OPTIMZATION OF BIODIESEL PRODUCTION FROM AN EDIBLE OIL AND ITS CHARACTERIZATION BY USING RESPONSE SURFACE METHODOLOGY (RSM)

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A report submitted in fulfillment of the requirement for the degree of Bachelor of Mechanical Engineering with Honours

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2019

APPROVAL

I declare that this report entitled “Optimization of Biodiesel Production from an Edible Oil and its Characterization by Using Response Surface Methodology (RSM)”is the result of my own work except as cited in the reference”.

Signature : ……………………..……………..

Name : …………………………...............

Date : ……………………………………

APPROVAL

I hereby declare that I have read this report and in my opinion this report is sufficient in terms of the scope and quality for the award of Bachelor of Mechanical Engineering with Honours

Signature : ………………………………………………

Supervisor’s Name : ………………………………………………

Date : ………………………………………………

DEDICATION

I would like to dedicate this project to my esteemed parents Mr. Sharif bin Othman and Mrs. Jamaliah Binti Long, my sagacious supervisor Dr Md Isa bin Ali, passionate family, lecturers, assistant engineers and fellow friends who gave me never ending support, love, encouragement, ideas and pray of day and night throughout this Undergraduate Project.

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ABSTRACT

The usage of motorized vehicle as a means of transportation have become so important in any daily activities that having a vehicle is normal and a must to possess. Since using vehicles shorten the length of time for transportation, the demand of vehicles generally never decline instead steadily inclining, thus lead to the rise of diesel consumption. However, throughout the year the petroleum reserve dwindle at an alarming rate in which trigger a new race of endeavor of producing an alternative fuel. Biodiesel was discovered to be one of the potential alternative as it could serve the purpose as fuel without remodeling much of the internal engine and release less pollutants. Most of the time, biodiesel is crafted by means of esterification and transesterification process. As for this study, transesterification is applied by mixing methanol and rice bran oil in the presence of sodium hydroxide to produce biodiesel. The three parameters with five level were chosen are reaction temperature, reaction time and molar ratio. Based on these parameter level, the results (biodiesel yield) were optimized by using Response Surface Methodology. The optimized biodiesel or the highest biodiesel yield that was computed by Minitab 18 can be produced by setting the reaction temperature at 45.5 °C, reaction time of 68.48 minutes and molar ratio of 8.1:1 with constant stirring speed at 400 rpm and 0.6% catalyst concentration. The optimized biodiesel was characterized based on its density which reported to be 0.856 SG or 865 kg/m^3 , viscosity of 7.618 cSt, cloud point of -4.7°C and pour point at -9.3°C. Meanwhile, the biodiesel yield of the optimized biodiesel was obtained at 88.11%.

ABSTRAK

Penggunaan kenderaan bermotor sebagai media pengangkutan telah menjadi suatu kepentingan dalam kehidupan seharian sehingga pemilikan kenderaan menjadi sesuatu perkara yang biasa, malah mempunyai kenderaan menjadi satu keperluan. Hal ini disebabkan oleh keupayaan kenderaan bagi memendekkan jangka masa yang diperlukan bagi tujuan pengangkutan. Seterusnya menaikkan permintaan bagi kenderaan bermotor secara tidak langsung meningkatkan penggunaan minyak bahan bakar diesel. Walau bagaimanapun, rizab petroleum berkurangan pada kadar yang tinggi setahun demi setahun yang mana mencetuskan satu lagi perlumbaan dalam bidang tenaga bagi menggantikan bahan bakar yang sedia ada dengan bahan bakar alternatif. Biodiesel merupakan salah satu alternatif bahan bakar yang berpotensi tinggi kerana ia dapat memenuhi tujuan sebagai bahan bakar tanpa pembentukan semula secara keseluruhan pada enjin dalaman malahan ia melepaskan bahan pencemar pada kadar yang minimum. Pada kebiasaannya, biodiesel dihasilkan menggunakan teknik esterifikasi ataupun transestrifikasi. Bagi kajian ini, transesterifikasi digunakan dengan cara menghasilkan tindak balas antara methanol dan minyak dedak beras bersama dengan natrium hidroksida sebagai pemangkin. Tiga parameter yang mempunyai lima aras dipilih bagi tujuan transesterifikasi iaitu masa tindak balas, suhu tindak balas dan nisbah molar. Berdasarkan tahap parameter yang telah dipilih, hasil dari eksperimentasi (peratusan biodiesel) dioptimumkan dengan menggunakan Kaedah Tindakbalas Permukaan. Biodiesel yang telah dioptimumkan atau hasil peratusan biodiesel yang tertinggi dikomputasikan oleh perisian statistik 'Minitab 18' dengan menetapkan suhu tindak balas pada 45.5°C, masa tindak balas 68.48 minit dan nisbah molar pada 8.1:1 dalam keadaan berputar pada 400 rpm dan kepekatan pemangkin sebanyak 0.6%. Hasil daripada biodiesel yang dioptimumkan, dicirikan berdasarkan ketumpatannya yang dilaporkan 0.856 SG atau 865 kg/m^3, kelikatan 7.618 cSt, takat awan pada -4.7°C dan titik tuang pada -9.3°C. Sementara itu, hasil peratusan biodiesel bagi biodiesel yang optimum oleh perisian 'Minitab 18' memperolehi nilai peratusan pada 88.11%.

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LIST OF ABBREVIATION

OFAT	One-factor-at-a-time
RSM	Response Surface Methodology
ASTM	American Society for Testing Materials
EN	European Standards
MS	Malaysian Standards
NRBO	Neat Rice Bran oil
RBOB	Rice Bran oil Biodiesel
FAME	Fatty Acid Methyl Ester
SVOs	Straight vegetable oils
MPOB	Malaysia Palm Oil Board
SIRIM	Standards Industrial Research Institute
PME	Palm Methyl Ester
CCD	Composite Central Design
MeOH	Methanol
NaOH	Sodium Hydroxide
DOE	Design of Experiment

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CHAPTER 1

INTRODUCTION

1.1 Overview

This chapter will elaborate on what the project is discussing about, henceforth the Project Background. From the Project Background shall the problem statement, objective of the project and the scope which would be the main focus for the project be developed and comes in order respectively.

1.2 Project Background

Biofuels is basically known for its use which serve as the substitute of what now known in the verge of exhaustion, the diesel fuel. This compound is usually the results of specific types of lipids such as vegetable oil and animal fat on which react chemically towards alcohol to produce fatty acid and glycerol, (Kareem et al, 2016). Since the purpose of developing and researching biofuels is to replace diesel fuel, the characteristics or the fluid properties of the compound would be characterize to bear about the same as the fluid properties of diesel fuel. Biofuels production could be done by using the method of Transesterification or Esterification (Noor et al, 2016).

The process of transesterification is a process on which chemical reaction took place between any kind of lipids assisted with fitting catalyst particular short-chain alcohols such as methanol and ethanol (Stasha and Soh, 2017). According to Kareem et al (2016), the molar ratio for transesterification required at least 3 mole of alcohol and a mole of triglyceride (oil) to yield 3 mole of fatty acid methyl esters (biodiesel) and a mole of glycerol. Meanwhile according to Stasha and Soh (2017), the production of glycerol to biodiesel ratio is 1:10 as oppose to of 3:1 glycerol to biodiesel ratio suggested by Kareem et al, 2016.

Moreover, a wide range of value-added products could be obtained through the microbial fermentation of crude glycerol. The production of glycerol for all intents and purposes could not be applied exactly for all cases of biodiesel transesterification or esterification production. It really going down on depending towards the oil (variation of lipids) and the catalysts afflicted by variation of transesterification factors. Thus, according to Stasha and Soh (2016), the conventional ‘one-factor-at-a-time’ (OFAT) approach is less practical because the estimation of the factor effects is inaccurate and point to a vague understanding of the research findings. This issue however, could be avoided by utilizing the optimization of the factors via designing of experiment using Response Surface Methodology (RSM).

RSM is a usually employed with mathematical and statistical techniques for experimental model building. By careful design of experiments, the objective is to optimize certain amount of dependent variables which is influenced by several independent variables. RSM is a tool that could determine the best conditions of the experiment and its required run to produce such results statically. This could be done by assessing the relative significances of numerous independence variables (Stasha and Soh, 2016). Meanwhile according to Ajala et.al, RSM is an effective tool for statistical analysis to find the optimal conditions for different complex process, which able to be applied in the optimization of multiples variable with minimum number of experiments.

Rice wheat oil positions first among the non-regular, cheap, poor quality vegetable oils. In this way, utilization of rice wheat oil as crude material for the creation of biodiesel not only makes the process economical but also generates value added bio-active compounds (Mayank et al, 2016). Rice can be easily collected from the rice husk of the paddy.

About 16 to 20% of crude rice bran oil can be obtained from rice husk. Rice bran oil can be defined as natural oil that is produced extracting from inside of the hull of the paddy It is very difficult to collect the rice bran separately from the hull of the paddy, so most of the cases rice bran oil is extracted from a mixture of rice bran and hull. In the beginning of rice bran oil production it was mostly used as a cooking oil because it has a higher smoke point (about 232 °C or 450 °F) than the other vegetable oils, which prevent the oil from breaking down to form toxic substances (Ahmed et al, 2014).

1.3 Problem Statement

Petroleum is known to be unrenewable resource since it’s a byproduct of fossil fuels and fossil fuels is the deposits of organic matter such as decayed plants and animals that had been exposed to heat and pressure beneath the surface of the Earth for over millions of years ago. To replenish such resources is actually impossible since it takes millions of years to form and the current known reserves are depleting faster than refilling.

Biofuels is basically the alternatives of petroleum due to the fluid properties gain somewhat similar value. According to the data accumulated by Ahmed et al (2014), the fluid properties comparison between Rice Bran Oil Biofuel and fuels correlates somewhat directly, such that the density value obtain for fuel and biofuel are 0.82 and 0.748 (g/cc at 30 degree Celsius) accordingly. The two most commonly use biofuel types are biodiesel and bioethanol which were derived mainly from vegetable oils, seeds and lignocelluloses. Biodiesel can be used to substitute diesel and bioethanol can be used in terms of petrol, (Masjuki and Md Abul, 2013)

In other issue, the biodiesel technology of the present is not sufficient. This is due to the fact that there are array of factor that influence in the quality of producing the biodiesel. In accordance to that, biofuels were used as a blend with fossil-fuels since there are still some distinct value in terms of the fluid properties. It is also described by El-Gald et.al (2014) that the application of biofuels on an industrial scale could not be recommended until it is proved to be economically feasible. Thus come to the conclusion, the purpose of this project is to identify on how to produced biofuels efficiently and yield considerably similar properties to the clarified biofuels standard established by American Society for Testing Materials (ASTM) Organization.

1.4 Objective

The main objectives of this project are:

- i. To produce biodiesel by means of transesterification from rice bran oil.
- ii. To optimize transesterification factors.
- iii. To characterize the biodiesel properties using ASTM D6751 standards.

1.5 Scope of Project

- i. Using the transesterification method to produce biodiesel from rice bran oil.
- ii. Using Response Surface Method to optimize the biodiesel produced emphasizing on the factor of reaction temperature, reaction time and molar ratio.
- iii. Some properties such as density, viscosity, cloud point and pour point were tested and compared to the ASTM D6751 standards.

1.6 The Importance of This Study

As of year 2000, Malaysian government introduced a new fuel policy called the Malaysian Fifth Fuel Policy on which the renewable energy is included as the fifth component in the gas-hydro-coal-fuel oil equation, (Maulud and Hamdani, 2012). Thus, the idea behind this study is not to replace petroleum consumption, but to help create a balanced energy consumption between all of the five components and subsequently reducing the depletion rate of petroleum.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

This chapter will discuss on the topic of biodiesel progression throughout time and its general information, conjointly with transesterification process and Response Surface Methodology (RSM).

2.2 Biodiesel Development

Biodiesel belongs to one of the types of biofuel. In late 1970s, during the period of energy crisis after world war two, the use of vegetable oils was accepted early despite the initial practicality complication. Following that, Belgian Patent 422877 reported a paper explaining the interchanging of glycerol for ethanol by preparing the ethyl esters of palm oil through a transesterification reaction (Gerhard and Luis, 2016). There are a lot of efforts and method in developing and improvising the properties of vegetable oil (biodiesel fuel) to be approximately to the properties of diesel fuels.

Among the methods developed are pyrolysis. It is a process of thermal decomposition of an organic matters in the absence of oxygen and presence of a catalyst. The substances could be vegetable oils, animal fats, natural fatty acids or methyl esters of fatty acids. According to Atabani et al (2012), the product yielded from pyrolysis of vegetable oil could result in high cetane number, low kinematics viscosity, tolerable amounts of sulfur, water contents and admissible copper corrosion values. Despite that, ash contents, carbon residues, and pour points were unsuitable to be called biodiesel.

Another method as described by Atabani et al (2012), diluting vegetable oils with diesel to reduce the viscosity and improve the performance of the engine does not require any chemical process. However substitution of 100% vegetable oil for diesel fuel is not practical. Fully using vegetable oils with or without their blends inside engines have been acknowledge to be problematic both short and long terms.

Some other method use solvents such as methanol, ethanol, hexanol, butanol and 1-butanol to produce methanol. For instances, such method is micro-emulsion which could be illustrated as colloidal equilibrium dispersion of optically isotropic fluid microstructure with dimensions generally into 1–150 nm range formed spontaneously from two normally immiscible liquids and one and more ionic or more ionic amphiphiles. According to Atabani et al (2012), biodiesel obtain through this approach yield the maximum viscosity requirement for diesel fuel. Following the results they obtained, it had been explained that short-term performances of both ionic and non-ionic micro-emulsions of aqueous ethanol in soybean oil are nearly as well as that of diesel fuel.

As stated by Atabani et al (2012), transesterification is regarded as the best method among other approaches due to its low cost and simplicity. Transesterification consists of a number of consecutive, reversible reactions. Some fuel properties can be improved through transesterification process such as kinematic viscosity, density, flash point, cetane number and several others shown in the Table 2.1.

Table 2.1: General parameters of the quality of biodiesel

(Source: Atabani et al, 2012)

Parameters	France (general official)	Germany (DIN)	Italy (Uni)	USA (ASTM)
Density at 15°C g/cm^3	0.87-0.89	0.875-0.89	0.86-0.90	-
Viscosity at 40 mm^2/s	3.5-5.0	3.5-5.0	3.5-5.0	1.9-6.0
Flash Point (°C)	100	110	100	130
Pour Point (°C)	-10	-	0/-5	-
Cetane Number	>49	>49	-	>47
Iodine Number	≤115	≤115	-	-
Ester Content (mass %)	≥96.5	-	≥98	-
Diglyceride (mass %)	≤0.2	≤0.4	≤0.2	-
Triglyceride (mass %)	≤0.2	≤0.4	≤0.1	-
Free glyceride (mass %)	≤0.02	≤0.02	≤0.05	≤0.02
Total glycerol (mass %)	≤0.25	≤0.25	-	≤0.24

2.3 Natural Resources of Biodiesel

There are a total of more than 350 crops containing oil identified as possible feedstock for purpose of biodiesel production. Biodiesels can be produced from straight vegetable oils (SVOs), oils extracted from various plant species and animal fats. Throughout all the option of resources presented, the availability and cost economy are the major factors affecting the large scale production of biodiesel (Salvi and Panwar, 2012). Table 2.2 shows some of the primary biodiesel feedstock use around the global.

Table 2.2: Main feedstock of biodiesel

(Source: Atabani et al, 2012)

Edible Oil	Non-edible Oils	Animal Fats	Other Sources
Soybeans	Jatropha Curcas	Pork lard	Bacteria
Rapeseed	Mahua	Beef tallow	Algae
Safflower	Pongamia	Poultry fat	Microalgae
Rice Bran Oil	Camelia	Fish oil	Tarpenes
Barley	Karanja	Chicken fat	Poplar
Sesame	Cumaru		Switchgrass
Groundnut	Cyanara		Miscanthus
Sorghum	Abutilon		Latexes
Wheat	Neem		Fungi
Corn	Jojoba		

2.3.1 Non-edible Oil

Non-edible oils are the variants of lipids that could not be consumed by human being due to certain factor that could affect direct or indirectly to human health.

