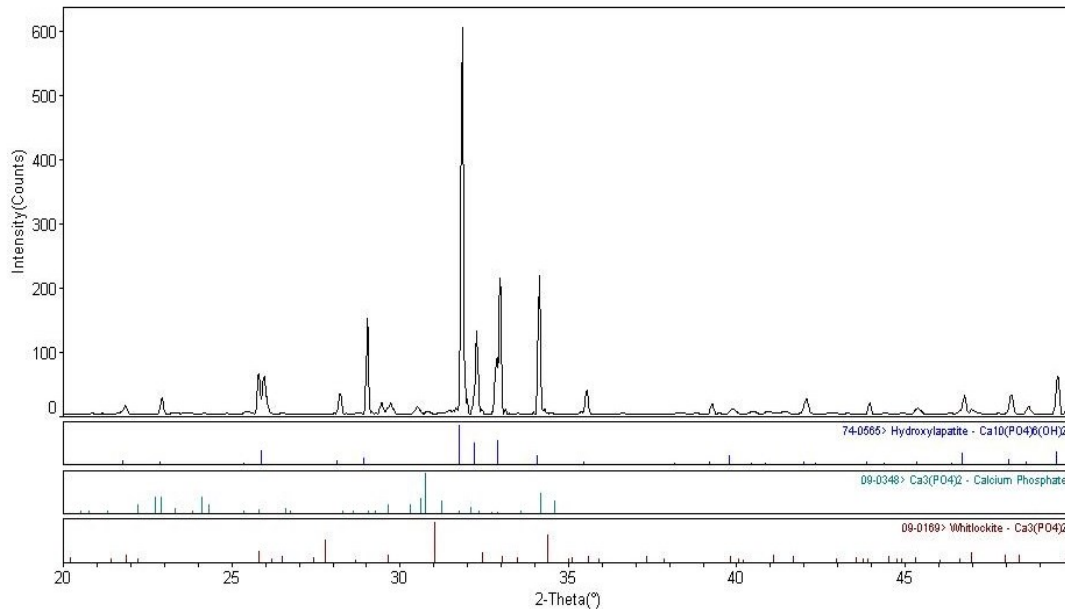


Figure 1: X-Ray Diffraction pattern of hydroxyapatite sintered at 1100°C

Based on Figure1 the X-Ray Diffraction indicates that the sample sintered at 1100°C peaks are consistent with that of hydroxyapatite which indicates that the sintered

material did not shift into a different material phase. The diffraction patterns show sharp, clear and high intensity corresponding to hydroxyapatite which proves phase purity and high crystallinity degree of the sintered sample produced.

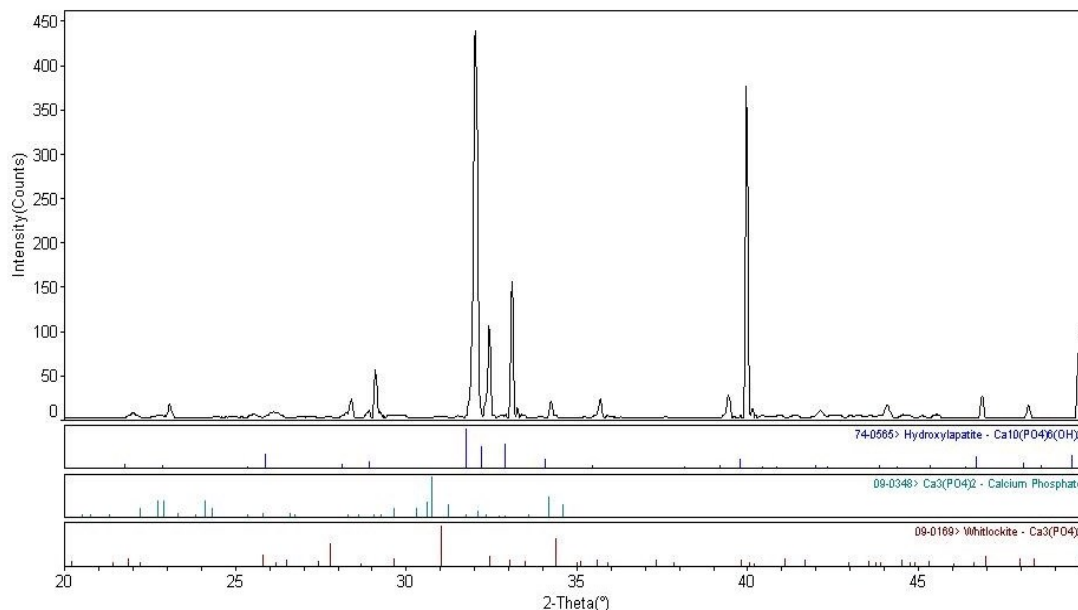


Figure 2: X-Ray Diffraction pattern of hydroxyapatite sintered at 1150°C

Based on Figure 2 the X-Ray Diffraction indicates that the sample sintered at 1150°C peaks are consistent with that of hydroxyapatite which indicates that the material did not shift phase into a different material. The diffraction patterns show sharp, clear and relatively high intensity corresponding to hydroxyapatite which proves phase purity and good crystallinity degree of the sintered sample produced.

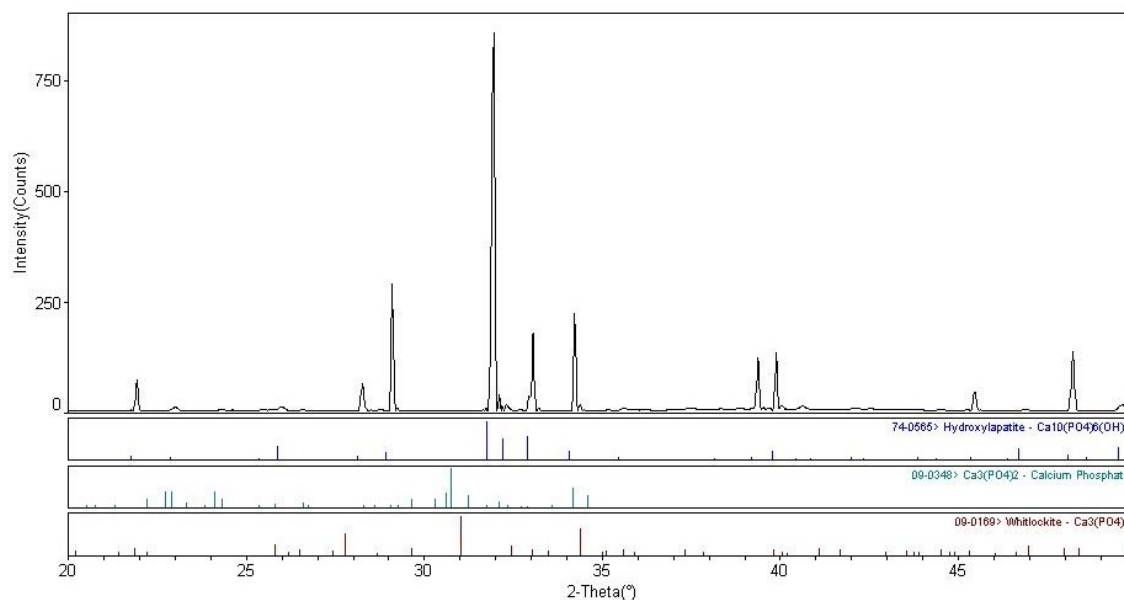


Figure 3: X-Ray Diffraction pattern of hydroxyapatite sintered at 1200°C

Based on Figure 3 the X-Ray Diffraction indicates that the sample sintered at 1200°C peaks are consistent with that of hydroxyapatite which indicate that the sintering did

not cause the material to shift phase into a different material. The diffraction patterns show sharp, clear and very high intensity corresponding to hydroxyapatite which proves phase purity and very high crystallinity degree of the sintered sample produced.

