# Methanolysis of Vegetable Oils and Parametric Optimization

by

Amirul Hasraff Bin Ridzuan

16844

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

MAY 2015

Universiti Teknologi PETRONAS,
32610, Bandar Seri Iskandar,
Perak Darul Ridzuan

# CERTIFICATION OF APPROVAL

## Methanolysis of Vegetable Oils and Parametric Optimization

by

Amirul Hasraff Bin Ridzuan

16844

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirements for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

__________________________________

(Dr. Sintayehu Mekuria Hailegiorgis)

UNIVERSITI TEKNOLOGI PETRONAS
BANDAR SERI ISKANDAR, PERAK
May 2015

# CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted I this project, that the original work is my own excerpt as specified in the references and acknowledgements, and that original work contain herein have not been undertaken or done by unspecified sources or persons.

AMIRUL HASRAFF BIN RIDZUAN

# ABSTRACT

The exploration for environmental friendly energy is important as the main source of current world energy consumption which is fossil fuel is getting depleted and also increasing in $CO_2$ emission. Renewable energy such as biodiesel is gain attention at now current world economic situation. Moreover, raw material and production cost are adversely affecting the economic viable of biodiesel production. Currently, more than 95% in production of biodiesel, the feedstock is from edible oil source which compete with food industry and also food processing that affecting both economic which in production of biodiesel and food industry. The problem why vegetable oil cannot directly use in diesel engine because the high viscosity contain in vegetable oil, by using transesterification reaction it can reduce the viscosity of vegetable oil. However, transesterification reaction is extremely slow due to the oil is sparingly soluble in lower alcohol and mass transfer between the two immiscible liquid is limited. The slow reaction rate of transesterification will increase the production cost of biodiesel which is also affecting increase in cost biodiesel as a fuel. Using non-edible oil such as castor oil can reduce the high cost of the feedstock because about 75% of production cost of biodiesel is come from feedstock alone. The slow reaction rate in transesterification reaction can be speed up by using reaction rate increasing technique such as microwave pre-treatment of oil and use rate enhancement agent such as phase transfer catalysis (PTC) along with conventional catalyst. In the current research work, in order to investigate transesterification of microwave pre-treated castor oil in the presence of alkaline PTC by using this two concept to utilize together. In order to design suitable transesterification reaction condition, chemical and physical properties of castor oil will be determined. The interaction and individual effects of transesterification reaction parameter will be study using design of experiment (DOE) software’s by using central composite design (CCD) of response surface methodology (RSM). After investigation of the optimum reaction condition and parametric effect for maximum yield will be established with the DOE tool.

# ACKNOWLEDGEMENT

First and foremost, In the name of Allah, the Most Beneficent, the Most Merciful. My first and most gratitude goes to my final year project supervisor, Dr. Sintayehu Mekuria Hailegiorgis who has been giving supervision, guidance, knowledge, time and support during the process of completing the final year project. A special thanks to chemical engineering department lab technician that help me a lot with all equipment and chemical in this project. Not forgetting also, my family and friends who are there to support me throughout the entire project completion. Last but not least, I would like to thank to Universiti Teknologi PETRONAS which have provide and equipped me with all the facilities to make this project a success.

# TABLE OF CONTENTS

## LIST OF FIGURES

## LIST OF TABLES

# ABBREVIATION AND NOMENCLATURE

NaOH : Sodium Hydroxide

KOH : Potassium Hydroxide

$H_2SO_4$ : Sulphuric Acid

MWHT : Microwave Heating Time

Wt. % : Weight Percent

w/wt. % : Weight per Weight Percent

℃ : Degree Celsius

% : Percentage

N : Normality

g : Gram

FAME : Fatty Acid Methyl Ester

FFA : Free Fatty Acid

min : Minute

cP : Centipoise

ml : Milliliter

rpm : Revolution per minute

J/g : Joule per gram

# CHAPTER 1

# INTRODUCTION

Nowadays, global energy consumption is rise that worrying us with increasing population and modernization. The total world energy demand in 2008 was 505 quadrillion British Thermal Unit (BTU) and its estimated will increase to 770 quadrillion BTU in 2035 this will become one of big concern all of the world because about 88% of world energy concern is based on fossil fuels. Moreover, in 2008 the world liquid energy consumption was 85.7 million barrels per day and its estimated will increase to 112.2 million barrels per day in 2035 (N. Yusuf *et al.*, 2011). As you know, fossil fuel is not permanent source and at this existing rate, it estimated that crude oil and natural gas will fully consume in another half century (Ong *et al.*, 2011).

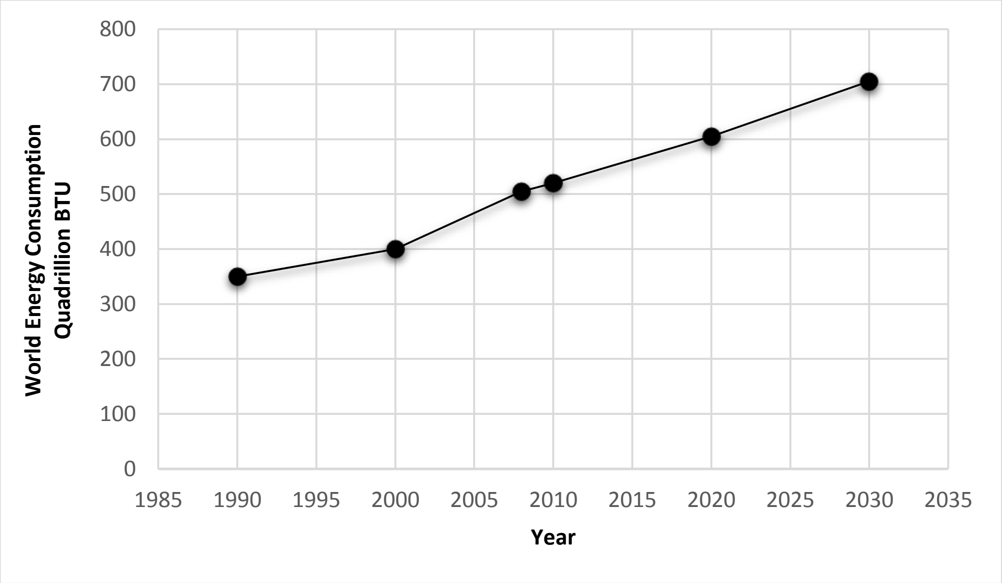


FIGURE 1.1 World energy consumption from 1990 to 2035 in quadrillion BTU (Chang *et al.*, 2012)

Furthermore, when increasing demand of energy from crude oil and natural gas, our environmental and ecosystem become polluted because of emission of greenhouse gases such carbon dioxide that release from combustion of fossil fuel in car engine. Emission of carbon dioxide in term used of energy is estimated will increase 30.2 billion metric tons in 2008 to 43.2 billion metric ton in 2035 (N. Yusuf *et al*., 2011). Therefore, with increasing emission of carbon dioxide it will causes such as global warming, glaciers, rising sea levels, melting of the polar ice caps and devastating weather patterns. Due to this concern, exploration of renewable fuels and chemical feedstock with zero net carbon dioxide emission is a must for sustainable development and one of the renewable fuels with zero net carbon dioxide emission is biodiesel.

Biodiesel can be one of alternative as a source of fuel replacing the common petroleum diesel fuel for diesel engines. Theoretically, biodiesel is produced by chemical conversion of animal fats or vegetable oils. Biodiesel was first develop by Rudolph Diesel in the early 1890s. During the time where the petroleum was not discovered yet, vegetables oils has been the commonly used and studied in the lab to produce biodiesel. The first public demonstration of vegetable oil as a base diesel fuel was conducted during the early 1900s, when the French government commissioned produce a diesel to run on peanut oil. After that, Rudolph Diesel did a further research on vegetable oil fuels and he believe in future that farmers could benefit by providing their own fuel. However this will take almost century to make the dream become true.

In 1940s, with petroleum discoveries and productions which the price is cheaper than production of biodiesel, diesel engines was changed due to match with properties of petroleum diesel fuel which is in lower viscosity. Therefore, the production of biodiesel were weakened in time and there is no significant effort were made to further discover the biodiesel full potentials. Increased demand for automobiles which used petroleum fuels make biodiesel to be forgotten. However in 1970s, speculation regarding the finite nature of the fossil fuel were arise and Organization of the Petroleum Exporting Countries (OPEC) was reduced oil supplies and increased the price because to meet with the shortage of petroleum crisis of that time.

Due to this crisis in 1979, South Africa start to commercialize the development on biodiesel by using a method of transesterification of sunflower oil and refined it to become more similar with petroleum diesel fuel. The result of the transesterification of sunflower oil has led to an important discovery of several sources and technologies which can improved diesel engine performance while reduced environmental impacts compared to petroleum diesel fuels with negative effect towards environment

Nowadays, many research was done by using various and cheap feed stock with various method of processing technique to produce a better and cheaper overall production cost of biodiesel.

## 1.1 Research Background

Due to the reasons of petroleum source become depleting over time and its known negative effects to the nature, biodiesel can be one of environmental-friendly alternative fuel to replace petroleum diesel fuel. Many research was done to produce a better biodiesel from a variety feedstock that make the overall production cost is low. Biodiesel was made from animal fats and vegetable oil as a feedstock by different several method. . Known for its high viscosity, lower volatility and high reactivity, vegetable oil cannot be used directly to existing diesel engine fuel. The problem that may be faced due to direct usage of vegetable oil in diesel engines are:

I. Cooking and trumpet formation on the injector
II. Oil ring sticking
III. Thickening and gelling of the lubricating oil
IV. Reduced power and fuel economy (Srivastava & Prasad, 2000)

To overcome the problem raised, different technique was used such as micro emulsion, dilution, pyrolysis and transesterification to modify chemical and physical properties of vegetable oil. However, transesterification is the most suitable method to lower the viscosity of vegetable oil or animal fats to produce biodiesel (Silitonga *et al.*, 2011).

Transesterification of vegetable oils is a reaction between of triglycerides which contain in vegetable oils or animal fats and alcohol to form ester as main product and glycerin as by product in the presence of catalyst (Leung *et al.*, 2010). There are many type of alcohol can used such methanol, ethanol, propanol and butanol but the most preferred alcohol is methanol because of it is the cheapest and available alcohol.

But when transesterification was conducted, it shown that not all the materials are readily mixed with each other. This is because the solubility of the two compound depends on existence of the OH groups. Compound that contain with OH group and not contain OH groups usually will not readily mixed. Therefore, the addition of catalyst will help to initiate transesterification reaction for producing biodiesel.

Generally, the selection types of catalyst depending on the type of vegetable oil and also operating parameter. There are several groups of catalyst that used in transesterification reaction process to synthesize biodiesel:

I. Homogenous alkaline catalyzed transesterification
II. Homogenous acid catalyzed transesterification
III. Homogeneous acid and alkaline transesterification (Two-step process)
IV. Heterogeneous alkaline and acid catalyzed transesterification
V. Enzyme catalyzed transesterification
VI. Non-catalyzed supercritical alcohol transesterification

As vegetable oil are sparingly soluble in lower alcohols, the reaction of transesterification is slower due to the limited mass transfer rate between two immiscible phases. Therefore, there are several techniques that have been done by researcher to enhance the reaction rate of the transesterification technique such as mixing, addition of co-solvent, higher temperature and pressure, super critical alcohol, ultrasonication and also microwave irradiation.

There are many type of vegetable oil was use as feed stock such as palm oil, castor oil, peanut oil, sunflower oil and etc. Currently, more than 95% of biodiesel was produced from edible oil source such as palm oil, sunflower oil and soybeans oil (Leung *et al*., 2010; Lin *et al.*, 2011).

However, the cost production of the biodiesel is quite high, which is about 75% of the biodiesel production is come from feedstock alone. This is because the competition between biodiesel industry and food processing industry that affecting the cost of production for both industry. Nowadays, researcher focus in non-edible and cooking oil as the feedstock because it has a potential to decrease the cost of biodiesel production compared to edible oil feedstock.