In the past decade, more than 95% of the biodiesel is synthesized from edible oil, there are many claims that myriad of complication may arise. By converting edible oils into biodiesel, food provisions are genuinely being converted into automotive fuels. It is believed that immensely colossal-scale production of biodiesel from edible oils may bring global imbalance to the food supply and demand market (Mushtaq et al, 2011).

To overcome this problem, a lot of new ideas and researches have been made to in order to exploit alternative or eco-friendly feedstock such as non-edible oils to produce biodiesel. The non-edible vegetable oils such as *Madhuca Indica*, *Jatropha Curcas* and

Pongamia Pinnata are discovered to be suitable for biodiesel production under the specific constraints of conditions (Mushtaq et al, 2011).

Following that, non-edible oil in some cases could be found in abundance in certain subcontinent. To name exactly, *Jatrophacurcas*, *Ricinuscommunis* (Castor oil), *Madhucaindica* Mahua, *Pongamia pinnata*-Karanja/Pongamia oil, Oleander (*Thevetiaperuviana*), Kusum (*Schleicheraoleosa*) and Bitter oil, *Azadirachtaindica*-Neem tree oil, Rapeseed oil (*Brassica napus*), Rubber seed oil (*Heveabrasiliensis*) could be found in the Indian subcontinent and adequate provisions are present for the extraction of the oils from these plats sources and conversion of them into biodiesel (Tanmay et al, 2018)

Jatropha Curcas L. is classified to *euphorbiaceae* family. It is a drought-resistant plant capable of surviving in abandoned and fallowed agricultural land. The plant is native to Mexico, Central America, Brazil, Argentina and Paraguay. *Jatropha curcas* is could adapt very well in semi-arid conditions, low fertility and capable to grow on little agriculture value soil. The result of two-step acid-alkaline catalyst transesterification from feedstock described earlier would an optimum yield of 98.23% fatty acid methyl esters (Silitonga et al, 2014). Figure 2.1 shows a sample of *Jatropha Curcas* L. plant.

Figure 2.1: *Jatropha Curcas* L (Jarak Pagar plant)

(Source: Ahmad et al, 2015.)

Calophyllum inophyllum L. oil is a type of non-edible oil and its low cost to produce makes it a significant feedstock for biodiesel production. *Calophyllum inophyllum* belongs to the *clusiaceae* family, generally known as the mangosteen family. A tree could be harvest up to 100–200 fruits per kg at one time. The seed of *calophyllum* inophyllum tree has been recorded to be 2000 kg per ha. The oil is tinted green, nutty smelling and the seed has very high oil content around 65-75%. The fatty acid methyl ester of this oil yield through two-step acid-alkaline catalyst transesterification is 97.72% (Silitonga et al, 2014). Figure 2.2 shows a sample of *Calophyllum inophyllum* L. plant.

Figure 2.2: *Calophyllum inophyllum* L. (Penaga Laut plant)

(Source: Ashok et al, 2017)

Ceiba pentandra L. (malvaceae) is an oleaginous species originate from Southeast Asia, India, Sri Lanka and tropical America. Ceiba pentandra L. oil is viscous, dark brown stable and non-dry oil. The seeds are brownish black in color and contain about 25-28% of oil in each fruit. The average oil yield could reach around 1280 kg per hectare. The result of transesterification of the oil extracted from this plant would yield fatty acid methyl ester of 97.72% with the assist of acid-alkaline catalyst (Silitonga et al, 2014). Figure 2.3 shows a sample of *Ceiba pentandra* L. plant.

Figure 2.3: *Ceiba pentandra* L. (Kapok plant)

(Source: Christopher et al, 2007)

Castor oil is a non-edible oil that has high oil content around 35 – 55% however this particular vegetable oil is recorded to have among the highest viscosity and molecular weight. Castor oil could yield considerable amount of biodiesel through production of biodiesel (batch reactor) which is 92% of the oil converted. Despite that, up until now no study had been conducted about the transesterification of castor oil in millichannel reactor to observe the efficiency of the reactor and compared with batch reactor (Muhammad et al, 2016). Figure 2.4 shows a sample of castor oil product.

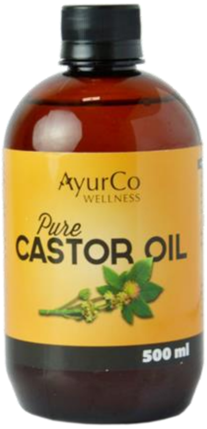


Figure 2.4: Castor oil

(Source: https://www.ayurco.com/products/pure-castor-oil)

Almond (*Prunus dulcis*) belongs to the family of *Rosaceae*, an endemic plant to the Mediterranean climate region of the Middle East. Throughout time, it spread into other regions by mean of humans. So far, it has been cultivated in Europe, Asia and Northern Africa, whereas lately also in California. Italy, Spain, Morocco, France, Greece and Iran are among the countries with the most noticeable almond harvest. The almond tree is able grows to a height in between 3 and 8 m (Mehdi and Hamid, 2011). Figure 2.5 shows a sample of *Prunus dulcis* plant.

Figure 2.5: *Prunus dulcis* (Almond tree)

(Source: https://www.mailordertrees.co.uk/products/prunus-dulcis-flowering-almond-tree)

The cottonseed oil as the name implied is able to be obtained from the cotton plant. The physic-chemical properties of cottonseed oil are somewhat closely identical to main plant oil. The result of transesterification of cottonseed oil with potassium hydroxide as catalyst yield cottonseed oil fatty acid methyl esters (FAME) of 71.9% (Fatah and Yoshimitsu, 2016). Figure 2.6 shows a sample of Cottonseed Plant.

Figure 2.6: Cottonseed plant

(Source: http://www.pinsdaddy.com/cotton-plant-care_7B0fSgmBG9wmSnLyZxAZGya*oDfYChHaKr0XT4ZGDNw/)

2.3.2 Edible Oil

Edible oil is the variants of lipids that is practically safe for human consumption. Despite the fact that researching production of biodiesel from edible oils means dwindling food resources, research of it is still being conducted as demand of energy sources ever increasing and petroleum reserves are depleting faster than refilling. Oil produces from Beniseed (*Sesamum indicum l.*), Cottonseed Plant, *Moringa Oleifera* (Drumstick Tree), Coconut Oil (*Cocos nucifera Linn*) and Sunflower oil (*Helianthus annus L.*) were among the edible oils that were found to be suitable for biodiesel production under experimental condition. The list of edible oil possible to be converted to biodiesel fuel does not end here on which it includes *Oryza sativa* (Rice Bran Oil).

Beniseed (Sesamum indicum L) is an herbaceous plant that could be found abundant in Nigeria, India, China, Sudan, Burma, Bangladesh, Indonesia, Egypt and Tunisia. It belongs to one of the *Pedaliaceae* family. Sesame seed is known to be one of the highest oil contents of any edible oil seed and is considered to be the oldest oilseed crop known to man highly resistant to drought and has the ability of growing where most crops fail (Dawodu et al, 2014). Figure 2.7 shows a sample of *Sesamum Indicum L.* plant.

Figure 2.7: *Sesamum Indicum L.* (Beniseed)

(Source: Aguoru et al, 2014)

Watermelon (*Citrullus vulgaris*) is commonly known for its drought tolerant capability. It belongs to one of the *cucurbitaceae* family of flowering plants. The fruit is suitable to be feedstock for biodiesel production is due to the fact that the seeds of the fruit are able to be extracted with high amounts of unsaturated fatty acids and oleic acids. The result of transesterification of watermelon seed oil is discovered to have maximum biodiesel yield around 70% that could be achieve with the assist of lowest concentration 0.13g anhydrous sodium hydroxide (Efavi et al, 2018). Figure 2.8 shows a sample of *Prunus dulcis* plant.

Figure 2.8: *Citrullus vulgaris* (Watermelon plant)

(Source: https://i.pinimg.com/originals)

Moringa oleifera is evergreen, fast growing, deciduous and widely cultivated species. It has some common English names such as moringa, drumstick tree, horseradish tree, benzoil tree etc. It grows in tropical and subtropical areas. It requires rainfall about 250-2000 mm depending on soil condition. It grows best in dry sandy soil and tolerates poor soil with pH range 5 to 9. It is distributed from Africa, Asia, Latin America and Oceana countries including Australia. This species is widely distributed in Queensland, Northern Territory and Western Australia. Moringa oil has many medicinal usages and also has significant nutritional value. Literature reported that moringa oil has good potential for biodiesel production based on a recent survey conducted on 75 indigenous plant derived non-traditional oils. The result of transesterification yield biodiesel with properties of 17°C for cloud and pour point, while having high content of behenic acid of 7.2% and density of 875 kg/m^3 at 15°C (Azad et al, 2015). Figure 2.9 shows a sample of *Moringa Oleifera.*

Figure 2.9: *Moringa Oleifera* (Drumstick tree)

(Source: Eman et al, 2009)

Coconut (*Cocos nucifera Linn*) or coconut palm is one of family member of the *Arecaceae*. Coconut is native to the tropical eastern regions. The plant can be found throughout the Asian continent, in Central and South America, and in some parts of Africa. Large palms have a single trunk that is able to grow up to 20–30 m tall, with pinnate leaves of 4–6 m long, and pinnae of 60–90 cm long palm. The cultivation of coconut requires sandy, saline soils with abundant of sunlight and regular rainfall throughout the year. Through dry processing, the coconut oil could be obtained and be converted to biodiesel (Habibullah et al, 2014). Figure 2.10 shows a sample of *Cocos nucifera Linn.*

Figure 2.10: *Cocos nucifera Linn* (Coconut palm)

(Source:

http://jogindernursery.com/index.php?route=product/product&product_id=463&landscape=1)

Sunflower (*Helianthus annuus L*.) is a plant that belongs to the *Asteraceae* family. The oil contents of the sunflower could vary from 38 to 50%. Sunflower is also one of the leading oilseed crops cultivated for the purpose of producing oil in the world. It is usually cultivated on non-irrigated clay loam soils in a rotation with winter cereals. About 80% of Europe's total biofuel is comprised of biodiesel produced from rapeseed and sunflower seeds (Mushatq et al, 2010). Figure 2.11 shows a sample of *Helianthus annuus L.* (Sunflower Plant).

Figure 2.11: *Helianthus annuus L.* (Sunflower plant)

(Source: https://plus.maths.org/content/sunflowers)

2.4 Rice Bran Oil

Rice (*Oryza Sativa Linn*) bran is one of the derivative of rice kernel that can be harvest from the outer layer of the brown (husked) rice kernel amid the milling process of producing polished rice. It comprises Hull, White Rice, Rice Bran and Germ as shown in Figure 2.12.

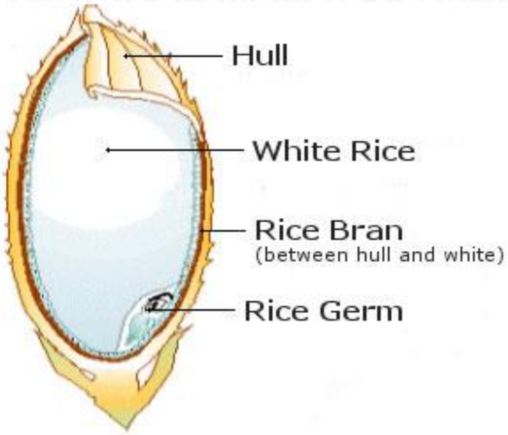


Figure 2.12: Cross section of rice grain.

(Source: http://www.oilmillmachinery.net/images/rice-bran-structure.jpg)

Rice bran oil abnormal, economical and substandard resource are also the cause of high added-value byproducts. The outcome of oil (rice bran oil) could be used as a feedstock for biodiesel production. The oil could also be extracted from the germ and inner husk of rice. The calorific value obtained from rice bran biodiesel is somewhat closer to diesel, (Jayaprabakar et al, 2017). Some properties of rice bran oil and rice bran oil biodiesel are shown in Table 2.3.

Table 2.3: Rice Bran oil and its biodiesel's fluid properties

(Source: Jayaprabakar et al, 2017)

Properties	Results	
	Rice Bran Oil	Rice Bran Oil Biodiesel
Free Fatty Acid	0.592%	
Kinematic Viscosity at 40°C	37.548 cSt	3.906 cSt
Density	0.910 gram/cc	0.873 gram/cc
Moisture Content	0.002%	0.001%
Flash Point (PMCC Method)	278°C	166°C
Fire Point (PMCC Method)	307°C	198°C
Copper Strip Corrosion at 60°C	1a (slight tarnish)	1a (slight tarnish)
Cloud Point °C	16°C	10°C
Pour Point °C	1°C	-3°C
Calorific Value	3808.3556 cal/gram	8214.692 cal/gram

2.5 Transesterification

The transesterification process is a reaction between oil and alcohol in the presence of appropriate catalysts which are acid or alkaline catalysts. Methanol is the most typical variant of alcohol due to its fluid properties and low cost. Alkaline catalysts, such as potassium hydroxide or sodium hydroxide are more practical in the transesterification process (Daming et al, 2012). The process of transesterification of converting triglyceride is explained in the Figure 2.13.

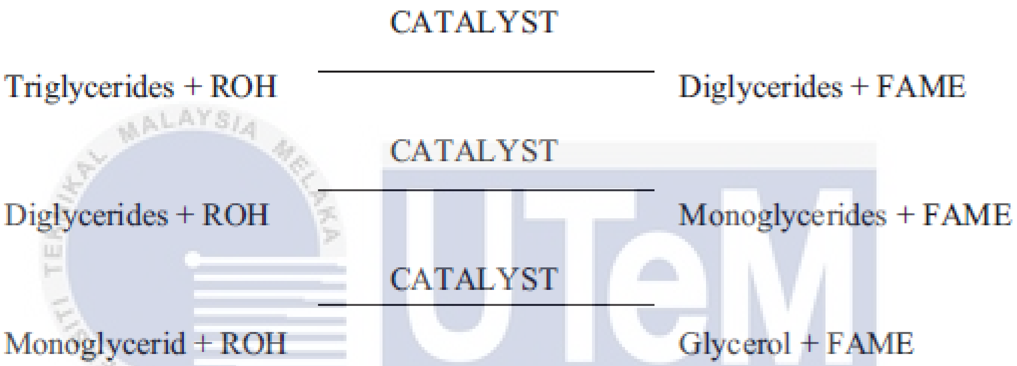


Figure 2.13: Equation of transesterification reaction in the present of catalyst.

(Source: Atabani et al, 2012)

Glycerol is an important by-product and can be burned for heat or be used as feedstock in the cosmetic industry. In this reaction, methanol and ethanol are the two main light alcohols used for transesterification process due to their relatively low cost. However, propanol, isopropanol, tert-butanol, branched alcohols and octanol and butanol can also be employed but the cost is much higher. As for the catalyst, it is vital in the process as alcohol is barely soluble in oil or fat. The catalyst enhances the solubility of alcohol and thus increases the reaction rate. (Atabani et al, 2012).

2.6 Factors affecting the transesterification process

The process of transesterification of biodiesel could be affected by several manipulated variables. Each respective variables could affect different aspects of the final product (biodiesel). Some of the factors that affect the process and its yield are alcohol to oil molar ratio, reaction temperature, catalyst concentration, reaction time, reaction temperature and stirring speed,

2.6.1 Alcohol to oil molar ratio

According to Mehdi and Hamid (2011), molar ratio of methanol to oil is one of the most important variables that affect the transesterification reaction. Their experiments were carried out using methanol to oil molar ratio in the range of 3:1–11:1, while other variables including KOH concentration and reaction temperature were set at 0.9% w/w and 50 °C, respectively. It was observed that with increasing the methanol to oil molar ratio from 3:1 to 7:1, the product yield increased from 91.8 to 97.2% while the biodiesel purity and yield increased from 74.6 to 92.7 and from 68.4 to 90.9, respectively. Thus the effect of methanol to oil molar ratio on the biodiesel purity and yield is more than its effect on the product yield.