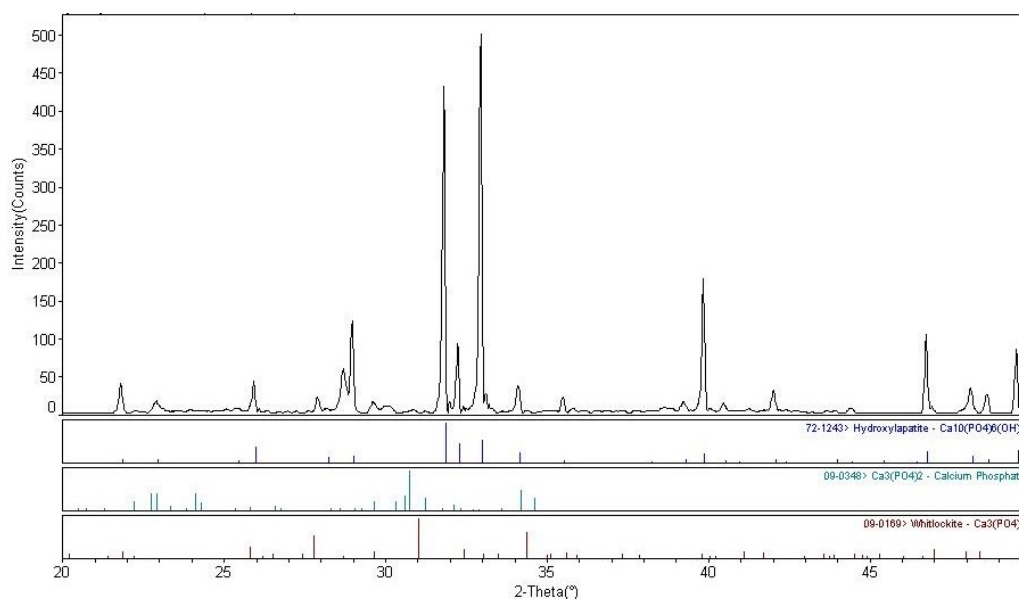


Figure 4: X-Ray Diffraction pattern of hydroxyapatite sintered at 1250°C

Based on Figure 4 the X-Ray Diffraction indicates that the sintered sample peaks are consistent with that of hydroxyapatite. This proves that the hydroxyapatite sintered at 1250°C did not cause the material to shift phase into a different material. The diffraction patterns show relatively intensity corresponding to hydroxyapatite which proves good phase purity and good crystallinity degree of the sintered sample produced but also indicates minor decomposition of hydroxyapatite as some low peaks do not correspond with hydroxyapatite.

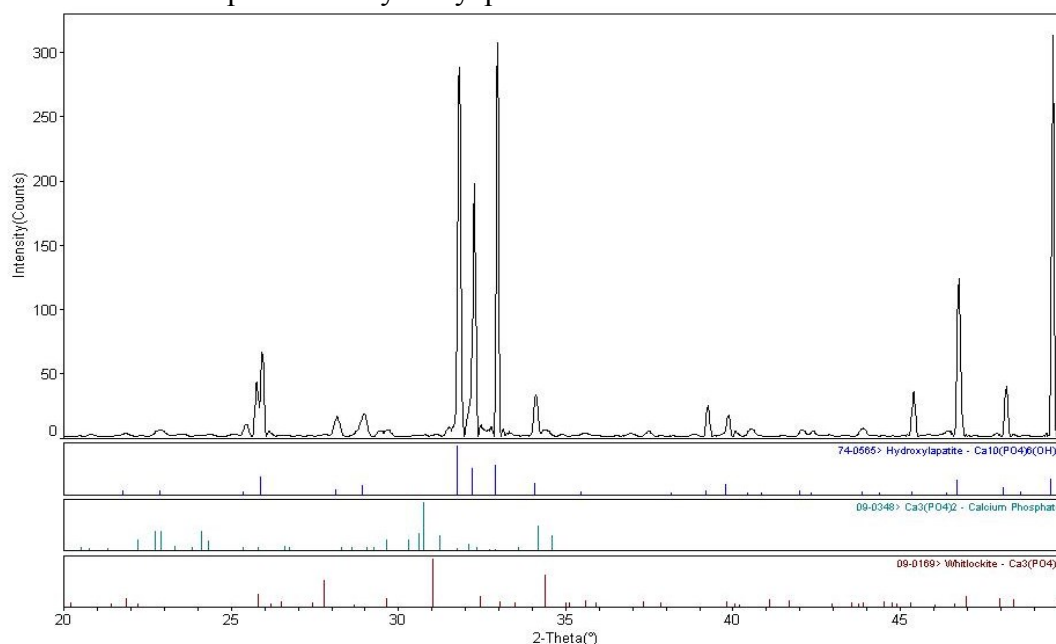


Figure 5: X-Ray Diffraction pattern of hydroxyapatite sintered at 1300°C

Based on Figure 5 the X-Ray Diffraction indicates that the sintered sample peaks are consistent with that of hydroxyapatite. This proves that the hydroxyapatite sintered at 1300°C did not cause the material to shift phase into a different material. The diffraction patterns show sharp, clear and high intensity corresponding to hydroxyapatite which proves phase purity and high crystallinity degree of the sintered sample produced. The diffraction patterns show sharp, clear and relatively high intensity corresponding to hydroxyapatite which proves phase purity and good crystallinity degree of the sintered sample produced.

The intensity of the X-Ray Diffraction decreases between the sintered hydroxyapatite at 1100°C and the sintered hydroxyapatite at 1150°C. The intensity of the X-Ray Diffraction then increases when the hydroxyapatite is sintered at 1200°C. The intensity of the X-Ray Diffraction then continues to decrease between the sintered hydroxyapatite at 1250°C and the sintered hydroxyapatite at 1300°C. The X-Ray Diffraction of the sample sintered at 1300°C is observed to have the lowest intensity indicating relatively low crystallinity as compared to the rest of the sintered samples. The clarity and sharpness of the pattern of the sample sintered at 1300°C indicate phase purity and a very high. The X-Ray Diffraction of the sample sintered at 1200°C is observed to have the highest intensity indicating phase purity and a very high crystallinity as compared to the rest of the sintered samples.

3.2 Bulk Density

For this experiment the bulk density is determined by weighing the sintered hydroxyapatite in different conditions to determine the density of the samples. Water temperature at the time of the test is at 28°C.