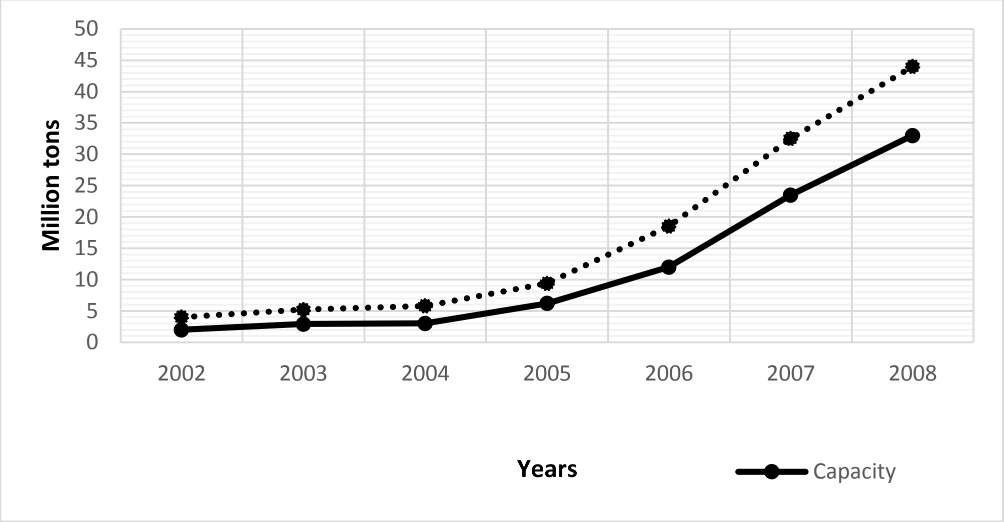


FIGURE 1.2 World biodiesel production and capacity from 2002 to2008 (Gude *et al.*, 2013).

The main purpose of this study will focused on the production of biodiesel by using transesterification technique by using microwave pretreatment method. Non-edible oil which is castor oil will be used in this study as the feed stock. Castor oil contain a high percentage of fatty acid which is more than 2%. This high percentage of fatty acid can cause saponification lead in affecting the yield of biodiesel and damage to diesel engines.

Therefore, firstly, the fatty acid in castor oil need to be lowered down. To lower down the fatty acid content, it need to react with acid which known as esterification technique. After that, the product will undergone transesterification technique. This step was called as homogeneous acid and alkaline transesterification (Two-step process).

## 1.2 Problem Statements

The production of biodiesel has been increase lately, this is due to increasing of petroleum price and also the environmental advantages. Due to increase in the price of the petroleum and the environmental concerns about the affect from car gases that can causes pollution, biodiesel become one of alternative method to overcome all the problems. There are different method of biodiesel production, with different kind of feedstock and also different type of catalyst being used to improve the reaction between triglyceride and alcohol

Nowadays, more than 95% of biodiesel is made from edible oil sources such as rapeseeds, soybeans, sunflower and crude palm oil. However usage of edible oils as a source of feedstock for biodiesel production not be cost efficient, as it is primarily used for food industry. Moreover, the use of edible oil as feedstock for biodiesel will compete with food industry, which will results in higher cost of production for both industry. It is necessary to keep the cost of production under control to make the biodiesel technology viable by using alternative cheap feedstock and effective environmental friendly reaction pathways which in this case the non-edible oil.

The production of biodiesel from castor oil is found to be one of good alternative to replace feedstock from edible oil due to reason of high cost of biodiesel production. Castor oil has a high viscosity which about tenth time higher than petro-diesel fuel, transesterification or methanolysis is the most promising method to lower the castor oil viscosity. Transesterification is a method by reacting the triglyceride in the castor oil with alcohol (methanol is being used) to produce biodiesel, but castor oil has high content of free fatty acid that will form soap. Therefore, reacting castor oil with acid before, will help to lower down the free fatty acid content in the castor oil.

## 1.3 Objectives

Based on the research background and problem statement described in the previous pages, the following are the objectives of this research:

I. To investigate transesterification reaction of castor oil and methanol in the presence NaOH as alkaline catalyst.

II. To investigate the effect of microwave pretreatment of castor oil on the rate and yield of methyl ester.

III. To study the individual and interaction effect of reaction variables and conduct parametric optimization of in situ transesterification of Castor oil.

## 1.4 Scope of Study

In the present research work, to achieve the affirmation research objectives, waste palm oils will be used as a source of non-edible oil sources and characterized to determine its physical and chemical properties. Oil purification from high free fatty acid will be conducted using esterification reaction. After esterification, the water formed during esterification will be removed from the purified oil. Transesterification reactions will be conducted to investigate the effect of reaction variables such as alcohol to oil ration, catalyst concentration, reaction temperature, mixing rate and reaction time on the yield of biodiesel. The interaction effect of reaction variables will be studied using statistical tools of response surface methodology (RSM) and optimum operating conditions will be established. Conversions of triglycerides with time at different reaction conditions will be measured to investigate the rate of reaction and order of reaction equations.

## 1.5 Relevancy of Project

Methanolysis of vegetable oils and parametric optimization is an important project because it discover the new source of renewable energy that replace fossil fuels that depleting nowadays which is in this case is replace the petroleum diesel. This issues become attraction to all of the world especially developed and industrialized that depend on fossil fuel source including Malaysia. Therefore, investigation to find an alternative and improve this problem is needed. This study will provide information for transesterification reaction rate of microwave energy pre-treated of castor oil.

# CHAPTER 2

# LITERATURE REVIEWS

## 2.1 Historical of biodiesel production from vegetable oils

Economic growth was measured by energy consumption per capita and also quality of livings. Pre-industrial revolution society at first was depend on animal strength and also agriculture for their energy needs. After that, energy source was come from combustion of wood and also biomass but it provide low efficiency of energy. However, in the era of industrial revolution in the late 18th century, combustion of coal was use because of released high efficiency of energy, and it was use as energy source for mechanical machine that use for industrial and transportation at that time. But later, when petroleum and natural gas was discover that contain more colorific value that enhance industrial and economic development. However, when economic development increasing, the number of vehicle on road also increasing, this was lead to a pollutants and greenhouse gases such as carbon, sulfur, and oxide of nitrogen that release by vehicles. Moreover, when use of fossil fuel sources increasing, another problem that arise is depletion of in fossil fuel that lead to unstainable energy source for long term period of energy supply. Therefore, many study was conduct by researcher to create efficient use of a renewable resources which is lead finding of biomass and vegetable oils as a renewable resources (Budau *et al.*, 2011; Knothe, 2012).

In early 1893, Rudolf Diesel was develop an engine that could run on vegetable oil as a source of fuel (Knothe, 2012). Unfortunately, due to high viscosity contain in vegetable oil, this was lead to poor performance of vegetable oil fuel compare to petroleum diesel. In 1912, Rudolf Diesel published an article related to vegetable oil as fuel resources which is “the use of vegetable oils for engine fuels may seem insignificant today, but such oil may become, in the course of time, as important as petroleum and the coal-tar products of the present time”

However, due to abundance source of petroleum fuel which have properties of low viscosity and also low cost production compared to vegetable oil fuel, diesel engine were modified because of to utilize petroleum diesel (Ma & Hanna, 1999).

As popularity of petroleum diesel was wide spread around the world, the fuel from vegetable oil based was received a less attention except when the energy shortage happen and high fossil fuel source prices (Lin *et al*., 2011). Therefore, in order to make a vegetable oil can run properly in diesel engine, a mechanism was required to decrease the viscosity of vegetable oil, so it can run on diesel engine. Many studies was done in order to reduce viscosity of vegetable oil such as pyrolysis, transesterification, blending with solvents etc. (Ma & Hanna, 1999; Sharma & Singh, 2008). Transesterification is one of the popular technique because of high yield of biodiesel. Transesterification is a reaction between triglyceride that contain in vegetable oils and alcohol in presence of catalyst.

Transesterification technique can convert vegetable oil into biodiesel which is it consist of three molecules of ester and a molecule of glycerol as a byproduct. This biodiesel less viscous and also suitable to use in existing diesel engine. First award for production of biodiesel was received in 1977 by Parante (Lin *et al*., 2011). At 1989, the first industrial-scale plant was established by an Austrian company, Gaskoks. Unfortunately, the economics of biodiesel production still unfavorable due to high cost of processing steps of vegetable oil and also high cost of vegetable oil itself. Furthermore, the quantity of vegetable oil that can produce a biodiesel is very less to been able replace entirely petroleum diesel.

Eventhough, presence of mercaptans or thiols in petroleum diesel is very useful to provide a lubrication for diesel engine operations, but it also can cause of pollution by emission oxides of sulfur. Nowadays, because of a bad environmental situation, a reduction of sulfur compound in petroleum diesel is necessary action (Knothe, 2012). It has been studies, by addition of small portion of biodiesel in petroleum diesel, the lubricity of sulfur free petroleum diesel can be restored. This method, can be complement usage of biodiesel with petroleum diesel and also it can lead in reduce pollution that cause by $SO_x$ emission. Another potential of using biodiesel, it has advantage in reducing the emission of $CO_2$. Eventhough, biodiesel have same or better performance as compared to petroleum diesel, but biodiesel is biodegradable, environmentally friendly and also it contain non-toxic (Srivastava & Prasad, 2000).

## 2.2 Different feedstock produce different yield of biodiesels

Production of biodiesel is can be produce by transesterification technique which is reaction between esters and lower alcohol. The ester that was used in transesterification is vegetable oil and fats which is contain of various fatty acid and glycerol. For alternative energy resources (I. M. Atadashi *et al.*,2010; Silitonga *et al.*, 2011) for producing biodiesel, vegetable oils and fats are available in wide ranges that enabling biodiesel as one of interesting alternative to replace petroleum diesel fuel. The planting of oil seeds was depend on climate, planting practice and soil conditions.

Vegetable oil can be divided by two categories, which is edible oils and another is non-edible oils. Production of biodiesel from edible oil such as palm, rapeseeds, sunflower, soybeans etc., received main attention because of the high cost due to competition with food processing industry. Basically, for produce biodiesel from edible vegetable oils it take about 75% of the biodiesel production cost for cost vegetable oil source itself (Lim & Teong, 2010; Silitonga *et al.*, 2011). Since increasing price of edible oils in current market due to competition for food industry, production of biodiesel from edible oil become limited. Therefore, choosing the cheapest feedstock is one of alternative to avoid high cost biodiesel production. Different feedstock will also produce different yielding capacity. Below table was shown that oil yield of different edible oil bearing plants.

TABLE 2.1 Oil yield of different edible oil crops (Leung *et al.*, 2010; Lin *et al.*, 2011; N. N. A. N. Yusuf *et al.*, 2011)

| **Type of oil** | **Oil yield (liter/hectare)** | **Oil yield (%)** |
|---|---|---|
| Palm | 5950 | 30-60 |
| Coconut | 2689 | 63-65 |
| Olives | 1212 | 38-46 |
| Rapeseed | 1059 | 45-55 |
| Sunflower | 952 | 25-35 |
| Soybeans | 446 | 15-20 |
| Corn | 172 | 48 |

By using non-edible as a source of feedstock such as castor, jatropha, used cooking oil, algae and animal fats can cut down the cost production of biodiesel and also can make technology economically viable. Basically, non-edible oils are not suitable for human used in food processing due to the presence of toxic compound in the oil such castor oil, jatropha, karanja, micro-algae, etc. Non-edible oil plantation cost lower compare to edible oil in terms of per kg (A. Kumar & Sharma, 2011). In table below, shows that the oil yield from in edible oil source in the order of volume and also percentage of oil in the oil bearing seeds.