This further coincide with the findings of Mathiyazhagan and Ganapathi, (2011) where they also claim that molar ratio of alcohol plays a vital role in biodiesel yield. They described that transesterification reaction would requires at least 3 mol of alcohol for one mol of triglycerides (oil) to three mol of fatty acid methyl ester (biodiesel) and one mol of glycerol. Excess amount of alcohol increases conversion of fats into esters within a short time. So the yield of biodiesel increases with the increase in the molar ratio of alcohol to oil. However further increase of alcohol content does not increase the yield of biodiesel but it also increase the cost of alcohol recovery.

2.6.2 Reaction temperature

Another variables that could alter the quality of biodiesel produce is the reaction temperature of the mixture. According to Mathiyazhagan and Ganapathi (2011), reaction temperature is another important factor that will affect the yield of biodiesel. For instance, higher reaction temperature increases the reaction rate and shortened the reaction time due to the reduction in viscosity of oils. Furthermore, research conduct by Leung and Guo (2006) and Eevera et al (2009) cited in Mathiyazhagan and Ganapathi (2011) discover that, increase in reaction temperature beyond the optimal level leads to decrease of biodiesel yield, because higher reaction temperature accelerates the saponification of triglycerides.

Meanwhile based on the results that Mehdi and Hamid (2011) achieved in their experiments, it is known that by using a setup with a reaction temperature ranging from 30 to 70°C with a preset value of 7 mol/mol molar ratio and 0.9% w/w of potassium hydroxide concentration would affect only a little change in the product yield. However when the experiment were conducted in the range of 50 to 70°C, the yield of biodiesel drop instead of increasing which means that 50°C is the optimum reaction temperature in their experiments. On top of that, in the range of 50 to 70°C the biodiesel purity decrease as well though are not significant as biodiesel yield. Past 70°C, the side saponification reaction of the triglycerides and the alkali catalyst is faster than transesterification process. Meaning more soap produce than biodiesel. In their experiment, a condensation system was not used, thus deter the transesterification process as methanol vaporize and reduce the biodiesel yield.

2.6.3 Catalyst concentration

Despite having said that molar ratio and reaction temperature are important other factor could not be neglected as they also have significant impact on the product yield. In the experiment conducted by Mehdi and Hamid (2011) potassium hydroxide (KOH) was used with a concentration of 0.1 to 1.7% w/w at the same time molar ratio and reaction temperature were put at constant of 7 mol/mol and 50°C accordingly. In the range of 0.1 to 0.9% of the concentration, the product yield were found to be constant and the biodiesel purity and yield increase. Meaning more biodiesel produce in the same amount of product yield. At 0.9% of concentration, the biodiesel yield reached the maximum output, meaning increasing the concentration further will decreased the biodiesel yield and its purity. This too is also the case for the product yield. Excess of catalyst increase the amount of soap formed through saponification.

Furthermore according to Mathiyazhagan and Ganapathi (2011), as the concentration of catalyst increase so shall the biodiesel yield increase as well. In conjunction to that, inadequate amount of catalyst would lead to incomplete transesterification process since the not all triglyceride could be converted into fatty acid esters. As mentioned in their article, the concentration of sodium hydroxide reached its peak at 1.5% w/w and further increasing it would decrease the amount of product yield and increase the amount of soap produced.

2.6.4 Reaction time

Reaction time is nonetheless an important factor that affect the rate of fatty acid esters conversion. In the experiment cited in Mathiyazhagan and Ganapathi (2011), the reaction of transesterification concluded or completed within 90 min. boundary. Exceeding this time boundary would not yield more product or biodiesel instead it could lead to decrease in the quantity of mono alkyl esters and probably even soap formation due to reversible reaction. The reaction time could not be limited too small since the dispersion of alcohol and oil needed to be taken into account (Mathiyazhagan and Ganapathi, 2011)

2.6.5 Stirring/agitation speed

Another factor that plays an important role in producing biodiesel is the stirring speed. Despite the fact that this factor enhance the production rate further, there are limits needed to be constraint with in order to achieve optimal condition. As such, at lower rpm the conversion rate of oil to biodiesel is slow while higher rpm creates higher amount of soap formation due to reversible reaction of transesterification. However, the final product of transesterification could be obtained nominally at 400 rpm with having little to none of soap formation (Mathiyazhagan and Ganapathi, 2011).

2.7 Response Surface Methodology (RSM)

Considering that there are numerous factor of transesterification, the conventional ‘one-factor-at-a-time’ (OFAT) approach is less practical because the estimation of the factor effects is imprecise and leads to an incomplete understanding of the research findings. Besides, the OFAT system is time-consuming due to the requisite of performing a number of experimental runs. These limitations can be replaced by optimizing the factors via designing a statistical experiment using RSM (Stasha and Soh, 2017)

Moreover, according to Chinyere et al (2017), the traditional one factor at a time method of analysis is time consuming and does not take into consideration about the interaction effects between the factors hence optimization method with respect to design of experiment via RSM could establish the best condition for biodiesel production.

In the experiment conducted by Giovanilton et al (2011), four factor of transesterification were picked as independent variables while having two of the variable counterpart. The four transesterification factor were temperature, ethanol-to-oil ratio, catalyst concentration and reaction time while production of ethyl ester and glycerol were taken as dependent variables. The experiment involved in employing second-order model and forming Central Composite Design using the variables and its range. As a result of optimization using RSM, the optimum concentration of catalyst, molar ratio, reaction time and reaction temperature were 1.3wt%, 9:1, 80 min and 40°C accordingly. Thus reducing resources since the optimal conditions had been discovered.

Meanwhile experiment conducted by Hoang et al (2018), five independent variables were chosen with only one corresponding dependent variable. These five variables are reaction times, molar ratio, enzyme loadings and reaction temperature with values ranges of 2 to 12h, 9:1 to 15:1, 10% to 20% and 30 to 50°C respectively. These variables and its range of values were employed in quadratic polynomial equation and Box-Behnken Design Matrix (BBDM). The outcome of optimizing using RSM and BBDM yield at reaction time of 12h, molar ratio of 14.64:1, enzyme loading of 17.58 and reaction temperature of 39.5°C that will result in optimum biodiesel yield of 98.28%.

2.8 Biodiesel Standard

Improvement of biodiesel standards began in the 1990’s, to help the ever expanding use of alkyl esters-based biodiesel and its blends as automotive fuels. In 1999, ASTM International (formerly American Society for Testing Materials) approved a temporary standard which was PS121. The first ASTM standard (ASTM D6751) was then been adapted in 2002 (ASTM 2002) (Hannu, 2009). Biodiesel fuel must conform to standard specifications for usage in diesel engine since diesel engine could not accommodate to the fluid properties of biodiesel.

2.8.1 Characteristic of Biodiesel according United States and European Union (US & EU) Biodiesel Standard

The US and EU standards have international impact in which they are the starting point for biodiesel specifications developed in other countries. Approaches to US and EU standards for biodiesel differ. In the USA, standard ASTM D6751 provide specifications for a biodiesel blend stock for fuels. At that point, despite the fact that the specification was written for B100, it is not intended for biodiesel (without blend property) used as automotive fuel. Rather, it is meant for the purpose of blending with diesel to produce biodiesel/diesel fuel blends. In Europe, standard specifications have been developed for unblended FAME biodiesel fuel (B100) and for specific larger amount of biodiesel blends, while low level blends are covered by EN 590. In Europe, EN 14214 biodiesel standard which largely based on biodiesel standard DIN 51606 was fully accommodated in October 2003. Biodiesel fuel fluid properties specifications according to ASTM D6751 and DIN 14214 are compared with Diesel Fuel of ASTM D975 are shown in Table 2.4. (Atabani et al, 2012)

Table 2.4: Diesel and biodiesel fluid properties according to ASTM and EN. (Source: Atabani et al, 2012.)

Fuel Properties	Diesel Fuel ASTM D975	Biodiesel ASTM D6751	Biodiesel EN 14214
Density 15°C (kg/m³)	850	880	860-900
Viscosity 40°C (cSt)	2.6	1.9-6.0	3.5-5.0
Cetane Number	40-55	Min.47	Min. 51
Iodine Number	38.3	-	Max. 120
Calorific Value (MJ/kg)	42-46	-	35
Acid (neutralization) Value (mg KOH/g)	0.062	Max. 0.50	Max. 0.5
Pour Point (°C)	-35	-15 to -16	-
Flash Point (°C)	60-80	Min. 100-170	>120
Cloud Point (°C)	-20	-3 to -12	-
Cold filter plugging point (°C)	-25	19	Max.+5
Copper Strip Corrosion (3h at 50°C)	1	Max. 3	Min. 1
Carbon (wt %)	84-87	77	-
Hydrogen (wt %)	12-16	12	-
Oxygen (wt %)	0-0.31	11	-
Methanol Content % (m/m)	-	-	Max 0.20
Water and Sediment content (vol %)	0.05	Max. 0.05	Max. 500^b

Ash Content % (w/w)	0.01	0.02	0.02
Sulfur % (m/m)	0.05	Max 0.05	10^b
Sulfated Ash % (m/m)	-	Max. 0.02	Max. 0.02
Phosphorus Content	-	Max. 0.001	10^b
Free Glycerin % (m/m)	-	Max. 0.02	Max. 0.02
Total Glycerin % (m/m)	-	Max. 0.24	0.25
Monoglyceride % (m/m)	-	0.52	0.8
Diglyceride % (m/m)	-	-	0.2
Triglyceride % (m/m)	-	-	0.2
CCR 100% (mass %)	0.17 $(0.1)^b$	Max. 0.05	Max. 0.03
Distillation Temperature (%)	-	Max. 360°C	-
Oxidation temperature (%)	-	3min	6min
Lubricity (HFFR; µm)	685	314	-

2.8.2 Characteristics of Biodiesel according to Malaysia Biodiesel Standard

According to Rahyla et al 2017**,** biodiesel manufactured in Malaysia is actually done under the Promotion of Investment Act 1986. Malaysia has extensive biofuel program since 1982. Since 1982, the National Biofuel Policy was devised through intensive discussion with all stakeholders based on the research discoveries made by Malaysia Palm Oil Board (MPOB). Following that, the Malaysian government invested in biodiesel technology research and development conducted by the Standards and Industrial Research Institute (SIRIM), the MPOB and Malaysian provincial universities. As part of the goals of the National Biofuel Policy, quality standards for Palm Methyl Ester (PME) biofuels were established by SIRIM Bhd. The quality standard for 100% biodiesel (B100) in Malaysia MS 2008:2008 was issued in 2008, on which most of the part refer to European standard EN 14214, with some slight alterations due to climate condition. Table 2.5 shows the fluid properties of biodiesel accede by MS 2008:2008.

Table 2.5: Biodiesel fluid properties according to Malaysian Standard (MS).

(Source: SIRIM, 2014)

Fuel Properties	MS 2008:2008
Ester Content %	96.5 (min)
Density 15°C (kg/m³)	860 to 900
Viscosity 40°C (cSt)	3.5 to 5.0
Cetane Number	51 (min)
Iodine Number	110 (max)
Acid (neutralization) Value (mg KOH/g)	0.5
Pour Point (°C)	-18 to 0
Flash Point (°C)	120 (min)
Cloud Point (°C)	-
Cold filter plugging point (°C)	-18 to 3
Copper Strip Corrosion (3h at 50°C)	Class
Carbon (wt %)	0.3 (max)
Water content (mg/kg)	500
Ash Content % (w/w)	0.02
Sulfur Content (mg/kg)	10
Sulfated Ash % (m/m)	0.02

Phosphorus Content	4.0
Free Glycerin % (m/m)	0.02
Total Glycerin % (m/m)	0.25
Monoglycerides % (m/m)	0.7
Diglyceride % (m/m)	0.2
Triglyceride % (m/m)	0.2

2.8 Conclusion

To summarize, the nature and origin of biodiesel are now known. The feedstock for the production of biodiesel had been researched into the extension of edible and non-edible oils. Rice bran oil fluid properties and its composition were found from previous research and tabulated in table for future references or for comparison to product. Meanwhile, the range of values for each of transesterification factor have been decided based on the justification from previous researchers on their published papers. Composite Central Design (CCD) and Response Surface Methodology (RSM) shall be employed based on results obtained in past research papers.

CHAPTER 3

METHODOLOGY

3.1 Introduction

Basically this chapter shall discuss about the elaboration of the project flowchart on which are the making samples preparation of Rice Bran Oil, extraction of fluid properties information of Neat Rice bran Oil, the preparation of catalyst, transesterification process along with washing process, characterization process for the product (biodiesel) and comparison between neat rice bran oil (NROB) and rice bran oil biodiesel (RBOB). Figure 3.1 show the flow chart of biodiesel production from Rice Bran Oil. Meanwhile Table 3.1 shows the fatty acid composition in rice bran oil that will be related to Equation 3.1, 3.2 and 3.3 in order to find mass of methanol and mass of catalyst.

In the transesterification process subtopic, it will elaborate on the method and precaution taken during the experimentation followed by biodiesel washing subtopic which covered the ground of how to process crude fatty acid methyl esters (which have cloudy-orange color) to refined fatty acid methyl esters (which have sparkling clear-orange color). After the washing process, the fatty acid methyl esters will be tested in biodiesel analyzer to obtain the value of biodiesel yield.

Design of Experiment (DOE) shows on how to manipulate the data using full factorial design and usage of Minitab software in order to obtain optimal parameter values to create optimized biodiesel. The optimized biodiesel produced went through characterization process which comprised of density, kinematic viscosity, cloud point and pour point test.

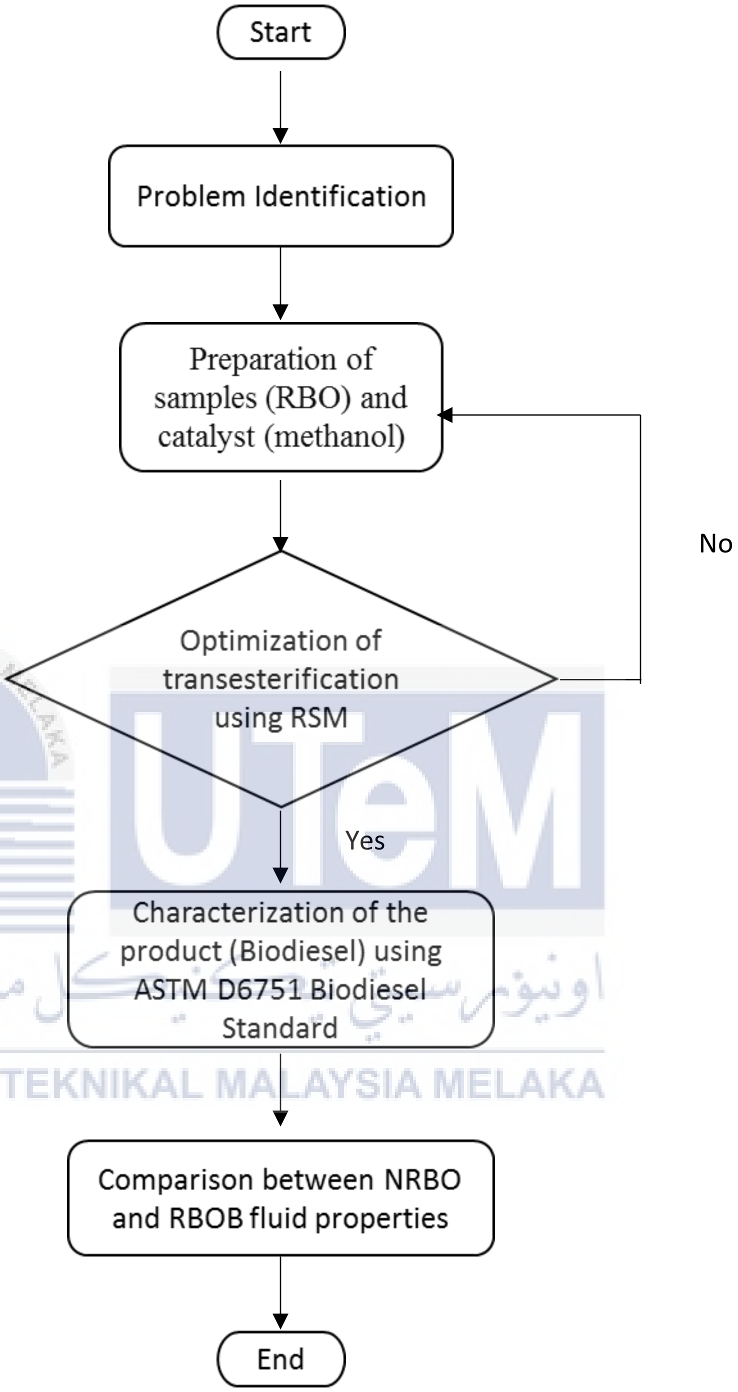


Figure 3.1: Project flow chart

3.2 Transesterification

3.2.1 Samples and Apparatus Preparation

Neat Rice Bran Oil (NRBO) obtained by buying from Mydin Supermarket, a local commodity located in Ayer Keroh, Melaka, Malaysia. Methanol (MeOH) and sodium hydroxide (NaOH) are supplied by University of Technical Malaysia Melaka (UTeM) as shown in Figure 3.2 and Figure 3.3. Catalyst is essential as alcohol (methanol) is barely soluble in vegetable oil (rice bran oil). In this case, alkaline catalyst (sodium hydroxide) is chosen because it perform well for transesterification process and cost effective when put in comparison to potassium hydroxide. For this particular project, various level of molar ratio, reaction time and temperature were used for each repeated experiment. The experiment required some apparatus which are thermometer, two digital stirring hot plate, glass rod, separatory funnel, two clamp stand, spatula, dropper, stopwatch and varying sizes of beaker.