Table 1: Tabulated density of sintered hydroxyapatite samples

Sintered temperature	1100°C	1150°C	1200°C	1250°C	1300°C
Weight in air, W_A (grams)	1.423	1.415	1.419	1.085	1.418
Weight in water, W_W (grams)	0.913	0.944	0.960	0.736	0.958
Weight in air after soaked in water, W_{A+W} (grams)	1.429	1.425	1.422	1.101	1.442
Bulk Density (grams/cc)	2.752	2.933	3.065	2.969	2.920

Based on Table 1 the hydroxyapatite sample sintered at 1100°C has the lowest bulk density at 2.752 g/cc and the hydroxyapatite sample sintered at 1200°C has the highest bulk density at 3.065 g/cc. The difference between the weight in air and the weight after being immersed in water in air is really small for the sample sintered at 1200°C which indicates that the porosity of the sintered sample is very low thus producing a sample with a high bulk density.

Based on a research done in a similar field the bulk density of hydroxyapatite sintered at 1200°C also resulted in a material with low porosity due to the elimination of residual porosity [10]. The temperature conditions are high enough to significantly reduce residual porosity of the sample while still being able to prevent the formation of undesired phases [10].

3.3 Young's Modulus

For this experiment the Young's Modulus of each of the sintered hydroxyapatite samples at different temperatures are determined.

Table 2: Tabulated data of Young's Modulus of the sintered hydroxyapatite.

Sintered Temperature (°C)	Young's Modulus (GPa)
1100	96.1
1150	110.9
1200	108.8
1250	106
1300	103

Based on Table 2 the hydroxyapatite sample sintered at a temperature of 1100°C has the lowest Young's Modulus at 96.1GPa and the hydroxyapatite sample sintered at a temperature of 1150°C has the highest Young's Modulus at 110.9GPa which indicates the resistivity of the material to elastic deformation. It can be observed from Figure 6 that the Young's Modulus increases between the samples sintered at 1100°C and 1150°C, while decreasing steadily between samples sintered at 1150°C and 1300°C.

Based on researches conducted on the sintering of ceramics, the average size of the pores present within the microstructure of the ceramic increases as the sintering temperature is increased [11]. The Young's modulus is directly correlated with the porosity of a material, as the porosity of a sample increases the Young's modulus decreases [12].

The hydroxyapatite samples are sintered in a repetitive thermal cycle at a set increment which can lead to crack nucleation which may result in a loss of strength [11]. The formation of cracks within the microstructure of the material can result in a significant influence on the Young's modulus of the material [13] and [14]. The decrease in Young's modulus can be attributed to the decomposition of the hydroxyapatite that prevented the formation of stronger inter-particle bonding within the ceramic matrix [11].

3.4 Hardness

For this experiment the Vickers's hardness is performed on each of the sintered hydroxyapatite samples at different temperatures are determined. Each hydroxyapatite sintered sample is tested three times in order to obtain an average hardness value. The test is performed by applying a load of 10N over a period of 5 seconds.

Table 3: Tabulated data of hardness test and mean hardness value.

Sintered Temperature (°C)	1100.00	1150.00	1200.00	1250.00	1300.00
Hardness (Hv) i)	376.00	507.00	549.00	577.00	519.00
ii)	396.00	498.00	548.00	527.00	577.00
iii)	371.00	499.00	575.00	548.00	522.00
Mean Hardness (Hv)	381.00	501.33	557.33	550.67	539.33

Based on Table 3 the hydroxyapatite sample sintered at a temperature of 1100°C has the lowest Vickers hardness at 381 HV and the hydroxyapatite sample sintered at a temperature of 1200°C has the highest Vickers hardness at 557.33 HV. The highest Vickers's hardness indicates a resistivity towards plastic deformation, penetration, and bending.

Sintering temperature of the sample is directly correlated to the hardness of the sample, the higher the sintering temperature the harder the sample produced. This however does not work infinitely as very high temperature have the tendency to eliminate the functional group OH in the hydroxyapatite matrix [15]. The elimination of the functional group OH from the hydroxyapatite matrix will lead to the decomposition of the hydroxyapatite phase that can result in lower mechanical properties [15].

3.5 Fracture toughness

Based on the Table 4 the hydroxyapatite sample sintered at a temperature of 1100°C has the highest fracture toughness at 0.93 and the hydroxyapatite sample sintered at a temperature of 1200°C has the lowest fracture toughness at 0.64. This indicates the material with the highest fracture toughness has the highest resistance towards the propagation of cracks present within the material.

Table 4: Tabulated data of fracture toughness.

Sintered Temperature (°C)		1100	1150	1200	1250	1300
Fracture Toughness (MPam ^{1/2})	i)	0.69	0.54	0.57	1.04	0.67
	ii)	1.31	0.71	0.54	0.44	0.84
	iii)	0.79	0.67	0.46	0.78	0.51
Mean Fracture Toughness (MPam ^{1/2})		0.93	0.64	0.52	0.75	0.67

Based on studies done on sintering of ceramics the thermal stress developed during the cooling phase of the sintering process can cause a variation in the mechanical properties of the sintered sample [16]. The samples that develop larger grains size during the cooling stage can create miniscule cracks that can affect the hardness and fracture toughness of the sintered sample [17]. A higher rate of cooling can result in a higher stress concentration that would be destructive towards improving the strength of the material [18]. These factors could have contributed to the fracture toughness obtained in this experiment.

3.6 Scanning Electron Microscopy

The purpose of this image is to observe the microscopic structure of the sintered sample and note the grain size and intergranular cracks present within it. Lower sintering temperature leads to formation of smaller grain size as compared to higher sintering temperature. The finer grain size of a material corresponds with a higher resistance to crack propagation and dislocation motion which in turn results in a higher fracture toughness. [19]

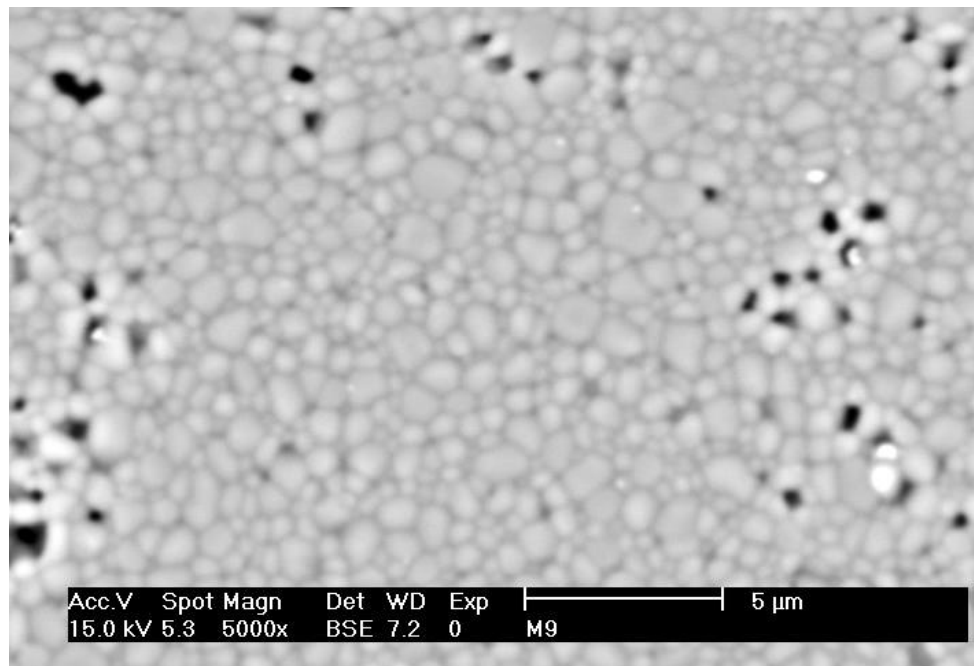


Figure 6: Scanning electron microscopy image of hydroxyapatite sintered at 1100°C