TABLE 2.2 Oil yield of different edible oil crops (Leung *et al*., 2010; Lin *et al*., 2011; N. N. A. N. Yusuf *et al*., 2011)

| Type of oil | Oil yield (liter/hectare) | Oil yield (%) |
|---|---|---|
| Jatropha cursas | 1892 | Seed:35-40, kernel: 50-60 |
| Castor | 1413 | 45-50 |
| Pongamia pinnata | 225-250 | 30-40 |
| Rubber seed | 80-120 | 40-50 |
| Sea mango | N/A | 54 |
| Cotton | 325 | 18-25 |
| Karanja | 27-39 | - |
| Moringa oleifera | N/A | 35-40 |

## 2.3 Quality and Standard of Biodiesel

Production of biodiesel by using transesterification reaction does not reach 100% completion reaction, it reaches equilibrium state at certain point. The final product of transesterification reaction may contain other impurities such as fatty acid ester, monoglycerides (MGS), diglycerides (DGS), and triglycerides (TGS) and other minor impurities. Biodiesel standards limit components of biodiesel such as glycerol, MGS, DGS, TGS, residual alcohol (by limiting flash point), moisture contents, and FFA (by limiting the acid number).

However, from all these parameters the glycerol content in the final product of transesterification which is free glycerol, MGS, DGS, TGS and acid value are the most important parameters. Thus, according to ASTM D6751 limit that the free glycerol contain in the biodiesel is less than 0.2%, and the acid value is less than 0.5 mg KOH/g as shown in Table 2.3;

TABLE 2.3 ASTM D6751 and DIN EN 14214 biodiesel standard (Knothe, 2012)

| **Property** | **Unit** | **Standard Limit** | | **Test Method** | |
|---|---|---|---|---|---|
| | | **ASTM D6751** | **DIN EN 14214** | **ASTM D6751** | **DIN EN 14214** |
| **K.Viscosity at 40℃** | Mm$^2$/s | 1.9-6.0 | 3.5-5.0 | D445 | EN ISO 3104 |
| **Density at 15℃** | Kg/m$^3$ | - | 860-900 | - | EN ISO 3675 |
| **Flash Point** | ℃ | 130.0 min | 101.0 min | D93 | ISO CD3679c |
| **Acid Value** | Mg KOH/g | 0.80 max | 0.5 max | D664 | pr EN 14104 |
| **Free Glycerol** | % (m/m) | 0.020 max | - | D6584 | EN 14106 |
| **Monoglycerides** | % (m/m) | - | 0.8 max | - | pr EN 14105m |
| **Diglycerides** | % (m/m) | - | 0.2 max | - | pr EN 14105m |
| **Triglycerides** | % (m/m) | - | 0.2 max | - | pr EN 14105m |
| **Total glycerol** | % (m/m) | 0.240 max | 0.25 max | D6584 | pr EN 14105m |
| **Methanol** | % (m/m) | - | 0.2 max | - | pr EN 14101 |
| **Cloud point** | ℃ | - | - | D2500 | - |
| **Distillation T90AET** | ℃ | 360 max | - | D1160 | - |
| **Iodine value** | - | - | 120 max | - | pr EN 14111 |
| **Water and sediment** | % vol | 0.050 max | - | D2709 | - |
| **Water content** | mg/kg | - | 500 max | - | EN ISO 12937 |
| **Cetane number** | - | 47 min | 51 min | D613 | EN ISO 5165 |
| **Sulphated ash** | % (m/m) | 0.020 max | - | D874 | ISO 3987 |
| **Carbon residue** | % (m/m) | 0.050 max | 0.3 max | D4530 | EN ISO 10370 |
| **Sulfur (S 15 Grade)** | ppm | 0.0015 max | - | D5453 | - |
| **Sulfur (S500 Grade)** | Ppm | 0.05 max | - | D5453 | - |
| **Oxidation stability 110℃** | h | - | 6 | - | pr EN 14112 |

## 2.4 Castor seeds as source of biodiesel feedstock

One of the popular non-edible oil that used in biodiesel synthesis is castor oil. Ricinus communis or castor tree was grow in the wild in large quantity which is originated from East Africa, and its available at low cost because of it can naturalize in temperature and also tropic region all over the world (Danlami *et al.*, 2015). Nowadays, India is one of the largest exporter of castor oil in the world, and others major exporter is China and Brazil. Castor oil has been used for coating fabrics and other protective coverings and also other used is for textile dyeing (Bean, 2010).

Many non-edible oil was used in biodiesel production because of low cost production, one of the most popular oil that use in biodiesel synthesis is castor oil (Gui *e al.*, 2008). Average yield of castor oil seen from the tree is about 1.1 t $ha^{-1}$ and usually castor oil seed contain about 40-55% oil. Therefore, castor is one of the top plants that highest oil yield potential (Scholz & da Silva, 2008).

Castor Oil appearance is pale yellow colour, and clear liquid at room temperature (27°C) and also at 0°C it shown no solid fat content. Eventhough, vegetable oil is high in viscosity, castor oil is more viscous compare to natural vegetable oils. This is because of the hydrogen bonding of hydroxyl groups in the oil. Furthermore, the high percentage of the unsaturated fatty acid make the castor oil in liquid form eventhough at low temperature (Bean, 2010). Table 2.4 and Table 2.5 shows the characteristic castor seed oil and also fatty acids composition in castor seed oil.

TABLE 2.4 Characteristic of Castor seed oil (Bean, 2010)

| **Parameters** | **Value** |
|---|---|
| Lipid content (%) | 43.3 |
| Moisture content (%) | 0.2 |
| Iodine value (mg/g) | 84.5 |
| Acid value (mg/g) | 4.9 |
| % free fatty acid | 3.4 |
| Peroxide value (mg/g) | 10.2 |
| Saponification value (mg/g) | 182.9 |
| Unsaponifiable matter | 3.4 |
| Viscosity (cP) | 332 |
| Refractive index at 25°C | 1.47 |
| Average molecular weight | 937.7 |

TABLE 2.5 Fatty acids composition of castor seed oil (Bean, 2010)

| **Fatty Acid** | **Value** |
|---|---|
| Palmitic; $C_{16:0}$ | 1.3 |
| Stearic; $C_{18:0}$ | 1.2 |
| Oleic; $C_{18:1\ \omega\ 9c}$ | 5.5 |
| Linoleic; $C_{18:2\ \omega 6}$ | 7.3 |
| Linolenic; $C_{18:3\ \omega 3}$ | 0.5 |
| Ricinoleic; $C_{18:1\ \omega\ OH}$ | 84.2 |
| Saturated fatty acids (SFA) | 2.5 |
| Unsaturated fatty acids (UFA) | 97.5 |

Castor oil contain such a unique composition that lead to advantages of biodiesel production because of its viscosity about seven times higher than other vegetable oils (Banković-Ilić *et al.*, 2012). Water contain in castor oil might be higher than expected because castor oil is highly hygroscopic. Therefore, one of method that has proven effective to overcome this problem is mixing with petrodiesel which is 10% blend of castor oil to make sure the specification meet the standards (Atabani *et al.*, 2012). Basically, production of biodiesel from castor oil has been done and also its properties has been studies, which is usually by carried out the analysis of the reaction in the transesterification of triglyceride that contain in the oil. Production of biodiesel from castor oil is very useful in biodiesel industry because low cost production and also can produce biodiesel fuel that environmental friendly.

## 2.5 Biodiesel production by using microwave technology

Microwave irradiation is one of technology available for biodiesel production which is it rapidly introducing energy into chemical system that different from traditional method which is thermal heating. In organic synthesis application, microwave-assisted organic synthesis is one of application that received a main attention. Microwave transfer its energy in $10^{-9}$ seconds for every cycle of electromagnetic energy and approximately $10^{-5}$ seconds kinetic molecular relaxation from its microwave energy when during microwave heating. This was shows that energy transfer rate is faster that the molecules can relax and giving non-equilibrium condition and also high instantaneous temperature that result in unaffected the orientation of the collision for the kinetic of the system and microwave (Yadav & Bisht, 2004). A greater movement of molecules which can cause a greater number of magnetic collision will enhance with an instantaneous increase in temperature. A small molecule can be built in a fraction of time required in microwave heating by conventional thermal method. As a result, it has gained increasing acceptance as a popular heating medium tool among process development and research product.

An acceleration of chemical reaction that produce by microwave irradiation can causes a selective absorption of microwave energy by polar molecules. Efficient internal heat transfer that produce from microwave irradiation will result in constant distribution and heating throughout sample compared to the traditional heat transfer that happen when a water or oil bath is applied as energy source (Nagariya *et al*., 2010). The study on microwave as heating source for biodiesel production was received a great attention since mid-1980s (Lidström *et al.*, 2001). By using the microwave irradiation many organic reaction were dramatically enhance. Many different research was done on microwave heating system, one of the study is stated that the microwave it is efficient method of heat supply which the reaction happen rapidly, safely and most important in production of biodiesel if high of product yields (Larhed *at al.*, 2002).

### 2.5.1 A basic mechanism in microwave heating

The microwave radiation part is located between infrared radiation and radio-wave in the electromagnetic spectrum. Usually, microwave frequencies is between 0.3 GHz and 300 GHz, it depend on the wavelength between 1 millimeter and 1 meter, respectively. A frequency 2.45 GHz is preferred for used in laboratory, this is because at this frequency has the right penetration depth for laboratory reaction conditions. Therefore, for heating mechanism, all domestic and commercial equipment use frequency at 2.45 GHz (Hernando *et al.*, 2007).The basic mechanism of microwave heating involve ions that oscillate electric or magnetic field or agitation of polar molecules. Particle will try to orient in phase with the field or orient themselves in the presence of oscillating field. The resisting forces restrict the motion of the particle (inter-particle interaction and electric resistance), which generate random motion and also restrict motion of the particle, it will producing heat (Lidström *et al*., 2001; Yadav & Bisht, 2004). Microwave radiation response to different material is different. Material can be classified based on their response to microwave radiations as material that can be transparent to microwaves for example sulfur. Other classified material based on their response to microwave radiations is material that reflect microwave such as copper and also material that absorb microwave such water. The only material that used in microwave chemical processes is material that absorb microwaves. These material can be conducted via polarization, interfacial polarization or conduction mechanism by microwave heating (Taylor *at al.,* 2005).

TABLE 2.6 Spectrum of electromagnetic radiation (Taylor *et al.*, 2005)

| Region | Wavelength (Angstroms) | Wavelength (centimeters) | Frequency (Hz) | Energy (eV) |
|---|---|---|---|---|
| Radio | $>10^9$ | >10 | $<3\times10^9$ | $<10^{-5}$ |
| **Microwave** | **$10^9$-$10^6$** | **10-0.01** | **$3\times10^9$ – $3\times10^{12}$** | **$10^{-5}$ – 0.01** |
| Infrared | $10^6$ - 7000 | 0.01 - $7\times10^{-5}$ | $3\times10^{12}$ – $4.3\times10^{14}$ | 0.01 - 2 |
| Visible | 7000 – 4000 | $7\times10^{-5}$ - $4\times10^{-5}$ | $4.3\times10^{14}$ – $7.5\times10^{14}$ | 2 – 3 |
| Ultraviolet | 4000 – 10 | $4\times10^{-5}$ – $10^{-9}$ | $7.5\times10^{14}$ - $3\times10^{17}$ | 3 – $10^3$ |
| X-Rays | 10 – 0.1 | $10^{-7}$ – $10^{-9}$ | $3\times10^{17}$ - $3\times10^{19}$ | $10^3$ – $10^5$ |
| Gamma Rays | < 0.1 | $<10^{-9}$ | $3\times10^{19}$ | $>10^5$ |

A process in which heat is generated in polar molecule on exposure is called dipolar polarization which is to oscillating electromagnetic field of appropriate frequency. While exposed to oscillating electromagnetic field, polar molecule will combine with themselves in phase with the filed. The random motion of particle is because of the polar molecules experience inertia forces and are restricted to follow the field. The random particle that experience inertia force, the interaction between of particle will generate heat. Basically, to allow adequate inter-particle interactions, the frequency range of oscillating field need to be appropriate. If the frequency range is high, it will causes inadequate inter-particle interactions, this is because inter-molecule force will stop the motion of the polar molecule before it tries to follow the field. However, if the frequency range is low, polar molecule get enough time to arrange itself in phase with the field. Hence, no random interaction takes beside itself in phase with the filed (Taylor *et al.*, 2005). Microwave radiation is a perfect choice for heating organic reactants because it has suitable frequency to oscillate polar particle and it can make enough for particle interaction.