Figure 3.2: Methanol

The catalyst that are supplied by UTeM are sodium hydroxide in pellet form. As for the methanol, a liter of methanol is required throughout the biodiesel production.

Figure 3.3: Sodium Hydroxide in pellet form.

The transesterification reaction were carried out by mixing methanol and sodium hydroxide (NaOH) that act as alkaline catalyst with NRBO. In order to avoid excess usage of catalyst, the amount of fatty acid contains in NRBO ought to be considered. This is due to the fact that 3 mol of alcohol are needed in order to properly react with one mol of triglyceride. The CH_3 broken down from methanol using sodium hydroxide will react with free fatty acid in the triglycerides to eventually from fatty acid methyl esters or in other word biodiesel. Table 3.1 elaborated the content of fatty acid in NRBO.

Table 3.1: Fatty Acid composition in Rice Bran oil

(Source: Yi-Hsu and Shaik, 2005)

Fatty Acid	Percentage in Oil (%)	Molar Mass (g/mol)	Moles
C14:0 Myristic Acid	0.21	228.38	0.00092
C16:0 Palmitic Acid	14.7	256.43	0.06
C16:1 Palmitoleic Acid	0.26	254.41	0.26
C18:0 Stearic Acid	1.86	284.49	0.007
C18:1 Oleic Acid	42.2	282.47	0.15
C18:2 Linoleic Acid	37.8	280.45	0.13
C18:3 α-Linoleic Acid	2.39	278.44	0.009
C20:0 Arachidic Acid	0.51	312.54	0.002
C20:1 Erucic acid	0.36	310.52	0.0012
C22:0 Behenic Acid	0.2	340.59	0.0006
C22:2 Docosadienoic Acid	0.22	336.56	0.00065
C24:0 Lignoceric Acid	0.3	368.65	0.0008

From the total amount of mole for fatty acid, equation 3.1 was used to calculate the total weight percentage of methanol meanwhile equation 3.2 and 3.3 were used to calculate the total mass of methanol and catalyst needed for the transesterification process. The concentration of catalyst have been selected based on several past research papers and on observation of a couple of trial and error test which is 0.6 wt. %. Table 3.2 shows the percentage of methanol's concentration according to corresponding molar ratio of alcohol to oil being used.

$$\text{Mass of Methanol} = \text{Total mole of Fatty Acid} \times \text{Molar Mass of Methanol} \qquad (3.1)$$

$$\text{Mass of Methanol} = 0.37 \times 32.04 \text{ g/mol}$$

$$= 11.76 \text{ g or } 11.76 \text{ wt. \%}$$

Table 3.2: Concentration of methanol corresponding to molar ratio used.

Alcohol to Oil (Molar Ratio)	Concentration of methanol (wt. %)
3:1	11.76
6:1	23.52
7:1	27.44
9:1	35.28
12:1	47.04

$$\text{Mass of methanol} = \frac{Concentration\ of\ methanol}{100} \times \text{Mass of oil used} \tag{3.2}$$

$$\text{Mass of Catalyst} = \frac{Concentration\ of\ catalyst}{100} \times \text{Mass of oil used} \tag{3.3}$$

3.2.2 Transesterification Process

The combination of these variables (reaction temperature, reaction time and molar ratio of alcohol to oil) applied central composite design for biodiesel production optimization by transesterification of rice bran oil with methanol. For this purpose, Response Surface Methodology (RSM) and Central Composite Design shall be employed to obtain optimal response. Once the optimum condition is obtained, the transesterification process is conducted according to the optimum condition to obtain product and biodiesel yield.

The full setup for the transesterification process is shown in Appendix A. At first, an approximate of 100 g or 100 ml of rice bran oil was poured into a beaker. The exact amount was needed to be taken from digital weighing scale with two decimal places to ensure the precision of the product. In order to ensure that the measurement have its precision valid, the stability indicator or in this case the bubble indicator as shown in Figure 3.4 needed to be adjusted to the middle. The weight of the oil needed to be measured in order to calculate the accurate weight of alcohol and catalyst based on equation 3.2 and 3.3.

Figure 3.4: Adjustment of Digital Weight Scale Balance indicator.

After measuring all three material aforementioned, the catalyst (sodium hydroxide) were mixed with alcohol (methanol) by crushing the pellets of sodium hydroxide and stirred it using glass rod and stirring hot plate respectively. Then the oil is heated up to the desired reaction temperature. The oil is left heated to ensure that the thermocouple is working properly and to determine whether the process can move forward to the next phase or to fix any issue occurring during that instance. After properly investigating the current situation and no issues were found, the oil stirred to 400 rpm using magnetic stirrer as shown in Figure 3.5.

Figure 3.5: Setting the rotation per minute to 400 RPM

The mixture of methanol and sodium hydroxide will be added and this point will be taken as the initial time of reaction. The mixture will be stirred constantly at 400 rpm according to appointed amount of reaction time as shown in Figure 3.6. Appendix B shows the closed up view of parameter setup on magnetic stirring hotplate.

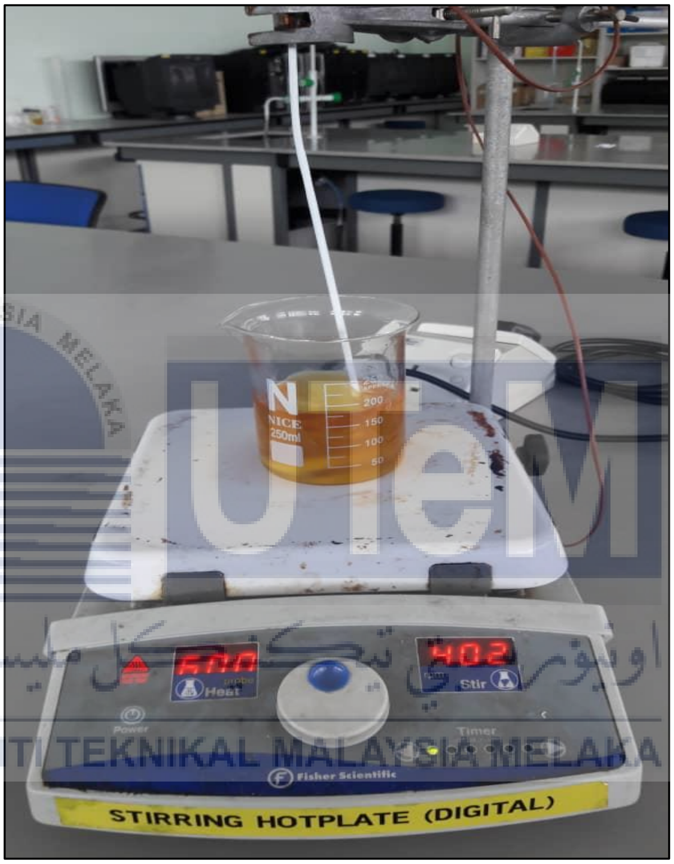


Figure 3.6: Mixture stirred at 400 RPM in 60°C

3.2.3 Biodiesel Washing Process

Afterwards, the reacted mixture that was left for selected amount of reaction time is poured into separatory funnel to be cooled down as shown in Figure 3.7. In a couple minutes, a clear separation was observed as the color of methyl esters (biodiesel) and glycerin contrast each other since methyl esters yield light yellowish cloudy color while glycerol produced dark orange color as shown in Figure 3.8.

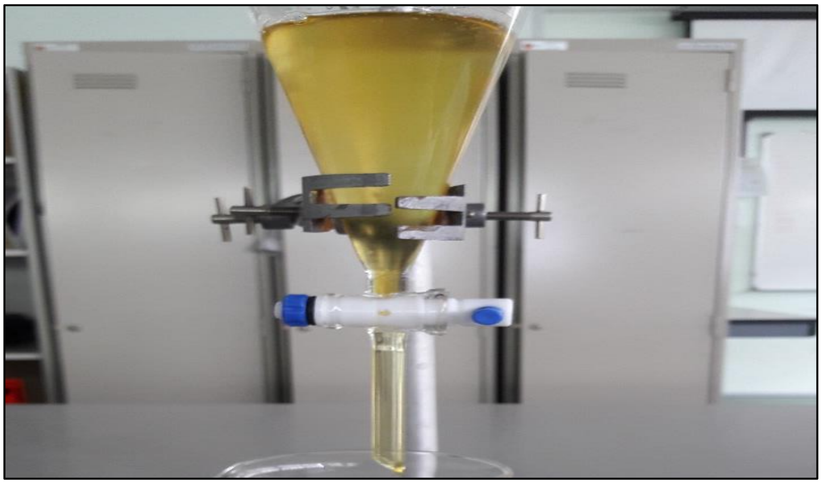


Figure 3.7: Mixture cooling down process in separatory funnel.

The glycerin is removed by utilizing the separatory funnel thus leaving behind the crude methyl ester layers. Appendix C shows the biodiesel after separation process. In order to produce a good sample of biodiesel, the crude methyl esters will be purified by washing gently with warm water until the color of the water and the methyl esters becomes clearer. This clear color indicates that soap and other water-soluble contaminants in the methyl esters had been removed as shown in Figure 3.9. The process were then repeated from preparation until washing process for different parameter at varying values.

Figure 3.8: Separation between Glycerin and Crude Fatty Acid Methyl Esters

Figure 3.9: Fatty Acid Methyl Esters after washing process.

Afterwards, to remove excess water cause by water purifying technic, the biodiesel is then heated up to 105°C as shown in Figure 3.10. This will caused the excess water which contains soap to evaporate leaving the soap to solidify and sink to the bottom in a form of small particles.

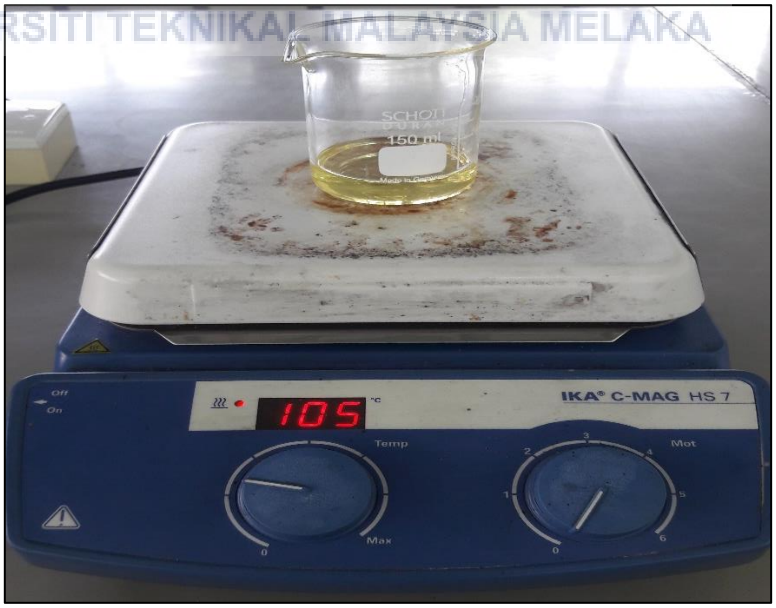


Figure 3.10: Reheating Biodiesel

3.3 Biodiesel Yield Test

Each of the product from varying parameter were put into biodiesel analyzer to measure the yield of biodiesel produced. The biodiesel required only in a small amount in order to be tested by the analyzer as shown in Figure 3.11. For each biodiesel sample, the test should be repeated five time in order to take the average value and get the results with the best accuracy.

Figure 3.11: Biodiesel Analyzer

3.4 Design of Experiment Using Response Surface Methodology

Response Surface Methodology (RSM) enable the possibility of identifying the relationship in between multiple variables and identifying the optimize value of each of said variables. Thus in order to obtain the optimum biodiesel yield, RSM was employed in this project in order to identify which of the three parameters and its setup values affect the production of Rice Bran Oil Biodiesel. In order to utilize RSM, the parameter was again clarified as the independent variables that influence the biodiesel yield which act as dependent variable. To have the full understanding of interactions between the factors, full factorial design is used. The independent parameter and levels created based on DOE is shown in Table 3.3.

Table 3.3: Independent Parameters and Levels

Independent Parameter	Levels				
	-α	-1	0	+1	+α
Alcohol to Oil Molar Ratio	3:1	6:1	7:1	9:1	12:1
Reaction Temperature (°C)	30	40	50	60	65
Reaction Time (min)	20	40	60	80	100

The level for each of the variables was chosen based on previous researches (Mathiyazhagan and Ganapathi, 2011), (Mehdi and Hamid, 2011), (Leung and Guo, 2006), (Eevera et al, 2009). However the highest reaction temperature was decided to be at 65°C due to the alcohol that being used was methanol that have its boiling point at 65°C. After that, a table is constructed in which consists of 20 set of experiment with different set of the independent parameters and levels as shown in Table 3.4

Table 3.4: Design of Experimental Data with Coded Values

Experiment	Independent Variables			Biodiesel Yield (%)
	Molar Ratio	Temperature	Reaction Time	
1	-1	-1	-1	To be determined
2	+1	-1	-1	
3	-1	+1	-1	
4	+1	+1	-1	
5	-1	-1	+1	
6	+1	-1	+1	
7	-1	+1	+1	
8	+1	+1	+1	
9	-α	0	0	
10	+α	0	0	
11	0	-α	0	
12	0	+α	0	
13	0	0	-α	
14	0	0	+α	
15	0	0	0	
16	0	0	0	
17	0	0	0	
18	0	0	0	
19	0	0	0	
20	0	0	0	

3.5 Characterization Test

The product of transesterification process (biodiesel) were characterized according to ASTM D6751 and EN 14214 biodiesel standard. Three selected fluid properties which were tested for characterization purposes are density, kinematic viscosity, cloud point and pour point.

3.5.1 Density test

Density is the weight per unit volume. Oils that are denser contain more energy. Following the standard mention before, parameter of density should be tested at the temperature reference of 15 or 20 °C. This is to ensure the accuracy of the hydrometer since at higher temperature biodiesel tends to expand the meniscus causing an error in reading data. For this project, the temperature for density test was set to 15°C. To identify the value of density, a hydrometer would be used within the specific confine of petroleum's test method which is ASTM D-4052. The hydrometer were sanitize firsthand. The biodiesel beaker was placed on a flat surface to get an accurate reading. The hydrometer's temperature calibration was checked to ensure that it coincide with the temperature on the biodiesel. For this purpose the temperature of the biodiesel was checked as well. The sanitized hydrometer was inserted in the biodiesel fluid to a point where it could float naturally. The hydrometer bulb was ensured not to touch anything besides the fluid itself. For accuracy purpose, the hydrometer was spun or shaken to dislodge air bubble clinging to the tool. As the movement of the fluid calm down, the hydrometer scale at the lowest point of the liquid's surface was taken. The reading should not be taken from the meniscus curve form by the fluid surface tension. Figure 3.12 and Figure 3.13 below shows an example of a hydrometer apparatus.