Figure 6 shows that the grain size of the material are very small and there are many intergranular cracks present within. This correlates with the results of this experiment indicating that the sample sintered at 1100°C possesses the highest fracture toughness in the entire experiment.

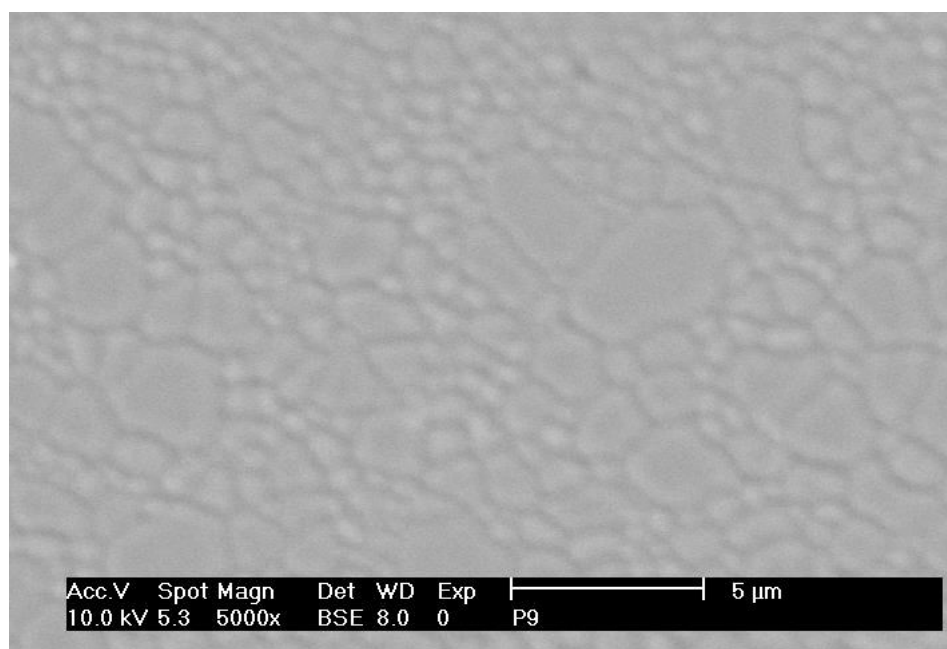


Figure 7: Scanning electron microscopy image of hydroxyapatite sintered at 1150°C

Figure 7 shows the grain size of the material are relatively small and there are many intergranular cracks present within. This correlates with the results of this experiment indicating that the sample sintered at 1150°C possesses a relatively high fracture toughness as compared to the other sintered samples in the experiment.

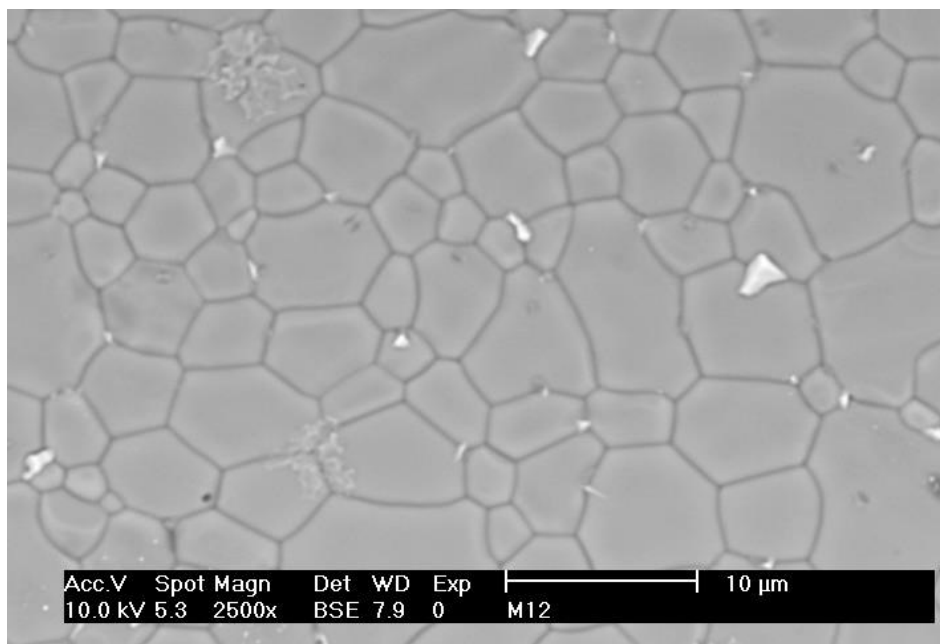


Figure 8: Scanning electron microscopy image of hydroxyapatite sintered at 1200°C

Figure 8 shows the grain size of the material are much larger in comparison with the grain size of the materials sintered at 1100°C and 1150°C. There are however much less intergranular cracks present within the sintered sample as a result of a larger grain size. This correlates with the results of this experiment indicating that the sample sintered at 1200°C possesses a very low fracture toughness as compared to the other sintered samples in the experiment.

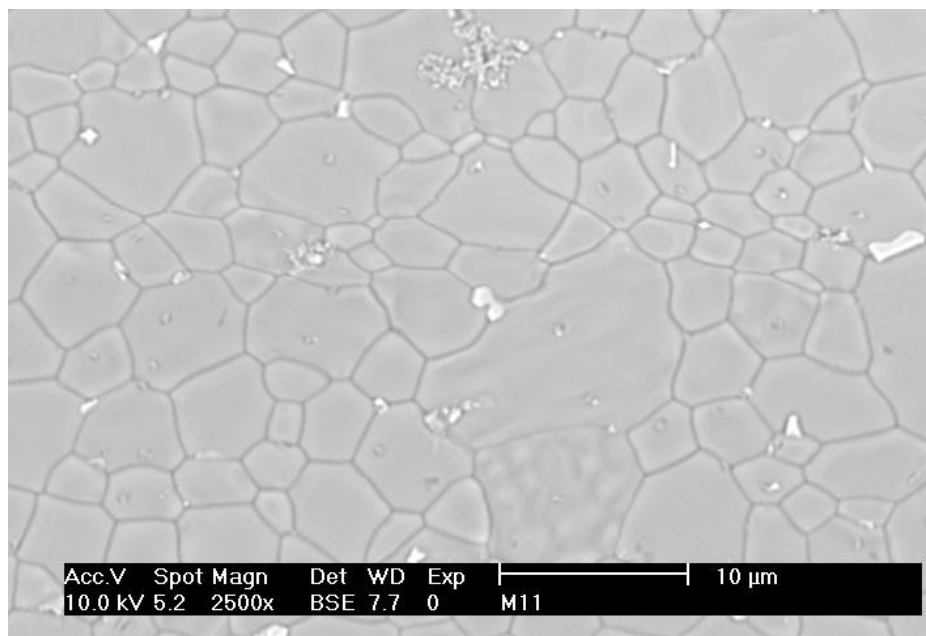


Figure 9: Scanning electron microscopy image of hydroxyapatite sintered at 1250°C