### 2.5.2 Transesterification reaction assisted by microwave heating

The function of microwave irradiation is to enhance transesterification reaction rate that recently used by many different investigators. The effect of by using microwave irradiation is to increase the rate of reaction and also it can obtain product yield in short time compared to other heating method (R. Kumar *et al.*, 2011; Patil *at al.*, 2011). The increasing rate of transesterification reaction is because microwave irradiation heating process can increase the solubility of oil and alcohol, it also can increase the conversion of triglycerides. Easy separation of the biodiesel in very short time is also one of advantage microwave heating process (Azcan & Danisman, 2008; R. Kumar *et al.*, 2011). Fundamentally, many studies was done by researcher that shows biodiesel synthesis under microwave irradiation is one of the method that have potential to increase the rate of reaction and most important in biodiesel production is obtain high quality yield of the biodiesels.

## 2.6 Transesterification of biodiesel by Methanol

Transesterification of biodiesel is a chemical reaction between triglyceride that contain in the vegetable oil or animal fats and alcohol to form ester as a biodiesel and the by product for this chemical reaction is glycerol (Lam *at al.*, 2010). Transesterification by using Methanol as an alcohol in the reaction is called Methanolysis. Methanolysis is a chemical reaction that involve of triglyceride and methanol in present of catalyst that will produce methylester (biodiesel) and glycerol.

Methylester have a one-third of molecular weight compare to its feedstock molecule and the viscosity of methylester approximately double petroleum diesel fuel instead the origin viscosity of the feed stock is 10 times or more compare to the methylester. Moreover, the physical characteristic of methylester is most likely same as petroleum diesel fuel. In methanolysis of vegetable oils, the stoichiometric of the reaction is one mole of the triglyceride will react with three moles of methanol to produce three moles of methylester and one mole of glycerol.

The reaction step is start with formation of diglycerides and after that is formation of monoglycerides, and the last step in the methanolysis of vegetable oils is formation of glycerol (Lotero *et al*., 2005). The reaction step was illustrate in Figure 2.1. Since, methanolysis is an equilibrium reaction, large amount of excess methanol is needed to shift the equilibrium toward formation of methylester and glycerol.

## 2.7 Transesterification Reaction Assist by Phase Transfer Catalyst (PTC)

Phase Transfer Catalyst (PTC) appear as a promising and important approach to mass transfer limitations during integration of the organic products. In order to transfer one of the reactant to the somewhere it can rapidly react with another reactant, PTC is used as a phase transfer agent in catalytic amount. Transfer one of the reactant to location where it can rapidly reacts, it's depend on ability of phase transfer agent to assist the phase with the past phase where the other reacting agent exist. By using PTC, it is possible to bringing the reaction between two reagents together which is originally in different phases. During reaction of PTC, it is also necessary to note that transferred reagent is in active condition for effective catalytic action (I. Atadashi *et al.*, 2010; Silitonga *et al*., 2011).

Eventhough, PTC is widely used in order to enhance the reaction of two or more immiscible reactants for synthesis organic chemicals but it is not fully exploited as a rate of enhancement agent in production of biodiesel except conducted by (Hailegiorgis *et al.*, 2013). PTC as an enhancement agent in for synthesis biodiesel was reported that it can increase the rate of reaction compare to reaction without using PTC. However, due to extraordinary ability of PTC to increase the solubility of two immiscible reactant, it can be used in catalytic quantity, its wide availability, the used of PTC to enhance the rate of transesterification reaction needs further detail research to develop suitable reaction mechanism and reaction properties (I. Atadashi *et al.*, 2010; Silitonga *et al*., 2011).

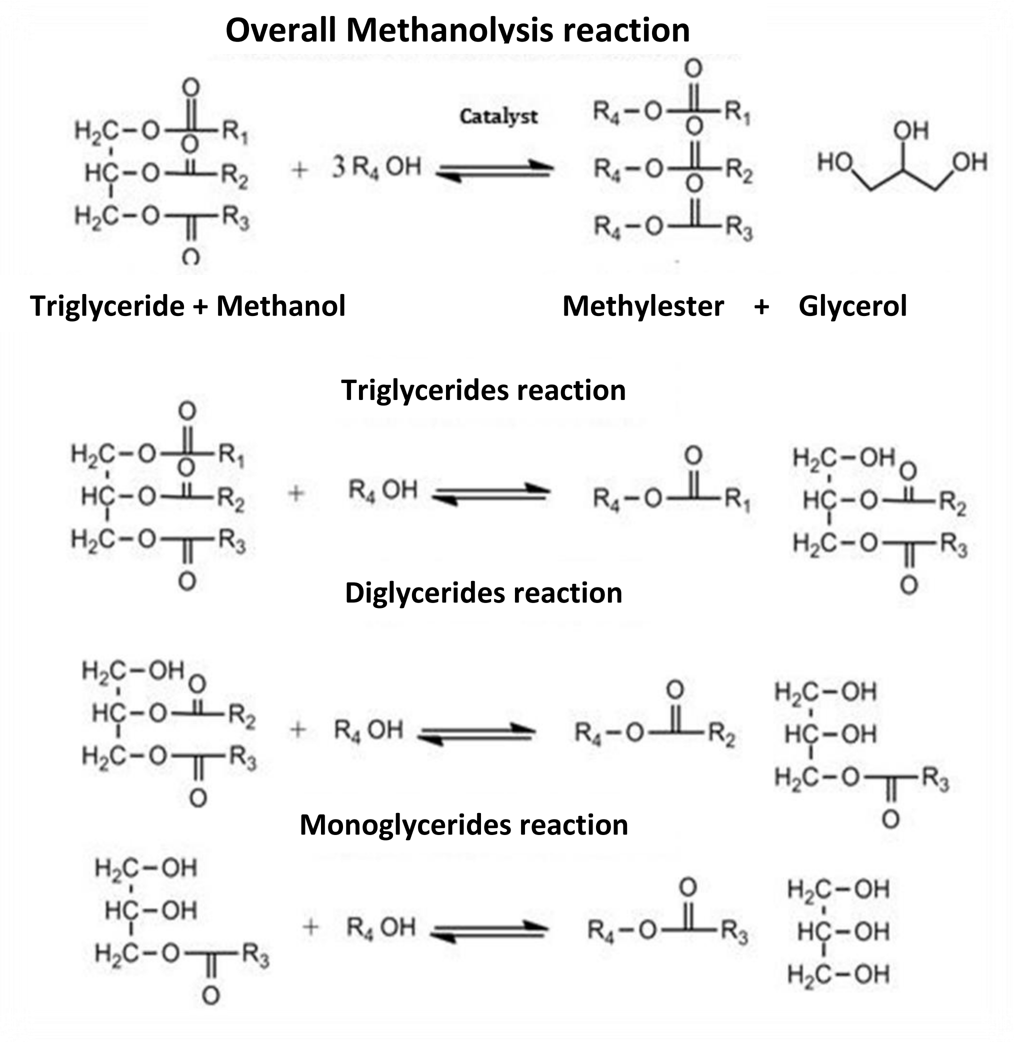


FIGURE 2.1: Formation of Methylester and Glycerol

# CHAPTER 3

# METHODOLOGY

## 3.1 Project Activities

**Literature Review**

- Further understanding on the concept of esterification and transesterification reaction of castor oil is carried out.
- More review on the literature in done to understand more about mechanism and effect of microwave pre-treatment on transesterification reaction.

**Experiment**

- Experiment was design for transesterification experiment with the microwave pre-treatment and without using microwave.
- Design of Experiment (DOE) was use in order to optimize the biodiesel yield.
- The results for both experiment is collected after the transesterification experiment is conducted with and without microwave pre-treatment.

**Data Collection**

- From the experiment conducted, the biodiesel is withdrawn, measured and the biodiesel yield was calculate.
- The data that collected from the experiment is entered into the DOE software in order to develop the model that predict the yield of biodiesel at the design reaction.

**Conclusion**

- The transesterification experiment will be concluded based on the result that gain at the end of the experiment.
- The dissertation report of the whole experiment was prepare.