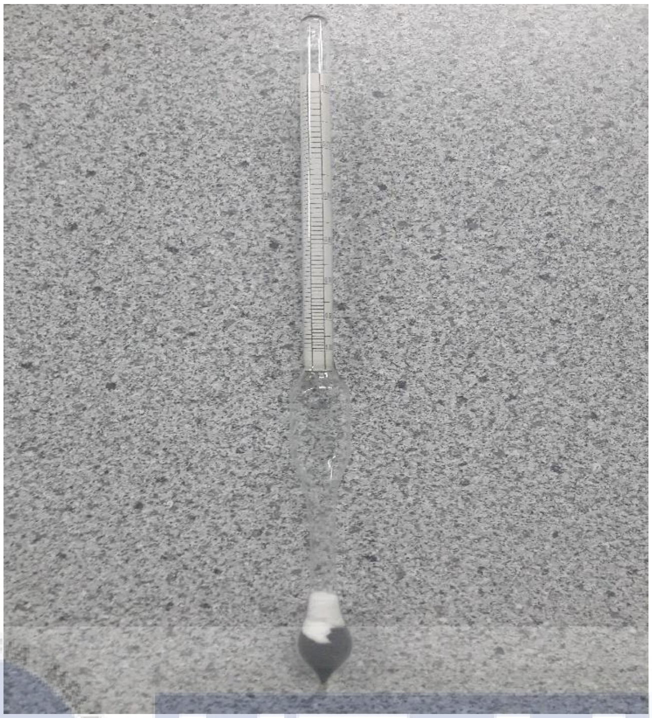


Figure 3.12: Hydrometer

Figure 3.13: Hydrometer submerged in biodiesel for testing purposes

3.5.2 Kinematic Viscosity

Viscosity is the most important property of any fuel as it indicates the ability of a material to flow. It therefore affects the operation of the fuel injection equipment and spray aoutomization, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel. The viscosity should be tested at a temperature reference of 40°C following the standard mentioned before. To determine the value of viscosity, Brookfield Viscometer DV-II+Pro was used following the test method of ASTM D-445. The specification of the instrument is shown in Table 3.5.

Table 3.5: Specification of Brookfield Viscometer DV-II+Pro

Temperature Sensing Range	-100°C to 300°C (-148°F to 572°F)
Analog Torque Output	0-1 Volt DC (0-100%)
Analog Temperature Output	0-3.75 Volts DC (-100°C to +275°C)
Viscosity Accuracy	±1.0% of full scale range. The use of accessory items will have an effect on the measurement accuracy.
Viscosity Repeatability	±0.2% of Full Scale Range
Temperature Accuracy	±1°C ǀ -100°C to +149°C ±2°C ǀ +150°C to 300°C
Operating Environment	0°C to 40°C temperature range (32°F to 104°F) 20%- 80% R.H.: non-condensing atmosphere.

The biodiesel should be put in a neatly clean container to avoid impurities during testing process. The water bath should be heated as shown in Figure 3.14. Once the temperature of the water bath reached 40°C the spindle was set to the required speed corresponding to spindle chosen (S81) and the viscometer was switched on. The indicator in the monitor is observed and the reading was recorded once the value stabilized as shown in Appendix D.

Figure 3.14: Viscometer and water bath apparatus.

3.5.3 Cloud Point and Pour Point

Cloud point and pour point are significantly important when dealing with cold climate. This is especially true when biodiesel is put to use in a country close to northern or southern hemisphere like Russia, Greenland and Canada. The reason would be thanks to biodiesel high cloud point and pour point. As shown in Chapter 2, biodiesel have its cloud point and pour point higher than diesel by 10-20 degree Celsius. Meanwhile diesel needs to be as low as -35 degree Celsius in order for it to reach its cloud point and pour point. This limit shows the ability to use biodiesel blend and even promote diesel usage in cold country. This is the particular reason on why should pour point and cloud point be identified.

To analyze the temperature of cloud point, the biodiesel must first cooled down is a small visible containers for observation purpose shown in Figure 3.15.

Figure 3.15: Optimized biodiesel poured into visible container.

During the start of its crystallization stage where small visible solid crystal formed, the temperature of the biodiesel should be taken and denoted as cloud point as shown in Figure 3.16.

Figure 3.16: Crystallization of biodiesel.

On the other hand, pour point temperature should be reported when the biodiesel that was frozen through and through starts to drips its content in liquid form as shown in Figure 3.17.

Figure 3.17: Biodiesel liquidation.

Instead of normal laboratories standard issue thermometer as shown in Figure 3.18, the temperature should be gauge by thermocouple instruments as shown in Figure 3.19. This method could be seen as imprecise technique, however the result could illustrate at which point is the range of the accurate temperature would be.

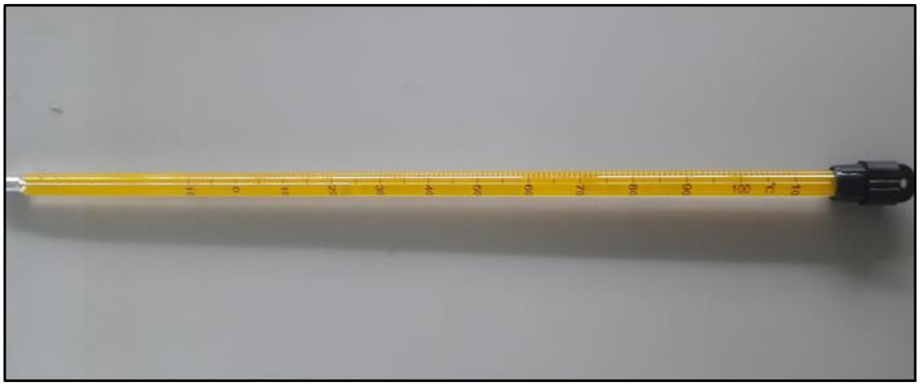


Figure 3.18: Standard issue laboratory thermometer.

Figure 3.19: Digital thermometer with thermocouple.

Since digital thermometer equipped with thermocouple are sensitive as it is accurate, the temperature illustrated in Figure 3.17 would not depict the actual results. Instead that figure shows temperature few degrees after the event happened.

3.6 Conclusion

All the aforementioned tests and procedures results were tabulated in an orderly manner within the results and discussion section of this written report. Most of the figure that depicted the methodology were attached to the appendix section.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Overview of Experimental Data

The dependent and independent variables is tabulated with respective levels as shown in Table 4.1. The Design of Experiment (DOE) for Response Surface Methodology (RSM)) with coded parameters values is shown in Table 4.2.

Table 4.1: Dependent and independent variables and levels.

Independent Parameter	Levels				
	-α	-1	0	+1	+α
Alcohol to Oil Molar Ratio	3:1	6:1	7:1	9:1	12:1
Reaction Temperature (°C)	30	40	50	60	65
Reaction Time (min)	20	40	60	80	100

Each sample of biodiesel have its biodiesel yield examined using biodiesel analyzer five times to ensure the accuracy by producing the average results. Only then that the value of average should be taken as biodiesel yield. Table 4.3 shows the DOE for RSM with parameters values.

Table 4.2 DOE of RSM with coded parameters.

Experiment	Independent Variables			Biodiesel Yield (%)
	Molar Ratio	Temperature	Reaction Time	
1	-1	-1	-1	76.82
2	+1	-1	-1	70.80
3	-1	+1	-1	53.80
4	+1	+1	-1	48.53
5	-1	-1	+1	75.32
6	+1	-1	+1	82.98
7	-1	+1	+1	60.90
8	+1	+1	+1	62.14
9	-α	0	0	61.30
10	+α	0	0	65.90
11	0	-α	0	61.06
12	0	+α	0	58.68
13	0	0	-α	56.72
14	0	0	+α	71.48
15	0	0	0	85.17
16	0	0	0	85.17
17	0	0	0	85.17
18	0	0	0	85.17
19	0	0	0	85.17
20	0	0	0	85.17

Table 4.3: DOE for RSM with parameters values.

Experiment	Independent Variables			Biodiesel Yield (%)
	Molar Ratio	Temperature (40°C)	Reaction Time (min)	
1	6:1	40	40	76.82
2	9:1	40	40	70.80
3	6:1	60	40	53.80
4	9:1	60	40	48.53
5	6:1	40	80	75.32
6	6:1	40	80	82.98
7	6:1	60	80	60.90
8	9:1	60	80	62.14
9	3:1	50	60	61.30
10	12:1	50	60	65.90
11	7:1	30	60	61.06
12	7:1	65	60	58.68
13	7:1	50	20	56.72
14	7:1	50	100	71.48
15	7:1	50	60	85.17
16	7:1	50	60	85.17
17	7:1	50	60	85.17
18	7:1	50	60	85.17
19	7:1	50	60	85.17
20	7:1	50	60	85.17

4.2 Influences of Parameters on Biodiesel Yield

4.2.1 Alcohol to Oil Molar Ratio

According to the previous study conducted by Mehdi and Hamid (2011), it is stated that using alcohol to oil molar ratio ranging from 3:1-7:1 will have the biodiesel yield to increase while having molar ratio past 7:1 will not increase the biodiesel yield any further. Thus, it is concluded in their discovery that using molar ratio exceeding 7:1 is not economical as it promoted wastage. Meanwhile, the previous study lead by Mathiyazhagan and Ganapathi, (2011) stated that the alcohol to oil molar ratio needed to be at least 3:1 for transesterification process as 3 mol of alcohol are needed to react with 1 mol of triglycerides.

The results of RSM using Minitab related to the molar ratio is presented with fitted line plot between alcohol to oil ratio and biodiesel yield as shown in Figure 4.1. Based on the graph, the biodiesel yield increase steadily as molar ratio were set in between 3:1 to 7:1. Correspondingly, the biodiesel yield at first increase from 61% towards 72%. However once the molar ratio were set above 7:1, the biodiesel yield steadily drops from 72% to 64%. This further supports the claim made by previous study that having molar ratio higher than 7:1 does not benefit on the outcome of biodiesel yield.

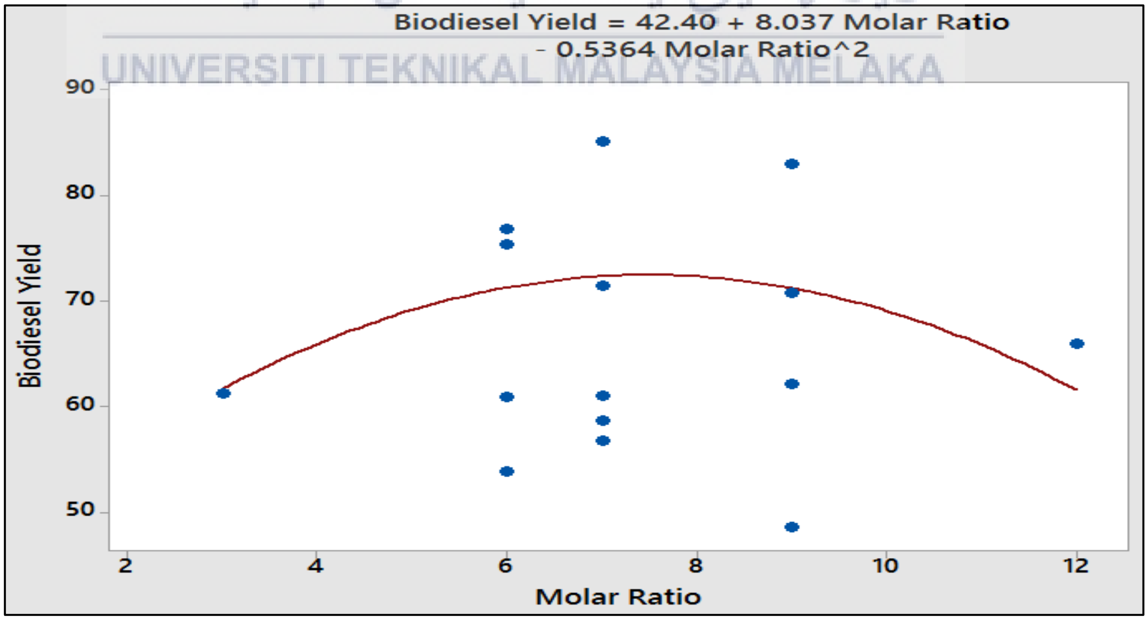


Figure 4.1: Fitted line plot for alcohol to oil molar ratio.

4.2.2 Reaction Temperature

As for the influence of reaction temperature, the previous study conducted by Mathiyazhagan and Ganapathi (2011) concluded that the higher the temperature the faster the rate of transesterification process of biodiesel. Meanwhile Leung and Guo (2006) and Eevera et al (2009) cited in Mathiyazhagan and Ganapathi (2011) concluded that having the temperature set higher than optimal level will cause the biodiesel yield to decrease due to saponification of triglycerides. On other note, having temperature set too high will cause the saponification of triglyceride to occur at a faster rate than the rate of transesterification. This in turn will cause the product to contain more soap than biodiesel which only means that the biodiesel yield decrease. In this project, methanol is used as the alcohol component. This means that the experiment must be conducted below the boiling point of methanol on which is 64.7°C.

However for the sake of simplicity and constraint by the instrument provided by the faculty, the highest temperature had been rounded to 65°C. The results of RSM using Minitab related to reaction temperature is presented with fitted plot between reaction temperature and biodiesel yield as shown in Figure 4.2. Based on the graph, the biodiesel yield increase momentarily in between temperature setups of 30 to 45°C while achieving yield from 62% up to 75%. Having the temperature setups past 45°C caused the biodiesel yield to drop from 75% to as low as 49%. Since the boiling point of methanol is 64.7°C, it is only natural that the biodiesel yield decrease severely as methanol do not have enough time to react before evaporating.

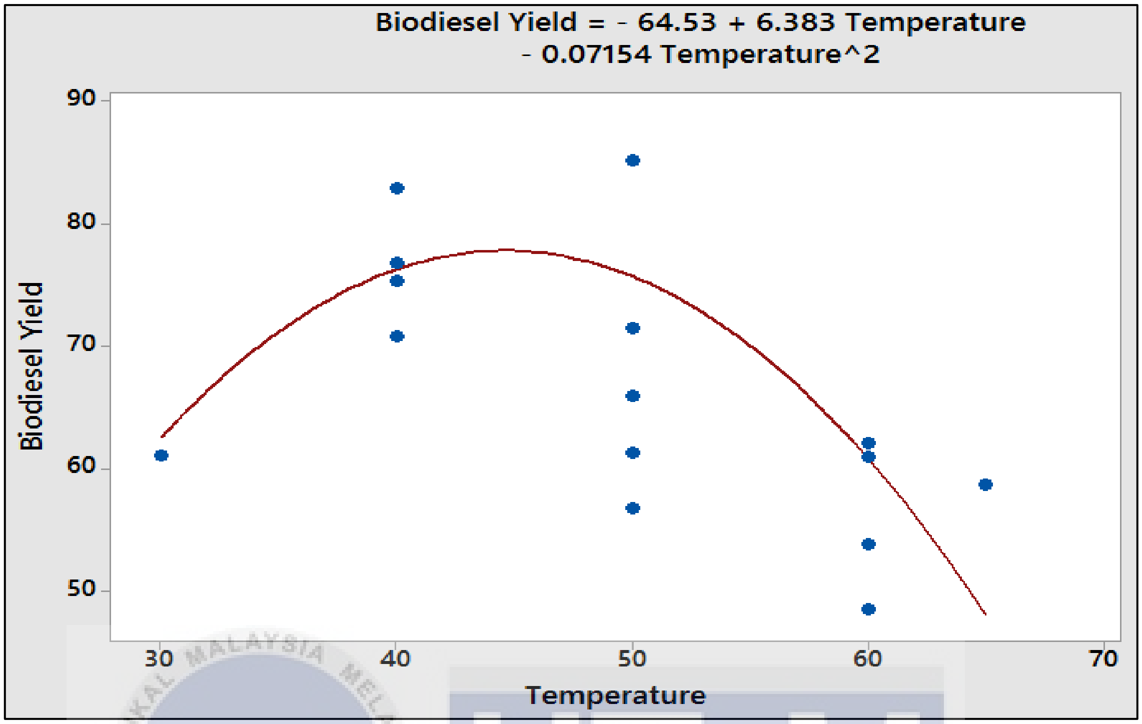


Figure 4.2: Fitted line plot for reaction temperature.