Figure 9 show he grain size of the material are larger in comparison with the grain size of the materials sintered at 1200°C. There are however much less intergranular cracks present within the sintered sample as a result of a larger grain size. The result however does not correlate with the results of this experiment indicating that the sample sintered at 1250°C possesses a relatively high fracture toughness as compared

to the other sintered samples in the experiment. The cause of the irregularity is not clear but could be attributed to the toughening effect of hydroxyapatite ceramics.

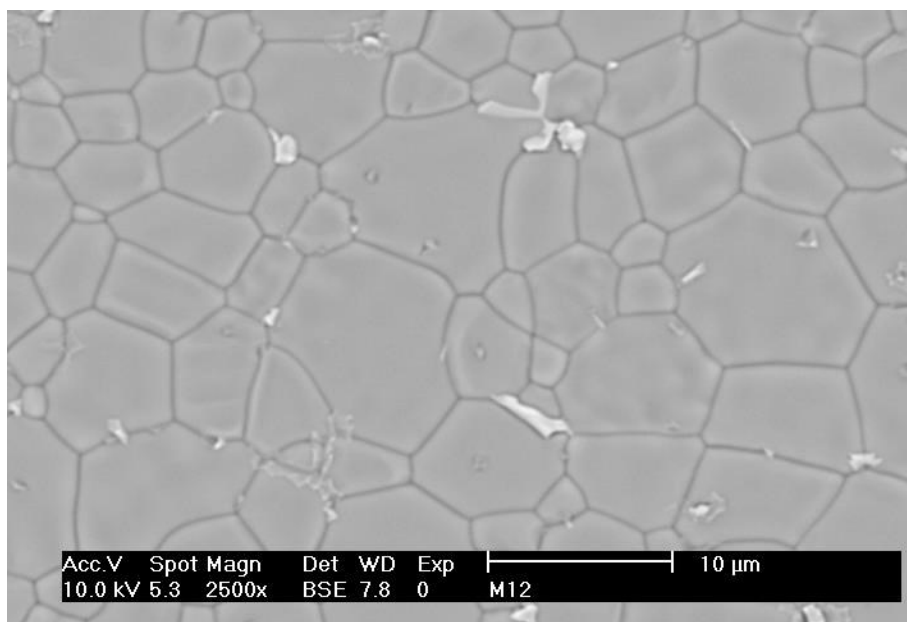


Figure 10: Scanning electron microscopy image of hydroxyapatite sintered at 1300°C

Figure 10 show the grain size of the material are is the largest in comparison with the grain size of the materials sintered at 1250°C. There are however very low intergranular cracks present within the sintered sample as a result of a larger grain size. The result however does not correlate with the results of this experiment indicating that the sample sintered at 1300°C possesses a better fracture toughness as compared to the sample sintered at 1150°C in the experiment. The cause of the irregularity is not clear but could be attributed to the toughening effect of hydroxyapatite ceramics.

4.0 Conclusion

This experimental research was conducted to study the sintering of commercial hydroxyapatite and determine the optimal sintering profile. The results indicate an initial increase in mechanical properties as the sintering temperature increased from 1100°C to 1200°C. The results however also indicate a decrease in mechanical properties at sintering temperatures of 1250°C and 1300°C. The optimal sintering profile that results with the best mechanical properties was determined to be the sample sintered at 1200°C with an increment of 10°C per minute and holding for one hour.

The future work in this field would include various different forms of sintering techniques which would result in different products. It would also include a two-stage sintering profile to further experiment on the effects of two-stage sintering on hydroxyapatite.

5.0 References

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Mechanical Simulation and Review of a Selected Electrical Car

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Abstract

Cars have always been the major contributor to reduction of earth's natural resources as well as being the frontrunner in green house effects, which is one of the main causes of global warming. Green vehicles have been taken to a new level through these years by extensive researching and constant improvements. This project focuses on the mechanical improvement and assembly of an energy efficient electrical car supported by an electrical hub motor and inside regenerative breaking implementation. Design and manufacturing of the electrical car have been done based on engineering facts with precise mathematical formulation and it is validated with computer simulations to ensure the safety and performance of the vehicle. Chassis and the knuckles of the electrical car were systematically designed and improved by 63% using static simulations and the final chassis and knuckle designs were then manufactured by 3d paper wrapping and CNC machining method respectively. The aerodynamic performance of the system was handled during the design stage and its components have been implemented. The contributing factors of the body shell were experimented and improved in terms of weight to strength ratio.

Key-Words: Chassis, Upright, Aerodynamic, Static simulation, Finite element analysis

1.0 Introduction

As the time passes by every year the reduction of petroleum in the world forces the automotive industry to alternate their source of energy to power vehicles. An alternative source of energy should be replaced to reduce the dependency to petroleum energy which is powering up more than 80% of transportation vehicles nowadays [1]. Statistics shows that 36.4% of energy is used by the transportation sector in Malaysia and this percentage is rapidly increasing everyday so in order to face this problem another source of energy should be replaced with petrol in this sector [2]. One of the best replacements would be Electrical power which is a clean energy. Higher efficiency, greater acceleration and reduction in carbon footprint are the benefits of an electric vehicle compared to the conventional internal combustion engine which this would help the world to save up this valuable source of energy for a better use. By the time of 2012 the global EV stock exceeded 180000 units [3]. At that time companies like Tesla Motors had the lead of EV market with their 130MPH speed and high range cars [4]. With the development of the electrical cars, being sustainable is not sufficient whereas efficiency should be taken into consideration as well. The most reasonable method to improve the efficiency is by reducing the weight of the vehicle while performing in the desirable boundary conditions [4]. In order to reduce the weight of the vehicle, every component has to be redesigned and mechanically developed which calls for extensive design and simulation stages.

Mechanical development of an electrical car is the main purpose of this project, which it focuses on designing and improving the chassis, upright and an aerodynamic body of an electric vehicle. To prove the capability of the design simulations are carried out to test design whereas experimental testing has also been done to fully ensure the generated results from simulation. In the case of chassis and upright weight/strength ratio is the most important criteria in the design stage and solid works simulations are done to further reduce the weight of both chassis and upright. Look and aerodynamic of the body is what that is considered in designing the body shell while SolidWorks flow simulation is used to test the aerodynamic aspect of the body. Finalized Designs are then manufactured and fabricated each with their respective chosen material. Chassis was fabricated using mild steel pipes with a diameter of 21mm. T6 (6061) aluminium alloy was used to manufacture the upright and it has been manufactured by a CNC machine. In this paper the design process of chassis, upright and aerodynamic body of an electric is explained into details and designs are optimized and validated by static simulations under defined real world conditions. These designs are manufactured using materials selected in the design stage and the manufactured prototypes are shown in this paper.