FIGURE 3.1 Project Activities

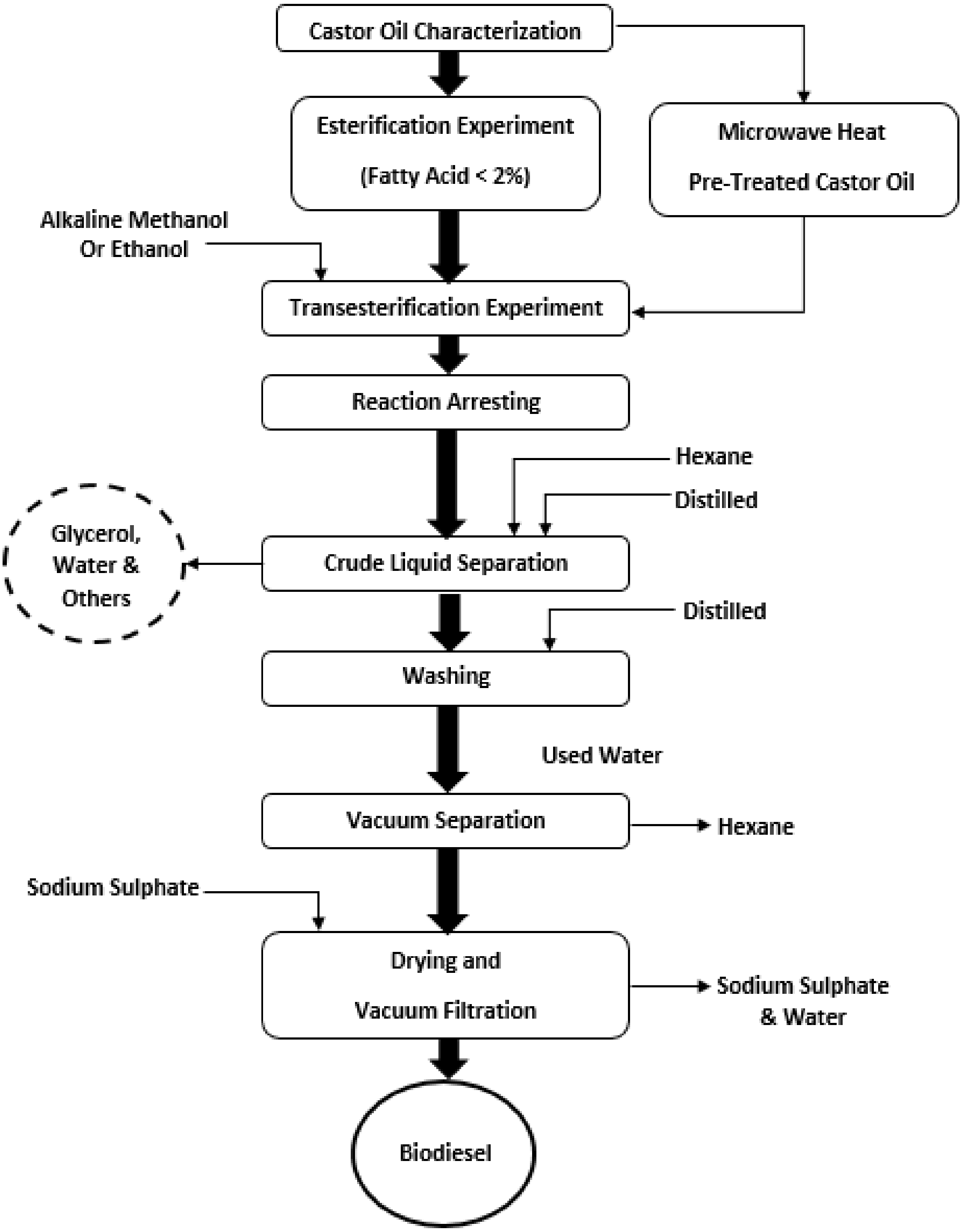


FIGURE 3.2 Work flow of the project

## 3.2 Key Milestone

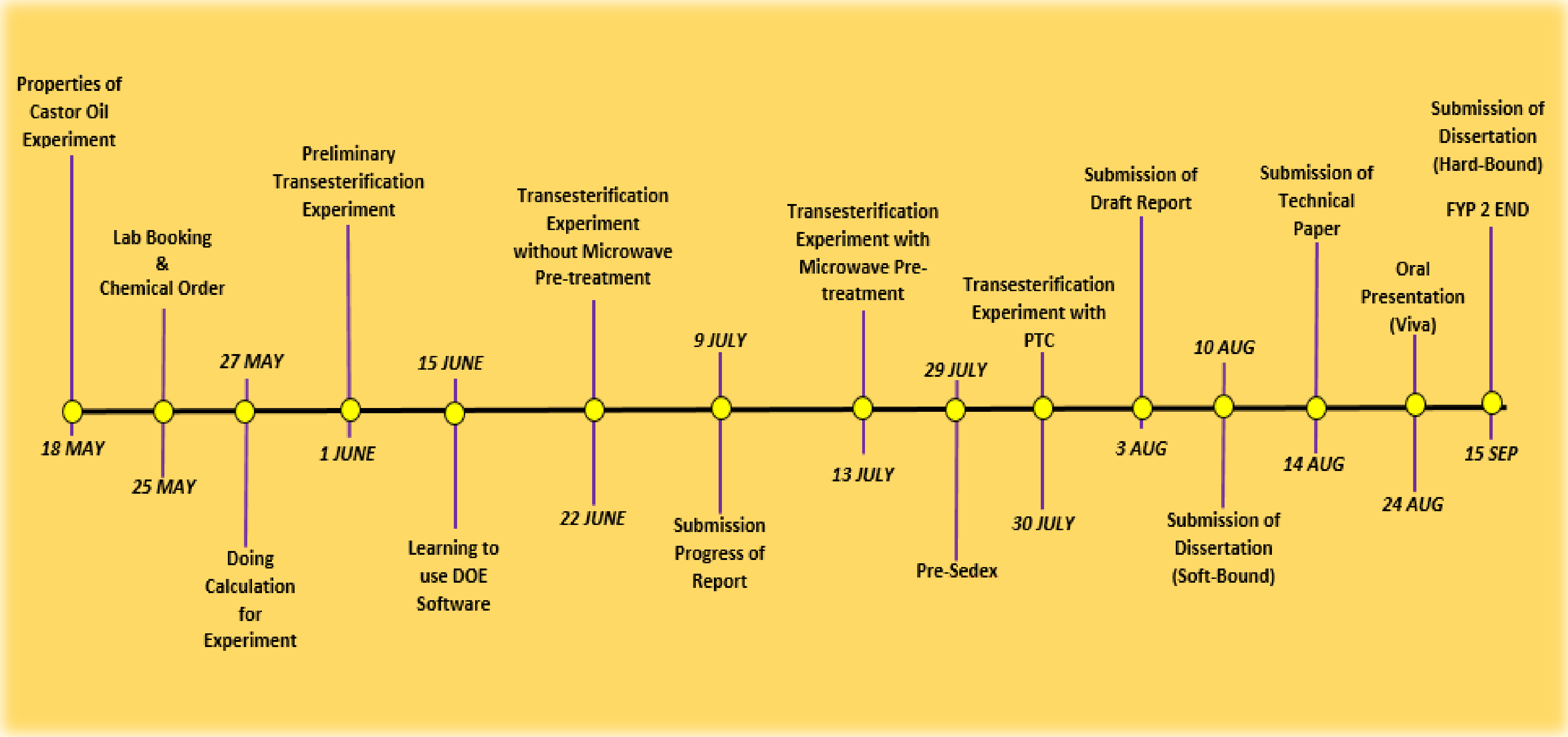


FIGURE 3.3 Key Milestone

### 3.2 Gantt Chart

| **No.** | **Details** | **Week** | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | **1** | **2** | **3** | **4** | **5** | **6** | **7** | | **8** | **9** | **10** | **11** | **12** | **13** | **14** | **15** |
| **1** | Castor oil Properties Experiment | 🟪 | | | | | | | **MID-SEM BREAK** | | | | | | | | |
| **2** | Preliminary Transesterification Experiment | | 🟪 | 🟪 | 🟪 | 🟪 | 🟪 | 🟪 | | | | | | | | | |
| **3** | Submission of Progress Report | | | | | | | | | ● | | | | | | | |
| **4** | Transesterification Experiment | | | | | 🟪 | 🟪 | 🟪 | | 🟪 | 🟪 | 🟪 | 🟪 | 🟪 | | | |
| **5** | Pre-Sedex | | | | | | | | | | | | ● | | | | |
| **6** | Submission of Draft report | | | | | | | | | | | | | ● | | | |
| **7** | Submission of Dissertation (soft-bound) | | | | | | | | | | | | | | ● | | |
| **8** | Submission of Technical Paper | | | | | | | | | | | | | | ● | | |
| **9** | Oral Presentation (Viva) | | | | | | | | | | | | | | | ● | |
| **10** | Submission of Dissertation (hard-bound) | | | | | | | | | | | | | | | | ● |

● Suggested milestone

🟪 Process

## 3.3 Materials and Chemicals

Castor oil sample was purchased from Best Formula Industries located at Jalan Batu Estates, Off Jalan Segambut, Kuala Lumpur, Malaysia. A sample of 5 liters of castor oil were bought and stored under room temperature. Other chemicals that used for transesterification process, pro-analysis chemicals, alkaline catalyst, acid catalyst, and standard chemicals for transesterification of biodiesel analysis in gas chromatograph are shown in Table 3.1;

TABLE 3.1 Standard Chemicals for Transesterification of Biodiesel

| Description | Purity | Supplier |
|---|---|---|
| **Alcohol** | | |
| Methanol | ≥ 99.7% | N/A |
| Ethanol | ≥ 99.7% | |
| **Catalyst** | | |
| Sodium hydroxide | ≥ 99% | Merck Chemical |
| Cetyltrimethylammonium bromide | ≥ 99% | Sigma Aldrich |
| **Pro-analysis chemicals** | | |
| Iso-propanol | ≥ 99.8% | Merck Chemical |
| N-hexane | ≥ 99% | |
| N-heptane | ≥ 99.5% | |
| Potassium hydroxide | 0.1 N | |
| Iodine | ≥ 99.99% | |
| Sodium sulphate | ≥ 99% | |
| α-Naphtholphthalein | ≥ 99% | |
| Acetic acid | Reagent Grade | |
| Diethyl ether | Reagent Grade | |
| **Reference standards kit for GC** | | |
| 1,2,4 butanetriol | GC Grade | |
| Tricaprin | GC Grade | |
| Glycerin | GC Grade | |
| Monoolein | GC Grade | |
| Diolein | GC Grade | |
| Triolein | GC Grade | |
| N-Methyl-N-trimethylsilytrifluoroacetamide (MSTFA) | GC Grade | |
| Pyridine | ≥ 99% | |

## 3.4 Experiment Methodology

### 3.4.1 Determination of Acid Value for Castor Oil

This experiment is to determine the FFA content in castor oil sample before undergo transesterification reaction. The FFA in the sample must be below 2% to ensure that no soap will formed during the transesterification process. The standard procedure for this test is follow the AOCS Official Method Cd 3d-63. The acid number can be calculated by AOSC Official Method cd 3d-63, revised 2003, which is calculated as below;

$$\text{Acid Value, mgKOH/g} = (\mathrm{A} - \mathrm{B}) \times \frac{\mathrm{N} \times 56.1}{\mathrm{w}} \quad (1)$$

Where: A = KOH solution required for titration of the sample, (ml)

B = KOH solution required for titration of the blank, (ml)

N = Normality of standard alkali KOH solution (mol/l)

w = The amount of sample used, (g)

Apparatus

1. Erlenmeyer flask – 250ml
2. Magnetic stirring device
3. Burette – 10ml, graduated in 0.05ml divisions with a tip drawn to a fine opening.
4. Analytical balance – accurate to 0.0001.

Reagent

1. Potassium hydroxide (KOH), 0.1N – Reagent Grade KOH having a carbonate specification of 0.5% Max, or 0.1N KOH with NIST traceable standardization to ±1 part in 1000 in water, methanol or ethanol.

2. Solvent mixture consisting of equal parts by volume of isopropyl alcohol and toluene. The mixture must give a distinct and sharp endpoint with phenolphthalein in the titration.
3. Phenolphthalein indicator solution – 1% in isopropyl alcohol.

Procedure

**a) Prepare standard solution (KOH with 0.1N reagent grade)**

Molar Mass of KOH = 56.1 g/mol, therefore, 1 mol of KOH = 56.1 g

$$\text{Normality} = \frac{\text{gram of solute}}{\text{amount solvent} \times \text{e.w}} \tag{2}$$

$$\text{e. w} = \frac{\text{Molecular weight of KOH}}{\text{valence } \bar{\text{e}}} = \frac{56.1}{1} = 56.1$$

$$\text{Gram of solute} = 0.1\text{N} \times 1000\text{ml} \times 56.1$$

$$= 5.61\text{g of KOH needed in 1L of water}$$

Therefore, for 250ml of water the amount of KOH needed is 1.4g.

**b) Prepare solvent**

The solvent needed in this experiment is 125ml of the neutralized solvent mixture which is contain 62.5ml of Isopropyl alcohol and 62.5ml of Toluene and about 2ml of Phenolphthalein.

1. Add the indicator solution to the required amount of solvent which is in ratio of 2ml of phenolphthalein to 125ml of KOH solution and after that neutralize it with alkali to a faint but a permanent pink colour.
2. By referring Table 3.2, the mass of castor oil was determine according to the acid value given.

TABLE 3.2 The mass of Castor oil according Acid Value

| **Acid Value** | **Mass, g of sample (±10%), g** | **Weighing accuracy ±g** |
|---|---|---|
| 0 – 1 | 20 | 0.05 |
| 1 – 4 | 10 | 0.02 |
| 4 – 15 | 2.5 | 0.01 |
| 15 – 75 | 0.5 | 0.001 |
| 75 and over | 0.1 | 0.0002 |

3. Weighed the specific amount of a well-mixed of castor oil into erlenmeyer flask and after that, 125ml of the prepare standard solution is added into the erlenmeyer flask that contain castor oil and make sure that the sample is completely dissolved before going to next step.
4. The sample that was prepared is titrated with the prepared KOH solution and need to shake vigorously until first permanent pink colour appear for 30s.
5. After the titration with the KOH solution, the blank titration is need to be done which is titration of KOH solution without castor oil.

### 3.4.2 Determination Specific Gravity and Density of Castor Oil

1. A 50 ml beaker was weigh on the weighing balance and the weight was record.
2. Pour 10ml of castor oil into the weighed beaker and weigh the beaker that contain castor oil.
3. Record the weight of the beaker with the castor oil. The density is calculated by using equation below;

$$\text{Density} = \frac{\text{Mass of beaker with oil (g)} - \text{Mass of beaker without oil(g)}}{\text{Volume of the oil (ml)}} \qquad (3)$$

4. To get the value of specific gravity of castor oil, the value of gravity is divided by density of water which 1g/m.

### 3.4.3 Determination Viscosity of Castor Oil

This experiment objective is to find out the viscosity of the castor oil before going to next step which is transesterification reaction.

Procedure

1. Turn on the switch that indicate ON button, which is located on the rear base of the console and after a few second the main screen will be displayed.
2. Select the number of spindle and after that attach to the console. Set the spindle number according state on the spindle and set the temperature to 50℃ and 20rpm.
3. Lower the handle and place the cone into the plate and after that lock the handle to its lowest position. Wait for around to ten minutes in order to make the cone equilibrium with the temperature of the plate.
4. Raised the handle of the console and place the castor oil sample into the plate that below the cone for measured. Lower the handle slowly towards the plate and be caution, do not put the spindle forcedly into the plate. The castor oil sample must be completely cover the face of the spindle and need to extend beyond the edge of the spindle about approximately 1.0mm.
5. Allow the spindle, plate, and castor oil sample to equilibrate to the set temperature of the control setting.
6. Set the run time to two at the console in order to rotating the spindle. Press the RUN key at the console and execute the viscosity measurement, read the result of the castor oil sample test.