4.2.3 Reaction Time

Following the study conducted by Mathiyazhagan and Ganapathi (2011), it was determined that setting the reaction to long or too short could impact the yield of transesterification process. Modifying the time too long would cause the soap formation due to reversibility of process. However adjusting the time too short would not allow the mixture to disperse thus leading to decrease in biodiesel yield as less alcohol is reacting with the oil. The reaction time needed in the previous study ranging around the boundary of ±90 minutes. The results of RSM using Minitab related to reaction time is presented with fitted plot between reaction time and biodiesel yield as shown in Figure 4.3. Based on the graph, the biodiesel yield increase when reaction time setup range from 20 to 70 minutes yielding up to 73% of biodiesel output. This observation however counteract with the previous study which claim that the biodiesel would yield the highest in range of 90 minutes.

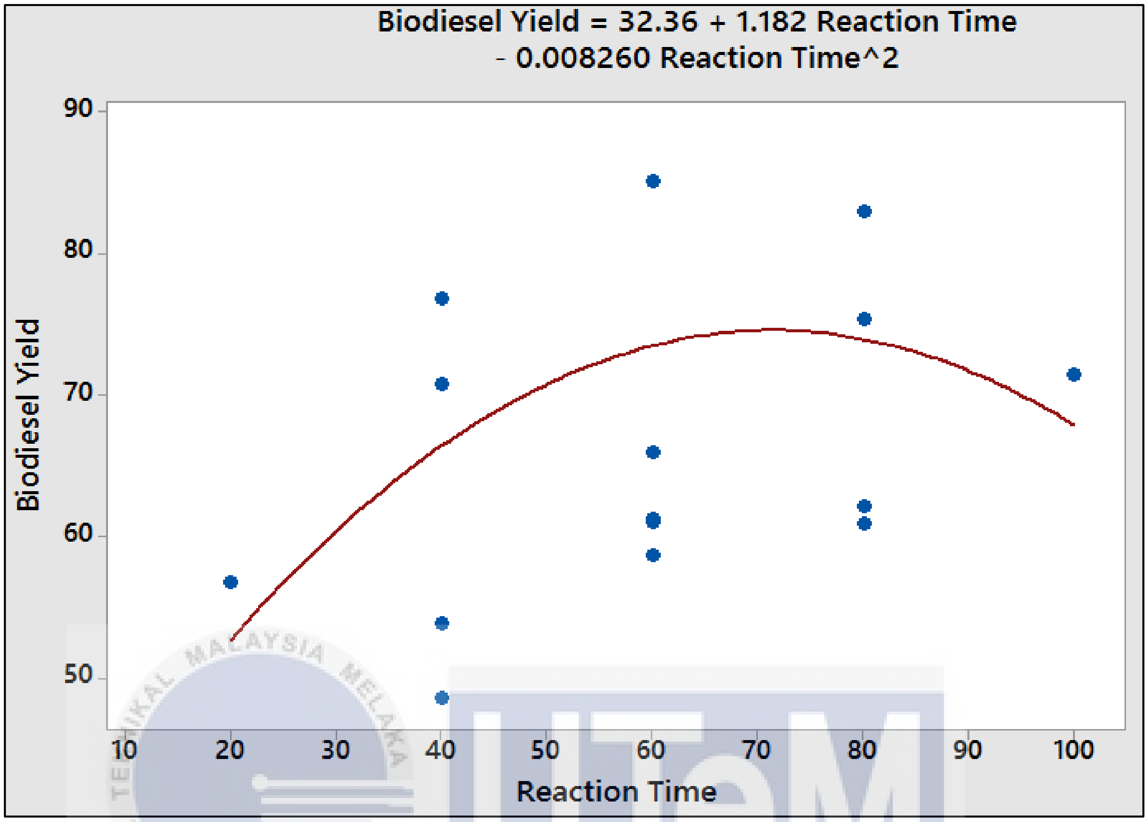


Figure 4.3: Fitted line plot for reaction time.

4.3 Interaction Plot between Independent Parameters

In order to study the regression model of different parameter for the project which are molar ratio, temperature and reaction time, Fitted Means Interaction graph is plotted as illustrated in Figure 4.4.

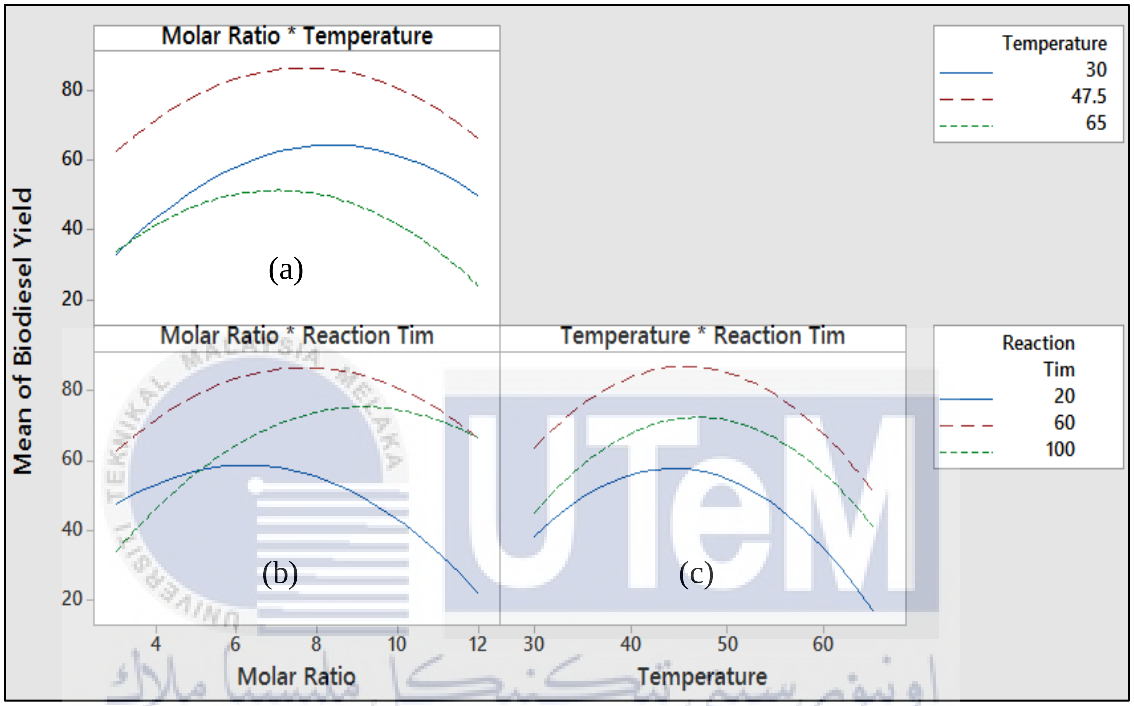


Figure 4.4: Fitted means interaction plot for biodiesel yield.

Figure 4.4 (a) is depicting the correlation between molar ratio (x-axis) and temperature (range from 30°C to 65°C) against biodiesel yield. This graph shows that when biodiesel production process sets up with temperature lower than 30°C or higher than 65°C will have significantly low biodiesel yield when molar is set lower than 6:1 or higher than 9:1. However, when temperature is sets close to 47.5°C the overall biodiesel yields are better than temperature lower than 30°C or higher than 65°C regardless of molar ratio. This really shows that temperature sets to 47.5°C is somewhere neat the optimum level for temperature.

Figure 4.4 (b) is portraying the interaction between molar ratio (x-axis) and reaction time (range between 20 to 100 minutes) against biodiesel yield. This graph shows that when biodiesel production process sets up with reaction time higher than 100 minutes with molar ratio lower than 5:1, the biodiesel yield will be at its lowest point. However, when molar ratio is increase higher than 5:1 with constant reaction time of 100 minutes, the biodiesel yield increase breaking through the biodiesel setup with reaction time of 20 minutes. The biodiesel yield for 100 minutes setup achieve almost the same as 60 minutes setup when molar ratio is set to be 12:1. This shows that, higher molar ratio will require more reaction time for transesterification process to turn Rice Bran oil (cooling oil) to biodiesel. However, as molar ratio increase, biodiesel yield also decrease as shown by reaction time setup of 60 minutes.

Figure 4.4 (c) is illustrating the interaction between temperature (x-axis) and reaction time (range between 20 to 100 minutes) against biodiesel yield. This graph shows that when biodiesel production process sets up reaction time lower than 20 minutes or higher than 100 minutes, the biodiesel would yield lower than reaction time setup of 60 minutes. Reaction time of higher than 100 minutes setup nonetheless shown to have somewhat higher level of biodiesel yield as compared to setup of reaction time lower than 20 minutes. This shows that 20 minutes of reaction time is merely not enough time to produce biodiesel. Meanwhile having a reaction time sets up to 60 minutes will have biodiesel yield at the highest level albeit the fact that it only increase from 30°C to somewhere around 45°C and starts dropping from there on forward.

Besides fitted means interaction plot for biodiesel yield, the fitted mean main effect plot from biodiesel yield was also plotted as shown in Figure 4.5. This graph was plotted explicitly for the purpose of seeing each of the independent parameter correlation against biodiesel yield. Thus based on the graph, molar ratio should be taken around 8:1, temperature about 47°C and reaction time somewhere 60-70 minutes in order to obtain the highest possible biodiesel yield value.

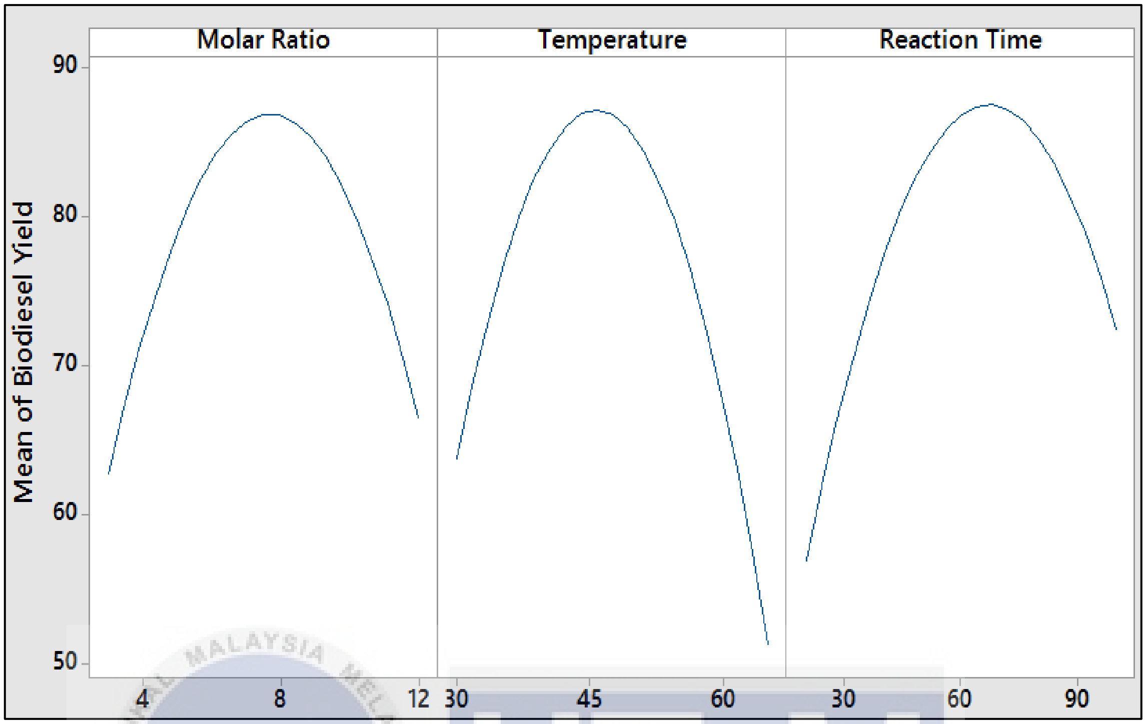


Figure 4.5: Fitted means main effect plot for biodiesel yield.

Other than using the fitted line graph between one dependent and independent variables for observation, analysis can also be conducted by using two independent and one dependent variables. Figure 4.6 shows the contour plot of biodiesel yield (independent variable) against molar ratio and temperature (independent variables). The dark green color shows that the biodiesel yield 80% and above. This dark green region exists in between temperature range of 33°C to 54°C and molar ratio range from 5.3:1 to 10.5:1. As the gradient moving outside of the mentioned contour, the color of the contour decreased in concentration from dark green to light green up until it turns to light blue and lastly dark blue. The lighter green contour range below 80% to 50% meanwhile the light and dark blue followed by having biodiesel yield of less than 50% to below 30%. To simplify, the biodiesel yield decrease as the experiment sets temperature below 33°C or above 54°C while molar ratio set below 5.3:1 or above 10.5:1. This data of contour plot can only be achieved by holding the value of reaction time constantly at 60 minutes.

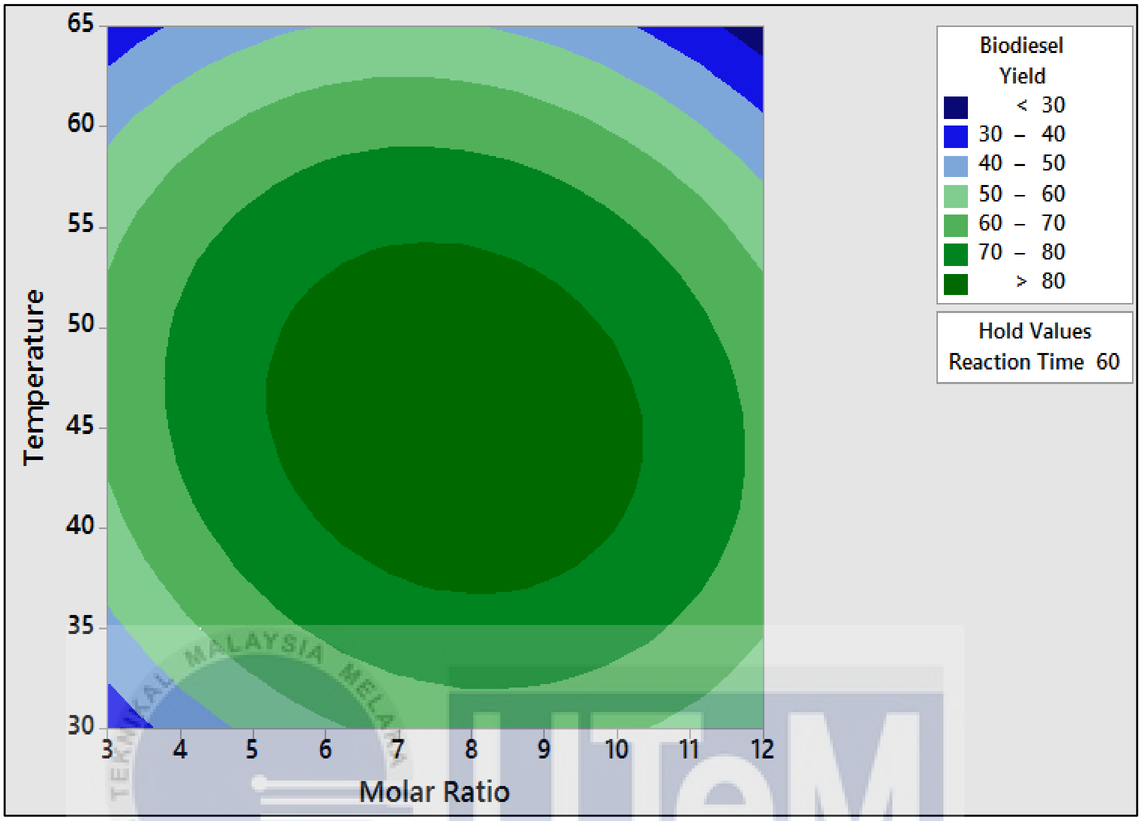


Figure 4.6: Contour plot of biodiesel yield versus molar ratio, temperature.