2.0 Design

2.1 Chassis

The main purpose of the chassis is to form the overall shape of the car and protect the passengers from any external invasion. A Space frame is used in this project as it is much lighter than other types like ladder or cruciform since metal tubes are used in prototyping them. Lightening the chassis while having a good response to stresses is the most important criteria of a chassis so in order to reduce the weight of the chassis there are a number of factors that should be taken into consideration. Firstly the size of the chassis should be minimized to the smallest size possible which in order to achieve that the chassis have been designed in a dimension of 1.75 m length and 0.5 m width which is the size of an average person ; this would

save the unnecessary weight. There are actually different types of static and dynamic forces acting on the chassis in different situations such as bending , torsion and lateral loadings which these are forces that have to be considered while designing a chassis .In order to increase the stiffness of the chassis diagonal braces are used in the design which is shown Figure1 [5].

The chassis is then designed in Solidworks based on the competition's criteria and have been optimized using solid works simulation in the simulation stage. The finalized design is then constructed using steel pipes.

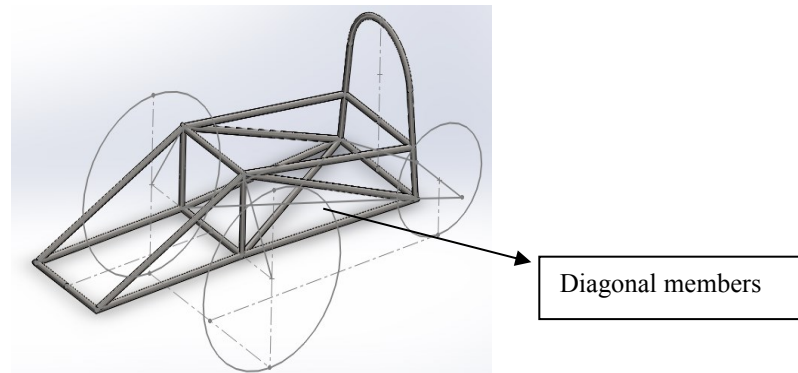


Figure 15. Chassis designed in Solidworks

2.2 Upright

The upright assembly of the car to provide a direct mounting from the suspension links to the wheels. The challenge of designing the front upright is to be able to support the electric car under common static and motional conditions [6] .The car will be subjected to forces unseen by naked eyes no matter it is static or motional and only the result of these forces can be seen. The design had to be done with concern safety measure to prevent damages and loss and even death. .Upright is one of the most critical components of car as it joins the chassis and the suspension unit to the wheels. There are quite a number of forces acting on the upright in different situations where lateral forces caused by the cornering of the car and normal force caused by the weight of the vehicle are the most considerable ones; these forces are shown in the simulation stage where 2 design solutions were provided for the upright shown in Figure 2 and 3 to find out whether a thinner steel design is better or a more complicated aluminium design.

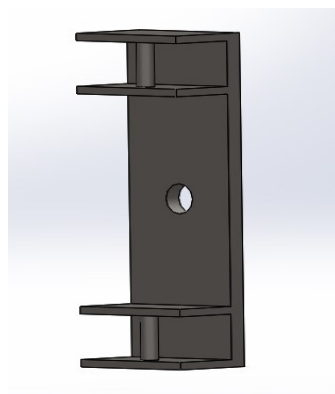


Figure2. First design solution for upright

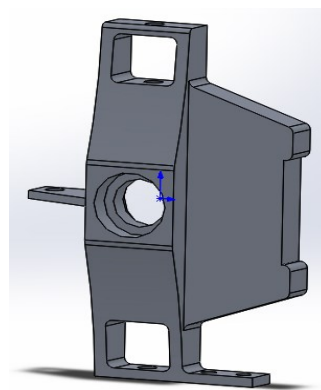


Figure3. Second design solution for upright

Comparison have been made in Table 1 based on the criteria needed for the upright where the second upright design is selected and it weights about 1006.37g. Upright is then simulated in the simulation stage for testing purposes and to look for any further improvement. Upright was found to be too strong whereas weigh reduction took place in the break pad and upright area (Figure 4). Finally the last stage of simulation is conducted to ensure the performance of the upright.

Table 1. Upright decision matrix

Attribute	weighing factor	steel design	Aluminium design	remarks
Mass	3	7	9	1st design:1763g 2nd design:1006g
Cost	0.5	9	6	aluminium is more expensive than steel
Reliability	2	7	8	Based on the simulations the second design is more reliable
Serviceability	0.5	9	7	steel can be easily welded while aluminium is not
Performance	2	7	8	the aluminium design is only one piece it has a better performance
Manufacturability	1.5	8	9	CNC manufacturing is more accurate than welding
Aesthetics	0.5	8	8	
Total	10	5.9	8.3	

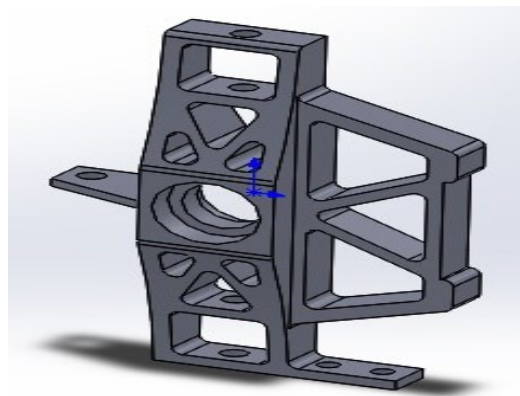


Figure4.Final upright design

2.3 Aerodynamic Body

In this stage the goal is to have the least amount of drag force and lightest body possible to directly increase the efficiency of the vehicle .The lowest drag coefficient and the smallest frontal area are desired in order to have a better aerodynamic performance since the drag force is directly proportional to the frontal area (Eq.1).An aerofoil shape has the best aerodynamic performance compared to

other shapes where in this case a NACA profile is what that is used as the basis of the design [7]. NACA 2420 was selected as the backbone of the design and generated from airfoil generator website since it is the smallest profile that can be fitted in to the chassis design and a canopy is added to cover the roll bar and act as a door for the vehicle. The body design is shown in Figure 5 where it shows the final assembly of the design to the other components.