### 3.4.4 Determination of the Calorific Value of Castor Oil using Bomb Calorimeter.

Procedure

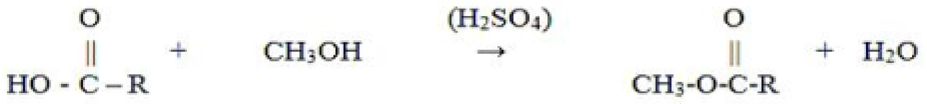
1. Switched on the system and you have acknowledged the opening screen with OK sign and it requires about 30 minutes until the temperature in stable conditions are prevalent in the measurement cell. Open the system menu then call sample. Enter the weight of the sample then call OK.
2. Prepare the decomposition vessel and the decomposition vessel must be clean and dry.

3. Suspend the decomposition vessel into the open measurement cell cover until it reaches the stopper. The message Bomb ↓ on the bottom line of the screen changes to a display of the function key assignment Start. If the function key assignment Start does not appear, check the ignition wire of the decomposition vessel.
4. Activate the Start and the measurement of cell cover is closes. The decomposition vessel is then filled with the oxygen and after that, the inner vessel is filled with water.
5. The sample is ignited and the change in the temperature of the inner vessel over time is recorded. After that, wait until the system displays the result of the experiment on the screen.
6. The decomposition vessel is vented and the measurement cell cover opens and as the message Bomb ↓ appears, remove the decomposition vessel and open it.
7. Check the crucible for combustion residue and for both cotton thread and the fuel sample must have been burned completely. The experiment need to be repeated if there are any sign of incomplete combustion.

### 3.4.5 Esterification of Castor Oil

1. The apparatus was setup as shown in figure below.
2. The reaction is carried out in 250ml of two neck flask, where the neck is for thermometer and reflux condenser.
3. Weigh the castor oil about 50g and put into the reactor flask.
4. A magnetic stirrer was placed into the reactor flask and was set the speed is 350 rpm.
5. The heat was turn on and allowed the temperature of the castor oil reach 70℃ - 80℃.
6. When the temperature reach to desired temperature put the methanol about 6ml to 7ml and leave about 5 minutes.
7. After that, put 0.8ml of $H_2SO_4$ and leave for 60 minutes.
8. After 60 minute, the reacted oil is place into separation funnel for separation of the castor oil and water.

9. Dispose the water from the separating funnel.
10. After that, put the remaining castor oil from the separating funnel into beaker and heat the castor oil about 100℃ to 150℃ to remove the excess water and also other impurities.
11. After that, the castor oil will be used in the transesterification reaction.



$$HO-\overset{\overset{O}{\|}}{C}-R + CH_3OH \xrightarrow{(H_2SO_4)} CH_3-O-\overset{\overset{O}{\|}}{C}-R + H_2O$$

FIGURE 3.2 Esterification of Free Fatty Acid

### 3.4.6 Transesterification of Castor Oil

### A) Catalyst Preparation Procedure

- **Sodium Hydroxide (NaOH) – 1.5% w/wt to oil**

1. The NaOH tablet was crushed into fine grain.
2. Weigh the crush NaOH about 0.15g on a weighing balance and placed into the beaker.
3. Based on 1:9 methanol oil ratio, 4.25 ml of methanol was pour into the beaker that contain the 0.15g of NaOH.
4. Mixed the solution well and now it's ready to use for transesterification experiment.

- **Cetyltrimethylammonium Bromide ($C_{19}H_{42}BrN$) – 0.5% molar ratio to NaOH**

1. Weigh 0.456g of cethyltrimethylammonium bromide and mix with 1% w/wt of prepared NaOH catalyst.
2. Mix the solution well and now it's ready to use for transesterification experiment.

**B) Transesterification process without phase transfer catalyst.**

12. The apparatus was setup as shown in figure below.
13. The reaction is carried out in 250ml of two neck flask, where the neck is for thermometer and reflux condenser.
14. Weigh the castor oil about 10g and put into the reactor flask.
15. A magnetic stirrer was placed into the reactor flask and was set the speed is 300 rpm.
16. The heat was turn on and allowed the temperature of the castor oil reach 50℃ (based of the desired temperature).
17. When the temperature reach to desired temperature put the prepared NaOH catalyst.
18. As soon as the NaOH catalyst is put into reactor flask, set the time to 30 minute (based on desired reaction time).
19. After the reaction time, the reacted oil is place into separation funnel for separation of the biodiesel and glycerol.
20. The biodiesel is washed with warm water (50℃) until a clear solution is seen at the bottom of the biodiesel layer.
21. If the biodiesel is not separate properly, pour about 40ml of N-hexane.
22. The bottom layer which contain water is removed from the separation funnel.
23. The biodiesel produce from the transesterification process, is the extracted and heated up to 120℃ in a dryer for 30 minute.
24. The FAME yield of the dried biodiesel oil is then calculated by weight.
25. The experiment is repeat according to the response surface methodology experiment that was designed.

**C) Transesterification process with phase transfer catalyst.**

1. The experiment was setup according the figure below.
2. The reaction is carried out in a 250 ml of two neck flask, where the neck is for reflux condenser and thermometer.
3. Weigh the castor oil about 10g and put into the reactor flask.
4. A magnetic stirrer was placed into the reactor flask and was set the speed is 300 rpm.

5. The heat was turn on and allowed the temperature of the castor oil reach 50℃ (based of the desired temperature).
6. When the temperature reach to desired temperature put the prepared PTC.
7. As soon as the PTC catalyst is put into reactor flask, set the time to 30 minute (based on desired reaction time).
8. After the reaction time, the reacted oil is place into separation funnel for separation of the biodiesel and glycerol.
9. The biodiesel is washed with warm water (50℃) until a clear solution is seen at the bottom of the biodiesel layer.
10. If the biodiesel is not separate properly, pour about 40ml of N-hexane.
11. The bottom layer which contain water is removed from the separation funnel.
12. The biodiesel produce from the transesterification process, is the extracted and heated up to 120℃ in a dryer for 30 minute.
13. The FAME yield of the dried biodiesel oil is then calculated by weight.
14. The experiment is repeat according to the response surface methodology experiment that was designed.

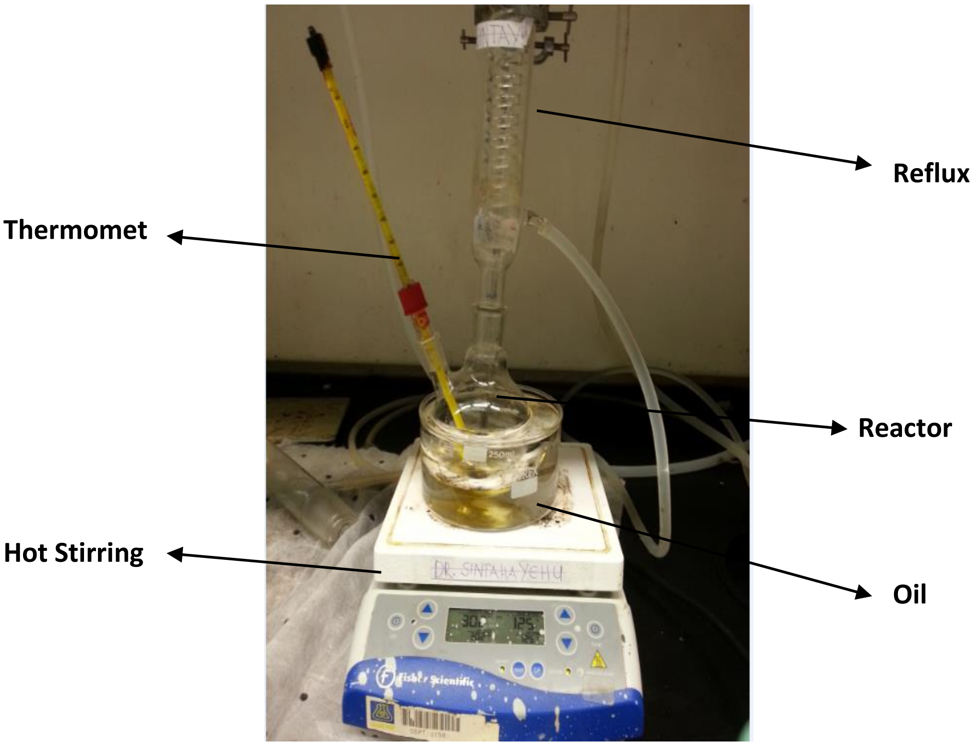


FIGURE 3.3 Batch Reactor for In-situ Transesterification of Castor Oil

### 3.4.7 Statistical Experimental Design for investigating the individual and cross effect of reaction variables to determine optimum operating conditions

Identification of optimum operating condition using conventional method was near impossible due to cross influence of different variables. The use of statistical method can be advantages in understanding interaction among process variables with minimum number of experiments that need to be performed and find the optimal condition. The response surface methodology (RSM) is one of software that widely used as statistical tool for experimental design and identification of optimal condition. In the present study of central composite design (COD) technique of RSM was used for experimental design to investigate the individual and interaction effects of reaction variables and to determine the optimum reaction condition for microwave as well as microwave heat pretreated transesterification of castor oil.

The experimental results were fitted using polynomial quadratic equation in order to correlate the response surface variables. The general form of the polynomial quadratic equation shown in equation (3.4) was used to develop a model that predicts the yield of alkyl esters (FAME) at designed reaction variables combination.

$$\mathrm{Y_i} = \beta_\mathrm{o} + \sum_{\mathrm{i}=1}^{\mathrm{k}} \beta_\mathrm{i} X_i + \sum_{i=1}^{k} \beta_{ii} X^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} X_i X_j \tag{4}$$

*Where:* $Y_i$ *is the predicted response and* $X_i$ *is the input variables for BTMAOH concentration, NaOH concentration, and volume of alcohol, reaction temperature and time. The term* $\beta_o$ *is the offset term (intercept),* $\beta_i$ *is the linear terms,* $\beta_{ii}$ *is the squared terms and* $\beta_{ij}$ *is the interaction terms and* $X_j$ *is the cross term to represent two-parameter interactions.*

The variable $X_\mathrm{i}$ was coded according to equation (3.5)

$$x_i = \frac{X_i - X_i^*}{\Delta X_i} \tag{5}$$

*Where: $x_i$ is the coded value of the $i^{th}$ variable, $X_i$ is the natural value of the $i^{th}$ variable, $X_i$* is the central value of $X_i$ in the investigated area, and $\Delta X_i$ is the step size.*

# CHAPTER 4

# RESULTS AND DISCUSSIONS

## 4.1 Properties of Castor Oil

### 4.1.1 The Determination of Acid Number

The free fatty acid composition of castor oil for this research work mostly composed of oleic acid and stearic acid. Thus according to AOCS Official Method Cd 3d-63, acid value need to be divided by 1.99 and 2.81 to obtain the free fatty acid (FFA) value. From the literature review, it was stated that the FFA content is high which 3.9%. This is a not a good condition in producing biodiesel because the presence of high FFA in vegetable oil can cause the formation of soap and this will happened during the alkaline catalyst will partially neutralized the FFA in the oil producing soap thus it will reducing the biodiesel yield during transesterification reaction. Several studies reported that FFA content in vegetable oil must be less than 2% to undergo transesterification reaction (He, 2015). As the FFA content in castor oil is high, therefore two-step transesterification reaction is required. Castor oil need to be undergo esterification reaction in order to reduce the FFA content before can proceed to transesterification reaction.