Figure 4.7 shows the contour plot of biodiesel yield (independent variable) against molar ratio and reaction time. The dark green color of the contour as establish before were drawn in the capacity of molar ratio ranging from 5.3:1 to 10.5:1 while reaction time range from 45 minutes up to 93 minutes. In this case when comparing biodiesel yield against molar ratio and reaction time, the reaction time constraint were bigger thus giving the contour shape of an oval. This means that the effective reaction time option to achieve optimized biodiesel yield is quite flexible as it lies within a big range of constraint. Only a small of portion of the contour graph could achieve biodiesel yield lower than 30% which is indicated by dark blue color indicator. However in order for this data to be achievable, the temperature of the setup need to be in constant of 47.5°C. To simplify the data, setting the value of reaction time below 45 minutes or above 93 minutes reduced the biodiesel yield. In addition, setting the value of molar ratio in between 5.3:1 and 10.5:1 increased the biodiesel yield.

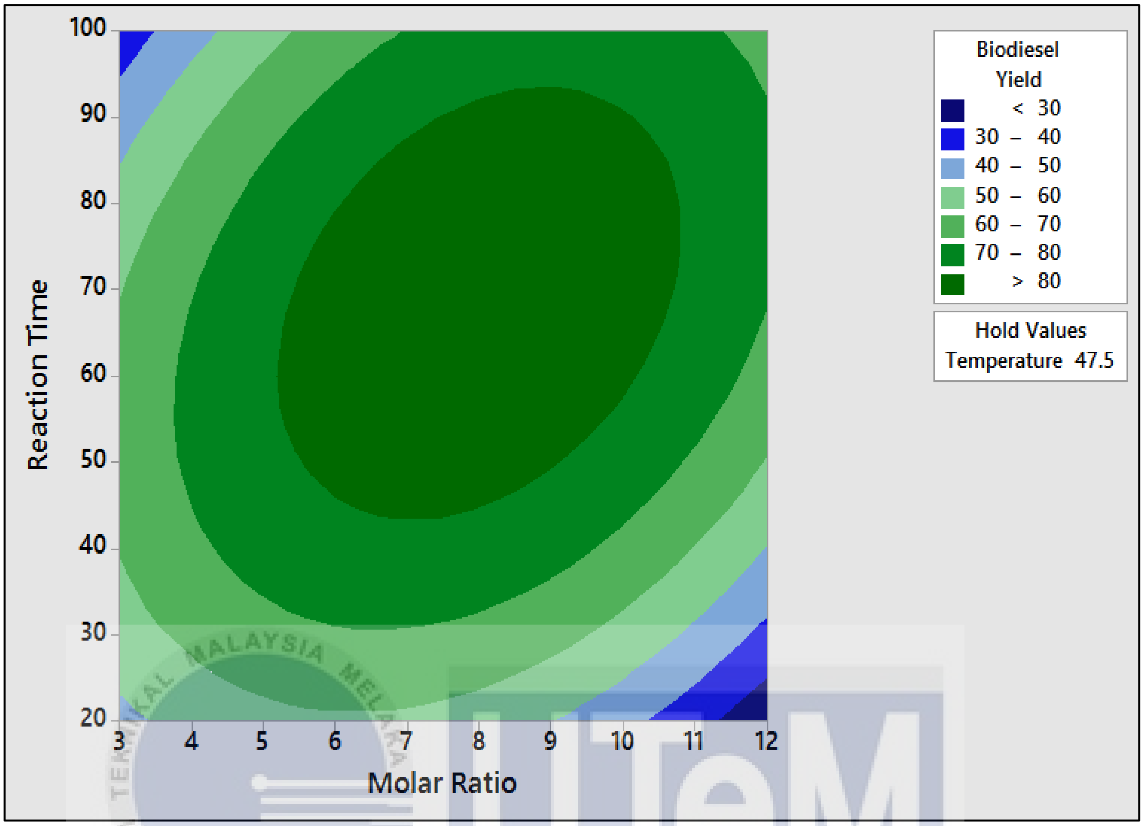


Figure 4.7 Contour plot of biodiesel yield versus molar ratio and reaction time.

Figure 4.8 shows the contour plot of biodiesel yield (independent variable) against temperature and reaction time (independent variables). The highest biodiesel yield is indicated with dark green color while the lowest biodiesel yield is indicated with dark blue color. The dark green color region range in temperature from 37°C to 54°C and reaction time from 45 to 88 minutes. The biodiesel yield region move somewhat uniformly away from the dark green region which lead to the conclusion that temperature will slowly loses its effectiveness on giving ideal design for biodiesel production when it leave its optimal level of 37°C to 54°C. Same thing could be said to reaction time which have its optimal level range from 45 to 88 minutes. However in order for this data to be obtained, the molar ratio of the setup need to be in constant of 7.5:1.

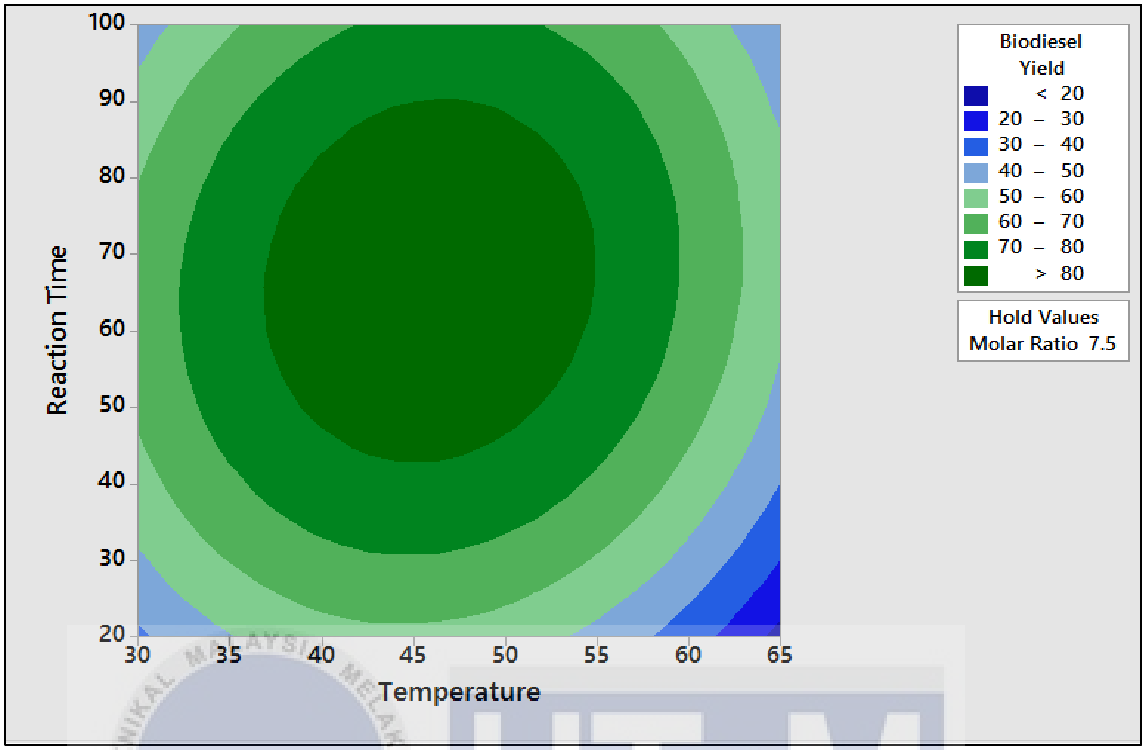


Figure 4.8: Contour plot of biodiesel yield versus temperature and reaction time.

In order to further study the correlation between independent and dependent parameter, several three dimensional surface graph were plotted. The Figure 4.9 shows the surface plot of biodiesel yield (independent variable) versus molar ratio, temperature (dependent variable). The white patch on the surface plot clearly indicates the highest point (peak) for biodiesel yield on which reside well within 5:1 to 8:1 for molar ratio and 48°C to 55°C for temperature. The biodiesel however would yield low when molar ratio sets close to 12:1 with temperature 30°C or lower. Lower when molar ratio is sets somewhere around 3:1 with temperature 30°C and lowest when molar ratio reach close to 12:1 and temperature more than 60°C. This data could only be obtained when reaction time is set to 60 minutes.

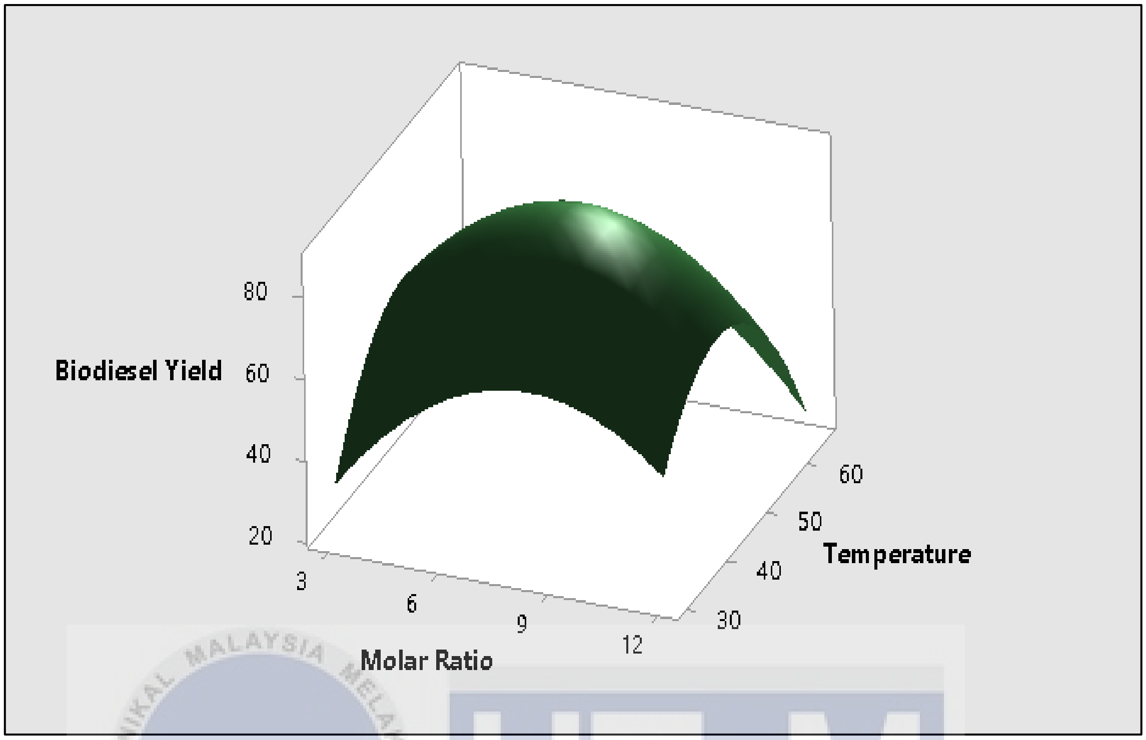


Figure 4.9: Surface plot of biodiesel yield versus molar ratio, temperature.

The Figure 4.10 shows the surface plot of biodiesel yield (independent variable) versus molar ratio, reaction time (dependent variable). This time around, the white patch (peak) appear in range of 8:1 to 10:1 for molar ratio and 68 to 88 minutes for reaction time. This means that optimal level of biodiesel yield could only be obtain when increasing molar ratio from 3:1 up to 8:1 while reaction time increase from 30 towards 68 minutes. The biodiesel will yield the lowest when molar ratio exceeds more than 12:1 and reaction time less than 30 minutes. Second lowest when molar ratio set to less than 3:1 while maintaining reaction time less than 30 minutes. Third lowest when reaction time sets more than 90 minutes and molar ratio higher than 12:1. This data can only be obtained when the parameter value is set to 47.5°C.

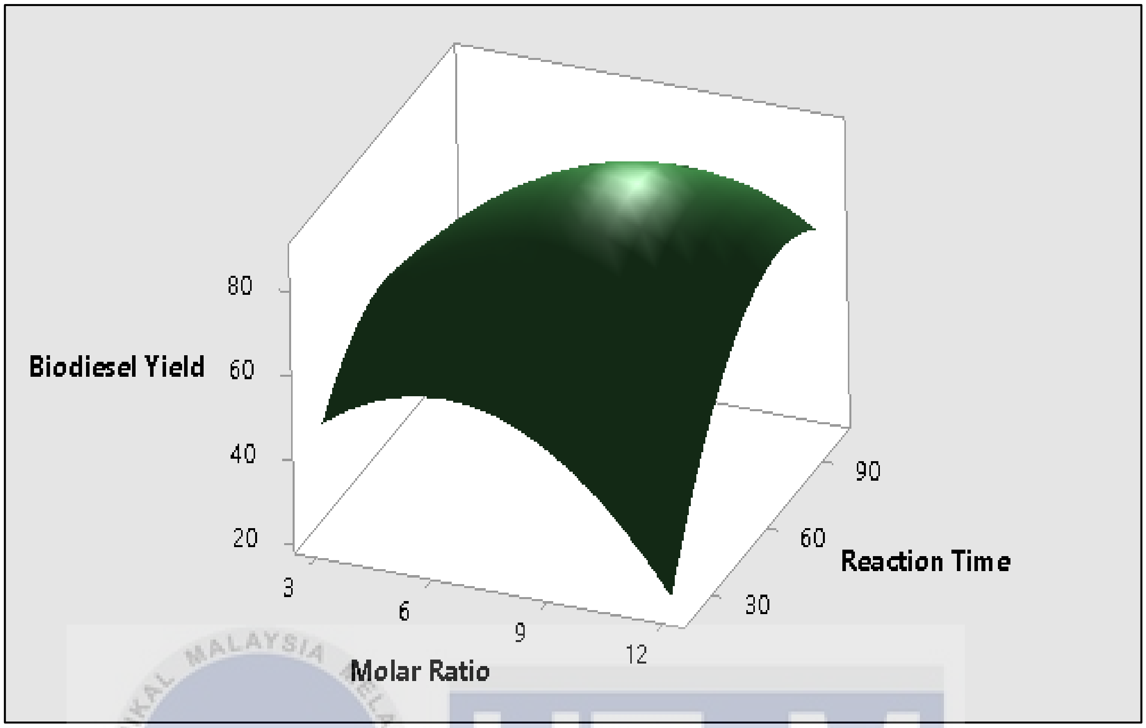


Figure 4.10: Surface plot of biodiesel yield versus molar ratio and reaction time.

Figure 4.11 shows the surface plot of biodiesel yield (independent variable) versus temperature, reaction time (dependent variable). The white patch (peak) this time exist in between temperature setup of 48°C to 55°C and reaction time setup of 68 minutes to 75 minutes. This peak can only be at the specified location when molar ratio is set to 7.5:1. Meanwhile the lowest biodiesel yield for this correlation graph is when temperature value set to more than 60°C while reaction time set less than 30 minutes of reaction time. Slightly higher when temperature set to lower than 30°C with reaction time maintaining to lower than 30 minutes and equal to biodiesel yield with setup of temperature more than 60°C and having reaction time higher 90 minutes.