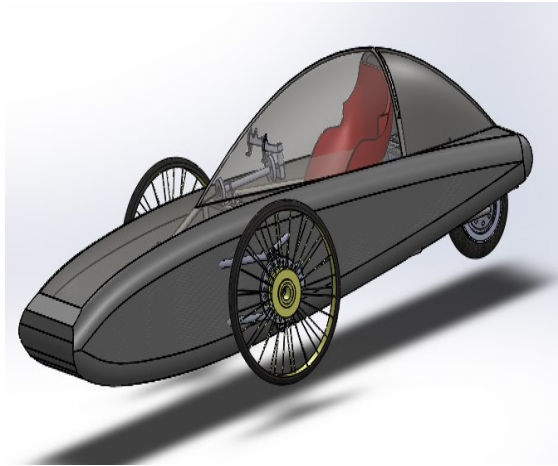


Figure 5.Final body design assembled to the chassis

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

where:

F_d = drag force

C_d = drag coefficient

Material selection is then carried out where Cambridge material selector application is used to compare the selected materials. Carbon fibre, fibre glass and aluminium were candidate as the materials of the body construction but carbon fibre was eliminated due to its high cost. Fibreglass and aluminium are compared (Figure 6) where fibreglass is selected because of its low density. There are a few processes required to manufacture the fibreglass body where in this case fibre glass cloth and matt are combined to achieve a higher strength and a smoother surface. Furthermore the ratio of the resin and hardener is also a critical factor for the hardening time of the body. Table2 is constructed showing all the factors associated in constructing fibre glass to find the best combination of factors. Layers of fibre glass matt and fibreglass cloth, resin to hardener ratio, the thickness produced, rated strength and the hardening time of the model is included in this table (The number in the resin and hardener section only shows the ratio between resin and the hardener).

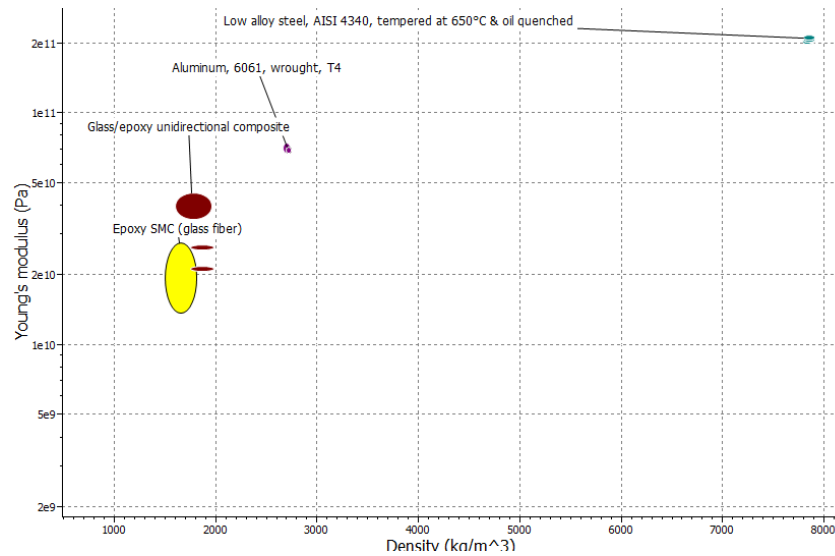


Figure 6. Material selection chart (young's modules VS density)

Table2. Fibre glass and resin-hardener ratio

Layer of fibre glass matt	Layer of fibre glass cloth	resin	hardener	Produced thickness (mm)	Strength Rated from 0 to 5	Hardening time (h)
1	1	2	1	3	2.5	11
2	1	2	1	4.3	3.5	11.3
3	1	2	1	5.8	4.5	12.43
2	1	3	1	4.5	4	18

3.0 SIMULATION

3.1 Upright simulation

In terms of weight distribution which is the portioning of weight within a vehicle, it can be calculated that the both front wheels together have 59% of weight distribution whereas the rear wheel yields a 41% [8]. The total weight of the electric car with load is about 140kg where by considering the safety factor of 4 it can be calculated as 560k. The possible cases here includes two major parts, which is the torque acting on the upright while the car is cornering at a required turning radius of 3.5m and when it encounter uneven surface when the cornering is done. When cornering, the electric car will have centrifugal force of 3275N acting away from the centre of the turning radius where this force must be opposed by the centripetal force

that is created from the lateral friction of the wheel tire sideways (Eq.2). This force will create a torque of 884 N.m on the upright. Moreover When the car go through a bump, the worst case scenario suggests that 2g of force will be acting to the car due to its weight and the force acting toward the wheel is the normal for which supports the car[9]. This results into 3241.2N of force and 228N.m of torque acting on the upright(Eq.3). Static simulations is done on the first and the second optimized model based on the values from above and the results are shown in Figure 8 and 9.

As it is shown below the deformation occurred in the first model is about 0.006 mm which is very low whereas the second model shows a deformation of about 0.1 mm.

$$F_c = m \times \omega^2 \times r \quad (2)$$

Where:

m = distributed mass supported by one front wheel, r = required turning radius

$$F_n = m \times g \times f \quad (3)$$

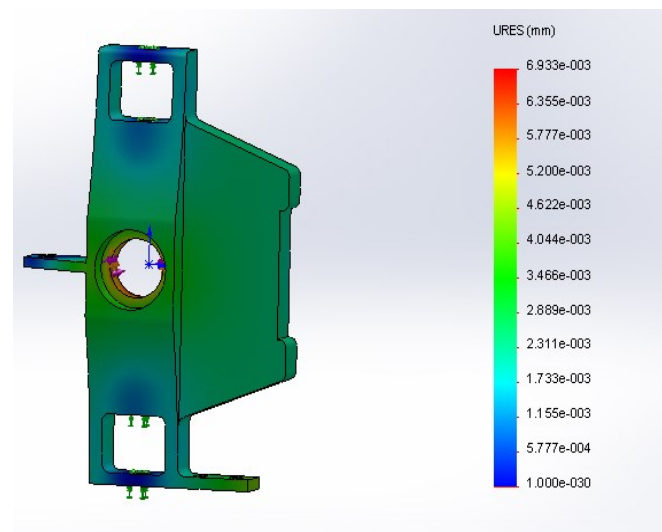


Figure 8. Simulation of the first model

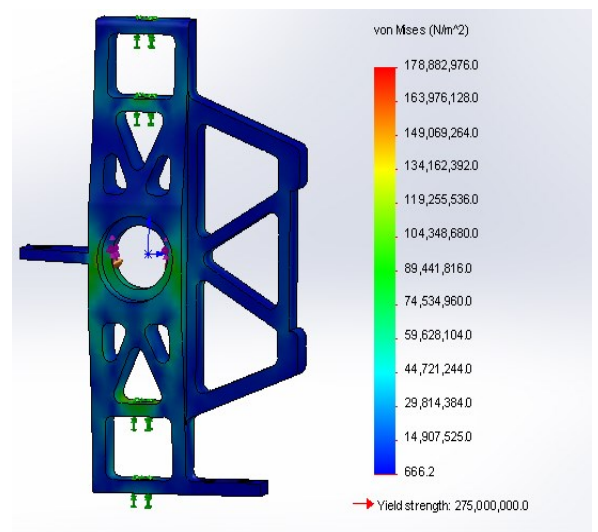


Figure 9. Final model simulation

3.2 Chassis Simulation

Frame torsion analysis is done on the chassis shown in figure 10 to study the torsional rigidity of the chassis Based on the weight distribution results from the upright simulation section. the weight acting on each front wheel considering a safety factor of 4 is 165kg where this value is used in the torsional rigidity testing. The torsional rigidity is calculated using Eq.(4) where the angular displacement is calculated from Eq.(5)[10]. The distance from the point of application and the centre of the car is 0.52m and the linear displacement in the Y direction is defined in Figure 10 where the linear displacement on both sides are taken and an average value is found to achieve a more accurate result.

In addition to that front impact analysis is done where 1800N is acting to the front plane of the chassis shown in Figure 11. This value is the force acting on the chassis when stopping the car with a speed of 30 km/h in 2 seconds considering a safety factor of 2.

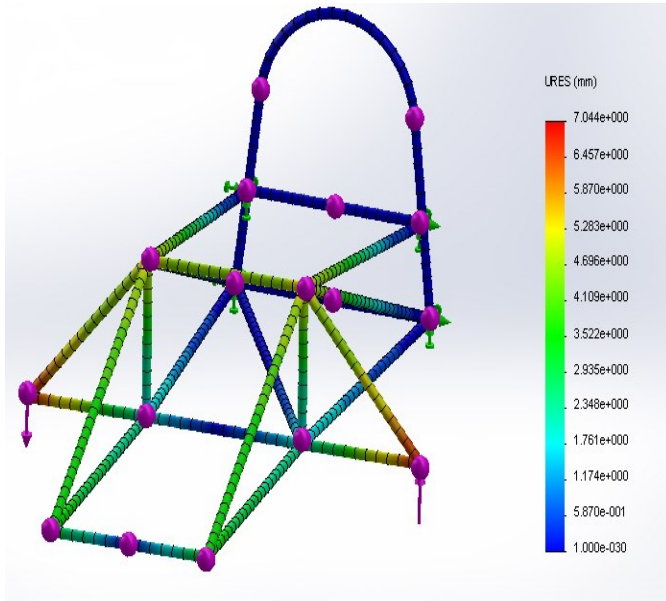


Figure 10. Torsional rigidity testing

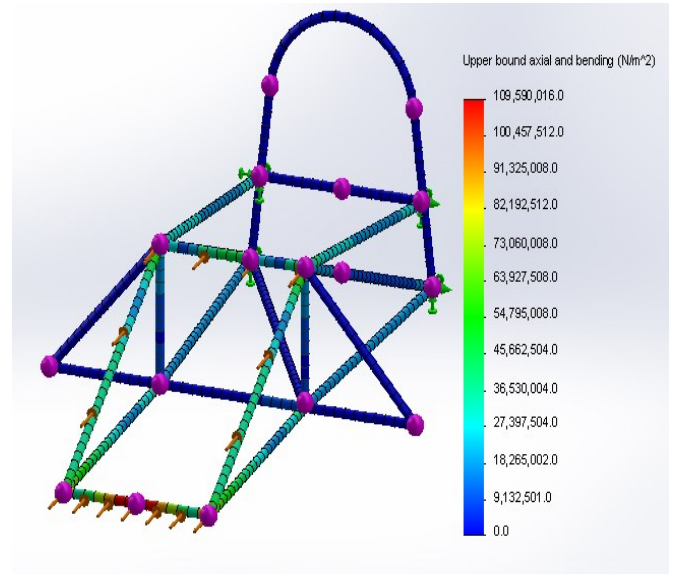


Figure 11. Front impact analysis

$$K = \frac{T}{\vartheta} \quad (4)$$

Where:

K= torsional rigidity (Nm/degree), F=force acting on the arm of the chassis=1650 N

L= distance from the point that the force is applied to the centreline of the car= 0.52m

T= FL = 858Nm

$$\vartheta = \tan^{-1} \frac{(Y_2 + Y_1)}{2L} \quad (5)$$

Where:

ϑ = angular displacement

Y = linear displacement of the right wheel in Y direction

4.0 Result and Discussions

4.1 Chassis

The stress acting on the chassis in the worst situation considering a safety factor of 4 is 179466144 N/m² while the yield strength of steel 1010 is 180000000 N/m². This means that the chassis can withstand the torsion force acting on its arms. Moreover the torsional rigidity of the chassis was found to be 554.33 Nm/ degree which is about 33.5kN/ radians, this value is about 50 % more than the stiffness target

for a vehicle which is 15-17 Nm/radians [11]. The obtained result from the second analysis on the chassis shows that the stress acting on the pipes is 109590016N/m^2 , which is much lower than the yield strength of the material used. The final constructed chassis shown in Figure 12 weighs about 10 kg which is very low in comparison with other prototypes made by steel.



Figure 12. Constructed chassis

4.2 Upright

The upright design shown in Figure 3 was selected based on Table 1 due to its better performance, precision in manufacturing and its lower weight which is about 57% lower than the first suggested design. This design was then simulated and found to be over designed under the defined condition because of its yield strength being much higher than the stress acting on it and its very small deformation.

The optimized design was introduced as it is explained in design section by removing the material from the places that are shown as blue colour in Figure 8. Simulation was also performed on this design shown in figure 9 where it shows a much higher stress than the first example but it is still way lower than the yield strength of aluminium 6061. This final design weighs about 630 g which is 63% lighter than its peer and it is manufactured by aluminium using CNC milling machine shown in Figure 13.



Figure 13. Manufactured upright using CNC milling machine

4.3 Aerodynamic body

The design of the aerodynamic body was based on a NACA profile to set a good backbone for the body design. Material selection was then showed in Figure 6 where fibre glass has a lower density in compare with aluminium which is why fibreglass is chosen. Table 2 is then constructed to show the strength and the thickness of the fibre glass dues to its layers and ratios. Using 1 layer of matt and cloth gives a low thickness fibreglass which is not suitable for this purpose whereas using 3 layers of matt and 1 layer of cloth can result into 5.8 mm of thickness which is too high, this is why 2 layers of matt and 1 layer of cloth was selected since it provides a good strength in compare with the first case and it has a sufficient thickness. 3:1 ratio of resin provides a longer hardening time which allows you to do the necessary changes if any issues occurred. It is concluded that the last case where 2 layers of matt is attached to 1 layer of cloth with resin-hardener ratio of 3:1 is selected. The constructed model of the body is shown in figure 14.



Figure 14: Final constructed model

5.0 Conclusion

To sum up in order to achieve the highest efficiency possible for an electric car, weight reduction is crucial. Material reduction without compromising the safety factors can directly affect the efficiency of the vehicle. In this paper upright and the chassis are designed based on engineering facts and mathematical formulation. Eventually these designs are tested and then altered based on the simulation results, where in this case, both chassis and the upright seem to have sufficient stability under static and torsional forces. 63% of improvement was achieved in the upright designs where the preliminary design was developed into a lighter system. Aerodynamic performance of an electrical car is the second most important characteristic of the vehicle, which is enhanced by innovative body manufacturing method and precise

experimentation in the material ratio used. The resin and hardener ratio was experimented in addition to the number of fiber glass matt used where results shows an about 25% of weight improvement. This paper summarizes all the steps to be considered and taken in order to design and manufacture an electric vehicle.

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