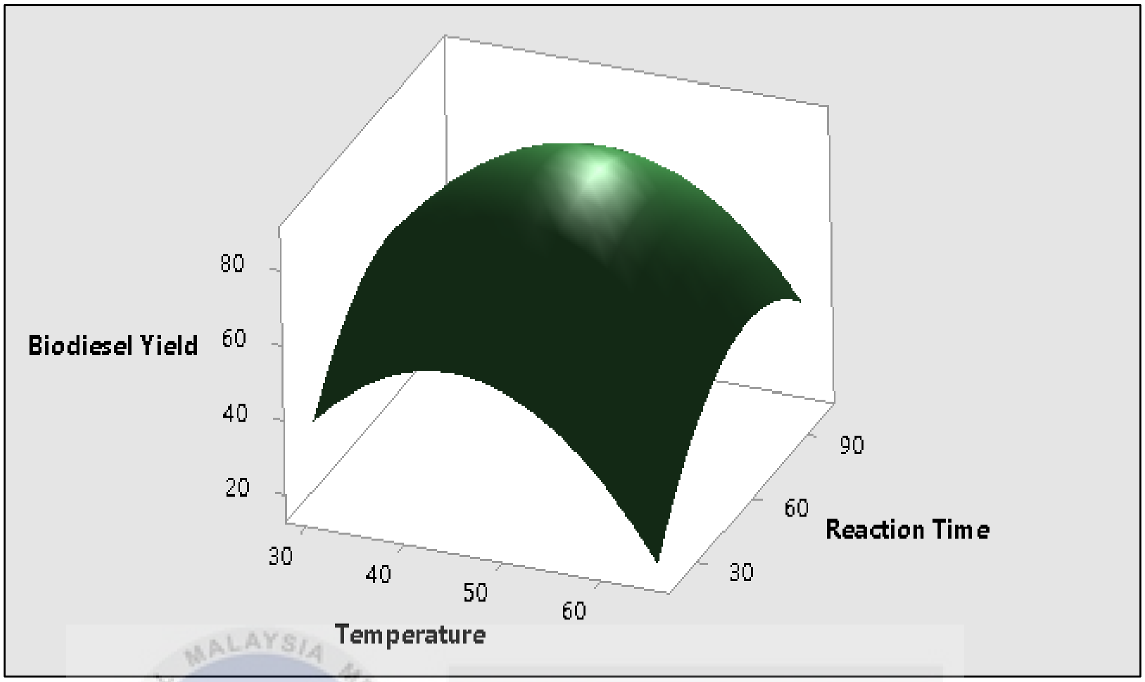


Figure 4.11: Surface plot of biodiesel yield versus temperature and reaction time.

4.4 Optimization of Independent Parameters

In order to characterize the biodiesel, first the biodiesel must undergone through optimization process. The process for this project is specifically to find the optimal values from each independent parameters to produce the highest biodiesel yield. Figure 4.12 shows the designed optimization plot.

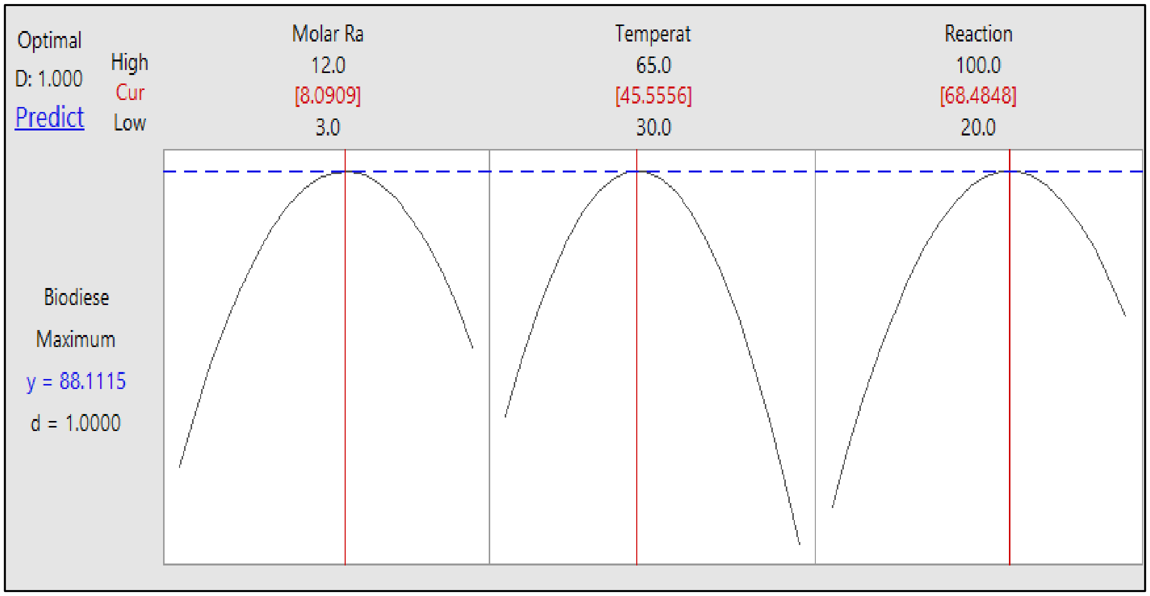


Figure 4.12: Designed optimization plot

From the designed optimization plot figure, the optimized value of molar ratio is found to be exactly 8.0909 in which was rounded of by two significant figures giving the molar ratio to be 8.1:1 for the sake of ease in transesterification process. Temperature was discovered to be 45.5556°C on which was rounded of by three significant figures that give temperature to be 45.6°C and later on to be rounded to two significant figures due to the limitations of apparatus. Meanwhile, reaction time was determined to be 68.4848 minutes which was rounded off to four significant figures which lead reaction time to be 68.48 minutes or one hour eight minutes and 48 seconds. All these values were only possible to get when Equation 4.1 is generated and used in Minitab 18 Statistical Software based on the experimental data. Based on the regression equation (Equation 4.1) the maximum biodiesel yield should be 88.1115%.

$$\begin{aligned} Y \;=\; & -229.9 + 15.09\,M + 8.87\,T + 1.814\,R - 1.127\,M{*}M - 0.0982\,T{*}T - \\ & 0.01375\,R{*}R + 0.028\,M{*}T + 0.0188\,M{*}R - 0.00336\,T{*}R \end{aligned} \qquad (4.1)$$

Where,

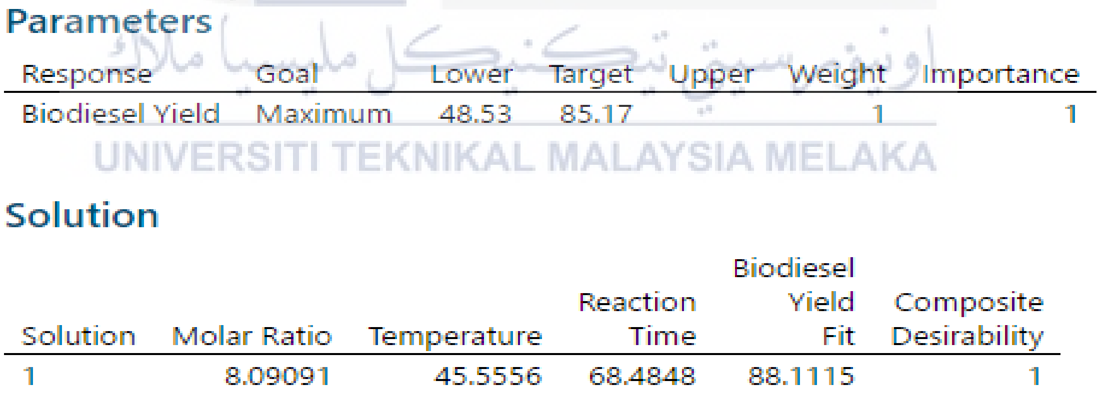
Y = Biodiesel Yield (%)

M = Molar Ratio

T = Temperature

R = Reaction Time

Based on the Equation 4.1, it is known that there consist of linear values for each independent parameter (molar ratio, temperature and reaction time) at the beginning of the equation. Meanwhile, in the middle part of the equation consist of quadratic notation for again each of the independent parameter. The last section of the equation consists the notation of correlation between the independent parameter. Through this equation on its resulting optimal values for each independent parameter, the biodiesel yield would obtain exactly 2.9415% more biodiesel yield. Figure 4.13 and 4.14 shows the solution obtain from Minitab 18 to optimized biodiesel yield based on the regression equation produced.



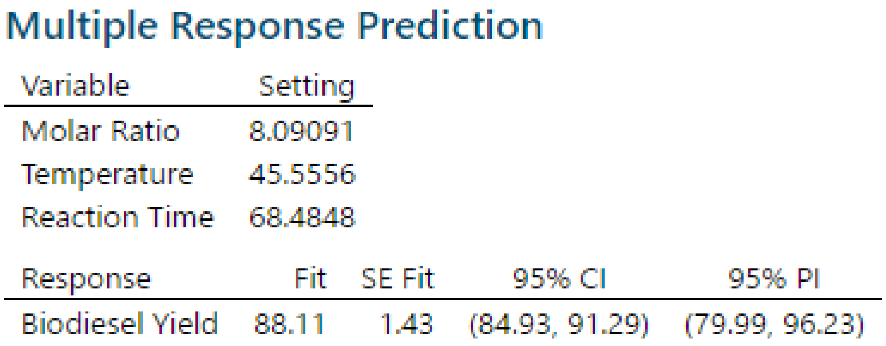
Parameters

Response	Goal	Lower	Target	Upper	Weight	Importance
Biodiesel Yield	Maximum	48.53	85.17		1	1

Solution

Solution	Molar Ratio	Temperature	Reaction Time	Biodiesel Yield Fit	Composite Desirability
1	8.09091	45.5556	68.4848	88.1115	1

Figure 4.13: Solution obtain through regression equation in Minitab 18 (1)


Multiple Response Prediction

Variable	Setting
Molar Ratio	8.09091
Temperature	45.5556
Reaction Time	68.4848

Response	Fit	SE Fit	95% CI	95% PI
Biodiesel Yield	88.11	1.43	(84.93, 91.29)	(79.99, 96.23)

Figure 4.14: Solution obtain through regression equation in Minitab 18 (2)

4.5 Characterization Rice Bran Oil Biodiesel

For this process, the characterization was done only for the biodiesel that was produced by the optimized independent parameter values obtain from Minitab 18. Characterization process only focus on density, viscosity, cloud point and pour point of the optimized biodiesel. To characterized density of biodiesel, test method ASTM D-4052 was applied when using hydrometer. On the other hand, when testing the viscosity of the biodiesel, the test method ASTM D-445 was applied when using viscometer. However, when testing for cloud point and pour point, ASTM D 2500 and ASTM D97-17b was not able to be applied properly due to the integrity of the available apparatus.

When using viscometer, the result obtain from it is shown in dynamic viscosity in unit of centipoise (cP) or x10^{-3} kg/ms. Meanwhile, in order to make comparison to ASTM D6751 and EN 14214, the viscosity should be kinematic viscosity which in unit of centistokes (cSt) or x10^{-6} m^2/s. Equation 4.2 is employed to calculate the dynamic viscosity of the biodiesel. The results of each of the test (density, viscosity, cloud and pour point) is tabulated in Table 4.4.

$$\nu = \frac{\mu}{\rho} \tag{4.2}$$

Where,

ν = Kinematic viscosity

μ = Dynamic viscosity

ρ = Density of biodiesel

$$\nu = \frac{6.59 \text{ x } 10^{-3}\ kg/ms}{865\ kg/m^3} \tag{4.2}$$

$$\nu = 7.618 \text{ cSt}$$

Or

$$\nu = 7.618 \text{ x } 10^{-6}\ m^2/\text{s}$$

Table 4.4: Characterized properties of Rice Bran oil biodiesel.

Test	Method	Unit	Results
Density	ASTM D-4052	kg/m^3	865
Viscosity	ASTM D-445	cSt or m^2/s	7.618
Cloud Point	ASTM D 2500	°C	-4.7
Pour Point	ASTM D97-17b	°C	-9.3

4.6 Comparison of Neat Rice Bran Oil and Rice Bran Oil Biodiesel

When the characterized biodiesel is put into comparison between ASTM D6751, EN 14214 and MS 2008:2008, it is found that the kinematic viscosity of the biodiesel is out of range by 1.618, 2.618 and 2.618 cSt respectively. However, this value is also tolerable since it does not deviated too far from suggested values set by all of the standards. Both the result of the viscosity test conducted and the value extracted from all the standards mentioned, had conducted the viscosity test at 40°C for biodiesel temperature. To support the argument for having viscosity value more than the standards values, the deviation is probably due to a big difference between the total number of fatty acid content between the characterized biodiesel and the biodiesel that is used to tabulate the data for table ASTM D6751, EN 14214 and MS 2008:2008.

On the other hand, the density of the characterized biodiesel was obtained within a good value range based from all of the standards by sitting on 865 kg/m^3. The biodiesel were subjected to a temperature of 15°C for comparison between the standards values. The density value shows that the biodiesel have a good amount of energy content comparable to that of the standards.

Meanwhile the cloud point and pour point albeit deviate in small amount from the standards values, it is understandable since different feedstock may have different cloud and pour point. Having different feedstock could probably diverge the physical properties of a certain biodiesel, however having different feedstock would definitely vary apart from the standards values. In order to have lower cloud point and pour point values, the biodiesel must undergoes through winterization process (Lee et al, 1996). The process remove saturated methyl esters by cooling the fuel to cause crystallization and then separating the high melting components by filtration. Table 4.5 shows the comparison between ASTM D6751, EN 14214, MS 2008:2008 and Rice Bran oil biodiesel.

Table 4.5: Comparison between ASTM D6751, EN 14214, MS 2008:2008 and Rice Bran oil biodiesel.

Test	Method	Unit	ASTM D6751	EN 14214	MS 2008:2008	RBOB
Density	ASTM D-4052	kg/m^3	880	860-900	860-900	865
Viscosity	ASTM D-445	cSt	1.9-6.0	3.5-5.0	3.5-5.0	7.618
Cloud Point	ASTM D 2500	°C	-3 to -12	-	-	-4.7
Pour Point	ASTM D97-17b	°C	-15 to -16	-	-18 to 0	-9.3

4.7 Conclusion

To summarize the results and discussion of this study, each of the independent parameters (molar ratio, reaction temperature and time) had been plotted in graph against the dependent parameter (biodiesel yield) using Minitab software in order to clarify the optimized values for each of the parameters. After that, the biodiesel that was produced from using the optimized values was subjected to characterization process in order to identify its fluid properties (density, viscosity, cloud and pour point). The fluid properties of the optimized biodiesel are then put into comparison with ASTM D6751, EN 14214 and MS 2008:2008 standard to fulfill the objective of this study.

CHAPTER 5

CONCLUSION AND RECOMENDATION

5.1 Conclusion

Upon completing the study, the following conclusion can be drawn:

a) Biodiesel could be and successfully be produced from Rice Bran oil by means of transesterification.

b) When the parameter of the biodiesel production is optimized, the molar ratio were found to be approximately 8.1:1, reaction temperature to be 45.5°C while reaction time set exactly at 68.48 minutes.

c) The optimized biodiesel were characterized on four different test. Density test which used hydrometer shows that the optimized biodiesel have a density of 865 kg/m^3 or its relative density of 0.856. Viscosity test which use viscometer shows that the optimized biodiesel have its viscosity at 7.618 centistokes or 6.59 centipoise or 7.6185 x 10^{-6} m^2/s. Cloud point which recorded through digital thermocouple read its temperature at -4.7°C while pour point was recorded to be at -9.3°C. All of the biodiesel properties have their values accepted well within ASTM D675, EN 14214 and MS 2008:2008 except for the viscosity. The viscosity is a bit higher from the standard probably due to high content of fatty acid as aforementioned in literature review and methodology.

Finally, the biodiesel was successfully produced using transesterification method and response surface methodology that shows satisfying physical properties. Thus, the biodiesel is deemed to be reliable and feasible for further development.

5.2 Recommendation

For future endorsement, the Rice Bran oil biodiesel could be test in real working engine of a vehicle in order to know whether it is ready for general usage for vehicle consumption or not.

The next project for the biodiesel could be increasing the range of parameter level from five (currently) to seven. The intention of increasing the parameter level is to provide the results with higher precision (biodiesel yield) and better understanding on the correlation between independent parameter.

After that, the characterization test could be extended to analyze corrosion test, calorific value and water (sediment) content (vol %). The corrosion test should be added if the biodiesel is to be subjected into a diesel engine to see the rate of its corrosion towards the engine. Identifying calorific value is self-explanatory since producing biodiesel means to replace an outdated fuel (diesel), thus the content energy inside a biodiesel should be known and achieve a value that is comparable to energy content of diesel fuel. Water (sediment) content value is needed in order to know whether the biodiesel needs to be reheated or not since having a biodiesel mixed with water could disrupt and complicate during the combustion process in real working engine.

Adding all of the suggested test (corrosion test, calorific value and water content) with density and viscosity test would be a better suggestion since density and viscosity are the most important properties of biodiesel to look out for.

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APPENDICES

Appendix A

Full setup during transesterification process

Appendix B

Example of parameter setup on magnetic stirring hotplate

Appendix C

Biodiesel (left) after Glycerol (right) separated

Appendix D

Viscometer computing viscosity