**First Experiment**

Mass KOH = 1.4011 g

Mass of castor oil = 20.014 g

A = volume of standard alkali used in titration

= 5.8 ml

B = volume of standard alkali used in blank titration

= 2.9 ml

Acid Value = $\frac{(A-B)\times N\times 56.1}{W}$

$$= \frac{(5.8-2.9)\text{ml}\times 0.1\text{N}\times 56.1}{20.014\text{ g}} = 0.813$$

**Second Experiment**

Mass KOH = 1.4009 g

Mass of castor oil = 20.021 g

A = volume of standard alkali used in titration

= 5.6 ml

B = volume of standard alkali used in blank titration

= 2.6 ml

Acid Value = $\frac{(A-B)\times N\times 56.1}{W}$

$$= \frac{(5.6-2.6)\text{ml}\times 0.1\text{N}\times 56.1}{20.021\text{ g}} = 0.841$$

Average of Acid Value = $\frac{0.841+0.813}{2} = 0.827$

** The experiment must be run at least three times but because of insufficient chemical it was run only in two times.*

### 4.1.2 The percentage of Free Fatty Acid (FFA)

$$\text{FFA }\% = \frac{\text{Acid value}}{\text{K}} \tag{6}$$

*Where: Oleic Acid = 1.99 and Stearic Acid = 2.81*

Total = 1.99 + 2.81 = 4.8

Oleic Acid $= \frac{1.99}{4.8} = 0.4146 \times 1.99 = 0.825$

$\text{Stearic Acid} = \frac{2.81}{4.8} = 0.5854 \times 2.81 = 1.645$

$\text{K value} = 0.825 + 1.645 = 2.47$

$\text{FFA \%} = \frac{0.827}{2.47} = 0.33\%$

The FFA percentage is 0.33% which is less 2%, therefore, transesterification experiment can be proceed.

TABLE 4.1 Summary Result for the Acid Determination Value

| Run | 1 | 2 |
|---|---|---|
| Mass of Castor Oil (g) | 20.014 | 20.021 |
| volume of standard alkali used in titration (ml) | 5.8 | 5.6 |
| volume of standard alkali used in blank titration (ml) | 2.9 | 2.6 |
| Mass of KOH (g) | 1.4011 | 1.4009 |
| Acid Value (mg KOH/g) | 0.813 | 0.841 |
| Average (mg KOH/g) | 0.827 | |
| Percentage of FFA before esterification reaction | 3.4 % | |
| Percentage of FFA after esterification reaction | 0.33 % | |

### 4.1.3 The Determination of Viscosity

The result of viscosity experiment by using viscometer was shown below:

TABLE 4.2 Summary Result for the Determination of Viscosity

| | **Spindle 1** | **Spindle 2** | **Spindle 3** | **Spindle 4** | **Spindle 5** | **Spindle 6** |
|---|---|---|---|---|---|---|
| **cP** | 554.3 | 358.6 | 23.4 | 0.4 | 84 | 60 |
| **Torque (%)** | 73.1 | 23.9 | 22.9 | 12.9 | 0.7 | 0.2 |

Based on the procedure of the experiment, the value for the viscosity was take with the highest percentage. By refer to above table, the highest percentage is spindle

1 which is 554.3 cP which is equivalent to 55.4 Pa.s and this value is higher than petroleum based diesel. Therefore, castor oil need to undergo transesterification reaction to reduce its viscosity.

### 4.1.4 Determination of Castor oil Calorific Value.

The calorific value of castor oil was obtain from bomb calorimeter experiment which is 37374 J/g. The value of calorific value of castor oil is lower than petroleum diesel which is 43100 J/g but the calorific value of castor oil is high enough to be considered feasible as a fuel.

### 4.1.5 Determination of Castor oil density.

$$\text{density} = \frac{\text{mass of beaker with oil} - \text{mass of beaker without oil}}{\text{the volume oil}} \qquad (7)$$

$$\text{density} = \frac{42.0439\text{g} - 32.6988\text{g}}{10\ \text{ml}} = 0.93451\text{g/ml}$$

### 4.1.6 Summary of Castor Oil Properties

The properties waste cooking oil such as FFA content, viscosity, calorific value and specific gravity are tabulated in the Table 4.3;

TABLE 4.3 Properties of Castor Oil

| Properties of Castor Oil | Value |
|---|---|
| Specific Gravity | 0.93451 |
| Dynamic Viscosity (cP) | 554.3 |
| Calorific Value (J/g) | 37374 |
| FFA Content (%) | 0.33 |
| Molecular weight (g/mol) | 933.61 |

### 4.1.7 Preparation of Transesterification Experiment

#### 4.1.7.2 Determination of Catalyst (wt %) to Oil ratio

For example to produce 0.5 wt% of catalyst to oil ratio

Mass of castor oil = 10g

$$0.5\ \mathrm{wt\%} = \frac{\mathrm{M_{NaOH}}}{\mathrm{M_{oil}}} \times 100\%$$

$$0.5\ \mathrm{wt\%} = \frac{\mathrm{M_{NaOH}}}{10\mathrm{g}} \times 100\%$$

$$\text{Mass of NaOH} = 0.05\mathrm{g}$$

Therefore, for 0.5 wt% of catalyst to oil ratio, the mass of NaOH needed for every 10 g of castor oil is 0.05 g.

#### 4.1.7.2 Determination of Methanol to Oil ratio (molar ratio)

For example to produce 6 molar ratio of methanol to oil.

Molecular Weight of Methanol = 32.04 g/mol

Density of Methanol = 0.791g/ml

Molecular Weight of Castor Oil = 933.61 g/mol

Density of Castor oil = 0.960g/ml

Therefore,

1 mol of methanol = 32.04 g 1 mol of castor oil = 933.61 g

6 mol of methanol is equal to 192.24 g of methanol.

For every 10g of castor oil, the volume of methanol needed in the reaction;

$$\text{Mass of Methanol} = \frac{\text{Mass of 6 mol methanol} \times \text{Mass of Castor oil needed in reactiom}}{\text{Mass of 1 mol castor oil}} \qquad (8)$$

$$\text{Mass of Methanol needed in reaction} = \frac{192.24\mathrm{g} \times 10\mathrm{g}}{933.61\mathrm{g}} = 2.06\mathrm{g}$$

$$\text{Volume of methanol needed in reaction} = \frac{\text{Mass of methanol needed in reaction}}{\text{Density of methanol}} \qquad (9)$$

$$\text{Volume of methanol needed in reaction} = \frac{2.06\text{g}}{0.791\frac{\text{g}}{\text{ml}}} = 2.6 \text{ ml} \cong 3\text{ml}$$

## 4.2 Preliminary Experiment Result

### 4.2.1 Transesterification Reaction

Two different conditions of transesterification reaction was carried out in order to determine the range of variables value in RSM experiment design. The result are tabulated below:

**Castor oil** : 10g

**Stirring speed** : 300 rpm

**Reaction temperature** : 50°C (without microwave heating)

: 30°C (with microwave heating)

**Reaction time** : 60 min (without microwave heating)

: 30 min (with microwave heating)

### 4.2.2 Reaction without microwave heating

In this experiment, the castor oil was not treated with microwave in order to study the FAME yield of biodiesel (methyl-ester). The transesterification reaction was done for 60 min reaction time for each experiment.

TABLE 4.4 Experiment Done with Constant Concentration of NaOH

| NaOH concentration (w/wt %) | Methanol to Oil Molar Ratio | FAME yield (w/wt %) |
|---|---|---|
| **1.5** | 4.5 | 65.48 |
| **1.5** | 6.0 | 84.03 |
| **1.5** | 9 | 77.71 |
| **1.5** | 12 | 67.44 |

TABLE 4.5 Experiment Done with Constant Methanol to Oil Ratio

| Methanol to Oil Molar Ratio | NaOH concentration (w/wt %) | FAME yield (w/wt %) |
|---|---|---|
| **6.0** | 1.0 | 75.11 |
| **6.0** | 1.5 | 84.03 |
| **6.0** | 2.0 | 83.37 |
| **6.0** | 2.5 | 70.15 |

### 4.2.3 Reaction with microwave pre-treatment of castor oil

In this experiment, the castor oil will undergo microwave pre-treatment before it goes for transesterification reaction in order to study the effect of microwave heating of castor oil towards the yield of biodiesel. The reaction time for this experiment is 30 min.

TABLE 4.6 Preliminary Experiment with Constant NaOH Concentration

| NaOH concentration (w/wt %) | Methanol to Oil Molar Ratio | FAME yield (w/wt %) |
|---|---|---|
| **1.5** | 4.5 | 76.61 |
| **1.5** | 6.0 | 89.34 |
| **1.5** | 9 | 82.74 |

TABLE 4.7 Experiment Done with Constant Methanol to Oil Ratio

| Methanol to Oil Molar Ratio | NaOH concentration (w/wt %) | FAME yield (w/wt %) |
|---|---|---|
| **6.0** | 1.0 | 69.43 |
| **6.0** | 1.5 | 89.34 |
| **6.0** | 2.0 | 76.42 |

The FAME yield is calculated by using the following formula:

$$\text{FAME Yield} = \frac{\text{weight of FAME after transesterification}}{\text{weight of castor oil used}} \times 100\% \qquad (10)$$

Based on the result obtained from the preliminary result, in order to produce higher FAME several range of variables are proposed for the design experiment. The range of variables is shown at below Table 4.8;

TABLE 4.8 Range of variables proposed for experiment

| **Variables** | **Range** |
|---|---|
| NaOH concentration (w/w %) | 1.0 - 2.5 |
| Methanol to Oil ratio (molar ratio) | 1 – 2.5 |
| Reaction Temperature (°C) | 30 – 70 |
| Reaction Time (min) | 30 – 60 |
| Microwave Time (min) | 2 - 4 |

## 4.3 Alkaline Catalyzed Transesterification

In this section, base catalyzed transesterification of castor oil was investigated. The objective is to conduct an optimization of base catalyzed transesterification reaction and to study the individual and interaction effect of the reaction variables on FAME yield.

### 4.3.1 Optimization of Base Catalyzed Transesterification of Castor Oil

In this section, yield of Fatty Acid Methyl Ester (FAME) produced is mainly depend on four independent variables: Methanol to oil molar ratio (A), NaOH concentration (B), reaction temperature (C), and reaction time (D). In all experiment, 10g of castor oil and 300 rpm stirrer speed were kept constant. The individual and interaction effect of process variables and the optimal conditions to get the maximum biodiesel yield were investigated by using central composite design (CCD) technique of response surface methodology (RSM) for base catalyzed transesterification reaction. According to RSM experimental design technique, it was considered that each reaction variable can take 3 different levels from low (-1), (0) and to high (1). The experiment range and level of the independent variables is shown in Table 4.9;

TABLE 4.9 Experimental Range and Level of the Independent Variables

| Variables | Coded Symbol | Range & Levels | | |
|---|---|---|---|---|
| | | -1 | 0 | 1 |
| Methanol: Oil | *A* | 4.5 | 6.75 | 9 |
| NaOH Conc. | *B* | 1.00 | 1.75 | 2.50 |
| Temperature | *C* | 30 | 50 | 70 |
| Time | *D* | 30 | 45 | 60 |

The experiment carried out as a function of the un-coded variables prompted by central composite design technique along with observed biodiesel yield for base transesterification are presented in Table 4.10:

TABLE 4.10 Experimental Design Matrix by CCD Technique for Base Catalyzed Transesterification along with Experimental and Model Predicted Yields

| No of Exp | NaOH (w/wt %) | MeOH:Oil (Molar Ratio) | Temperature (℃) | Time (min) | Mass Biodiesel (g) | Yield % of Biodiesel | Predicted Value |
|---|---|---|---|---|---|---|---|
| 1 | 1.75 | 6.75 | 50 | 45 | 8.1376 | 81.376 | 83.1156 |
| 2 | 1.75 | 6.75 | 50 | 45 | 7.9081 | 79.081 | 83.1156 |
| 3 | 2.5 | 4.5 | 70 | 30 | 4.7437 | 47.437 | 40.3078 |
| 4 | 2.5 | 9 | 70 | 30 | 7.5503 | 75.503 | 63.6997 |
| 5 | 1 | 4.5 | 30 | 60 | 6.5477 | 65.477 | 63.4919 |
| 6 | 1 | 9 | 70 | 30 | 5.6068 | 56.068 | 60.0498 |
| 7 | 1.75 | 11.25 | 50 | 45 | 6.8445 | 68.445 | 80.4578 |
| 8 | 1.75 | 6.75 | 50 | 45 | 8.3476 | 83.476 | 83.1156 |
| 9 | 2.5 | 9 | 30 | 60 | 7.4805 | 74.805 | 63.4329 |
| 10 | 0.25 | 6.75 | 50 | 45 | 5.5298 | 55.298 | 55.8583 |
| 11 | 2.5 | 9 | 30 | 30 | 6.4324 | 64.324 | 45.2098 |
| 12 | 1.75 | 2.25 | 50 | 45 | 4.6951 | 46.951 | 59.5663 |
| **13** | **1.75** | **6.75** | **50** | **45** | **8.8627** | **88.627** | **83.1156** |
| 14 | 1 | 9 | 30 | 60 | 6.4702 | 64.702 | 60.9915 |
| 15 | 1.75 | 6.75 | 50 | 75 | 8.1761 | 81.761 | 81.4635 |
| 16 | 1.75 | 6.75 | 50 | 45 | 8.8611 | 88.611 | 83.1156 |
| 17 | 2.5 | 4.5 | 70 | 60 | 5.3916 | 53.916 | 50.1304 |
| 18 | 2.5 | 4.5 | 30 | 30 | 3.1176 | 31.176 | 20.2292 |
| 19 | 2.5 | 9 | 70 | 60 | 7.7714 | 77.714 | 83.923 |
| 20 | 1.75 | 6.75 | 50 | 45 | 7.9563 | 79.563 | 83.1156 |
| 21 | 1 | 4.5 | 70 | 60 | 6.9153 | 69.153 | 77.4275 |
| 22 | 1 | 4.5 | 70 | 30 | 7.6956 | 76.956 | 74.5397 |
| 23 | 1.75 | 6.75 | 50 | 45 | 8.1075 | 81.075 | 83.1156 |
| 24 | 1 | 4.5 | 30 | 30 | 7.9653 | 79.653 | 62.6043 |
| 25 | 1.75 | 6.75 | 10 | 45 | 0 | 0 | 32.1868 |
| 26 | 3.25 | 6.75 | 50 | 45 | 0 | 0 | 24.0678 |
| 27 | 1 | 9 | 30 | 30 | 5.9706 | 59.706 | 49.7032 |
| 28 | 1 | 9 | 70 | 60 | 7.618 | 76.18 | 73.3384 |
| 29 | 2.5 | 4.5 | 30 | 60 | 4.2873 | 42.873 | 28.0515 |
| 30 | 1.75 | 6.75 | 50 | 15 | 3.5427 | 35.427 | 60.3526 |
| 31 | 1.75 | 6.75 | 90 | 45 | 7.2171 | 72.171 | 64.6123 |

Based on Table 4.10, it is observed experiment number 13 has the highest yield of FAME which is 88.63% and 83.12% experimentally observed predicted yield by RSM model equation at 6.75 methanol to oil ratio, 1.75% w/w of NaOH concentration, 50℃ reaction temperature time and 45 minutes reaction time.

TABLE 4.11 Regression Coefficient for FAME Yield (base catalyzed transesterification)

| **Coefficient** | **Estimate** |
|---|---|
| *Constant* | -5.5590 |
| *A:Methanol :Oil Ratio* | -1.7898 |
| *B: NaOH Concentration* | 4.9268 |
| *C: Temperature* | 2.3221 |
| *D: Reaction Time* | 0.6995 |
| *AA* | -0.6471 |
| *AB* | 5.6121 |
| *AC* | -0.0088 |
| *AD* | 0.0770 |
| *BB* | -19.1789 |
| *BC* | 0.1357 |
| *BD* | 0.1541 |
| *CC* | -0.0217 |
| *CD* | 0.0017 |
| *DD* | -0.0136 |

FAME yield obtained during base transesterification were statistically analyzed by ANOVA in order to determine the constants of the quadratic equation which is shown in above table. Based on the constants of quadratic equation, statistical model equation are shown in equation 3.9;

$$\text{FAME yield} = -5.5590 - 1.7898A + 4.9268B + 2.3221C + 0.6995D - 0.6471A^2 + 5.6121AB - 0.0088AC + 0.0770AD - 19.1789B^2 + 0.1357BC + 0.1541BD - 0.0217C^2 + 0.0017CD - 0.0136D^2 \quad (11)$$

Where;

A = Methanol to Oil ratio

B = NaOH Concentration

C = Reaction Temperature

D = Reaction Time

The diagnostic plot as shown in figure below compares the experimental FAME yield with the predicted values obtained using quadratic model equation. Linear trend are shown between experimental values versus predicted values of the FAME yield. Since the P-value in the ANOVA table is less than 0.05, there are statistically significant relationship between FAME yield and Predicted yield at the 95% confidence level. The R-squared statistic indicates that the model as fitted explains 72.3% of the variability in FAME yield. The correlation coefficients equal 0.83116, indicating a relatively strong relationship between the variables. This indicate that the experimental value are nearly same to predicted values. Apart from that, the R-squared statistic (R2=0.723) indicates that the model as fitted explains 72.3% of the variability in FAME yield. This implies that 72.3% of the experiment values for base catalyzed transesterification is reliable.

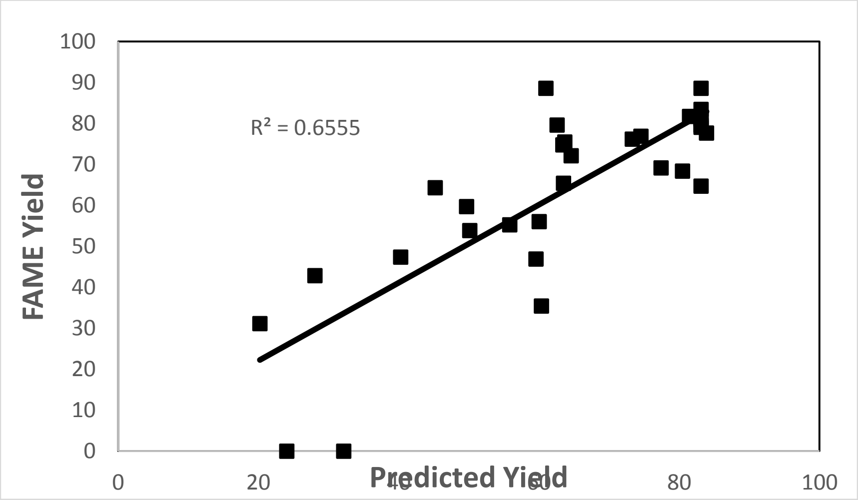


FIGURE 4.1 The Diagnostic Plot of Experimental FAME Yield (observed) Versus Predicted FAME Yield for Base Catalyzed Transesterification.

### 4.3.2 The individual and interaction effect of the reaction variables n FAME yield.

The response surface plots for the yield of FAME as function of two factor at a time while keeping the factors at their center point level wee plotted in the two-dimension surface with the response surface contour.

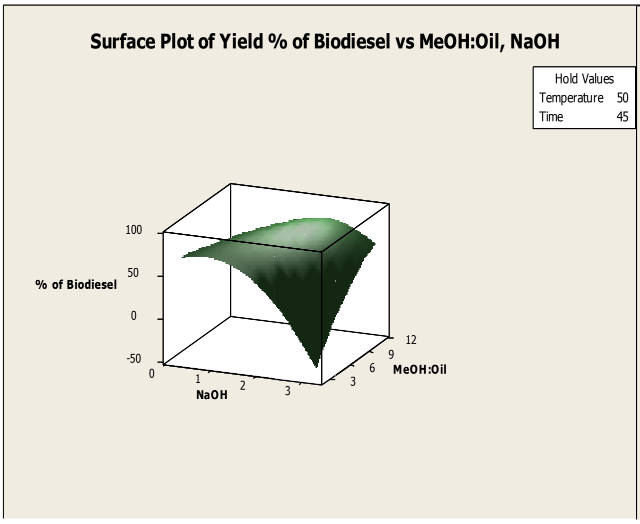


FIGURE 4.2 Surface Plot Yield % of Biodiesel vs MeOH:Oil, NaOH

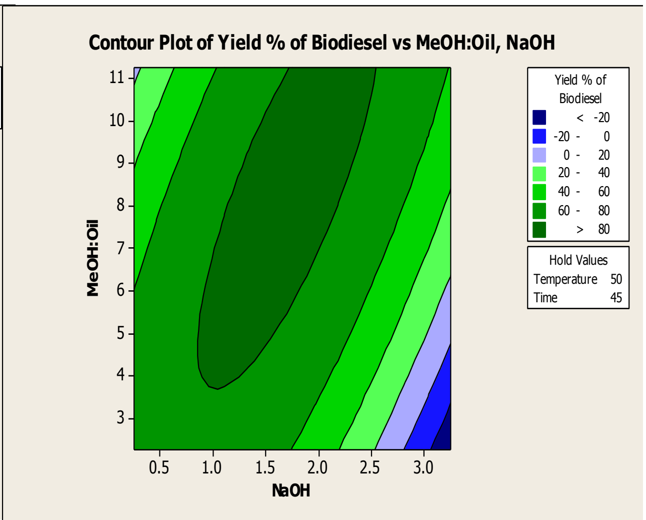


FIGURE 4.3 Contour Plot Yield % of Biodiesel vs MeOH:Oil, NaOH

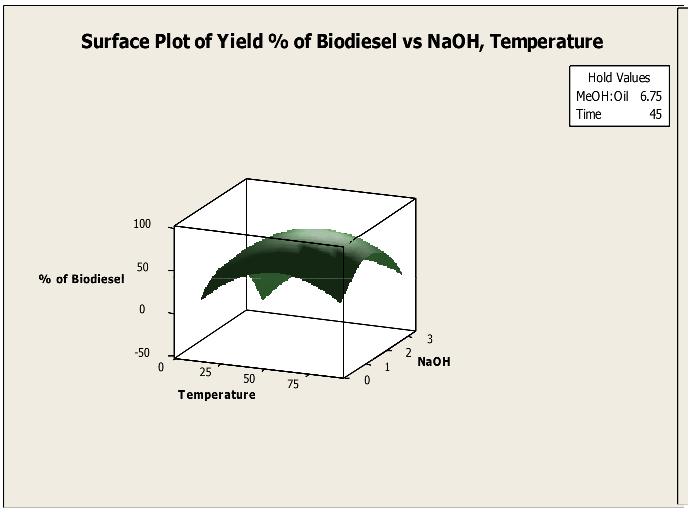


FIGURE 4.4 Surface Plot Yield % of Biodiesel vs NaOH, Temperature

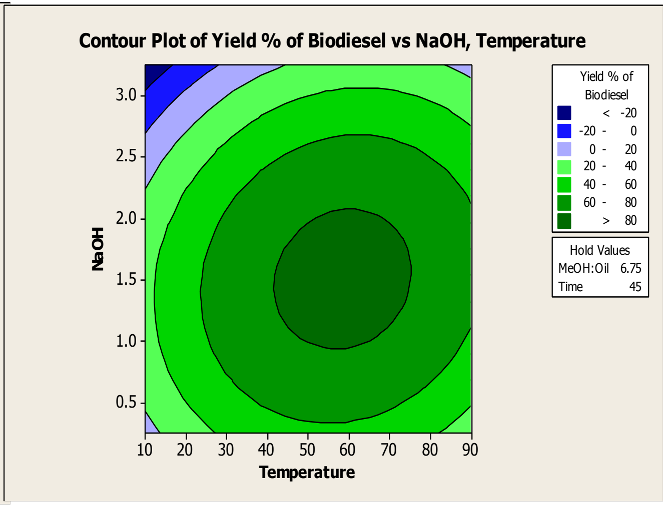


FIGURE 4.5 Contour Plot Yield % of Biodiesel vs NaOH, Temperature

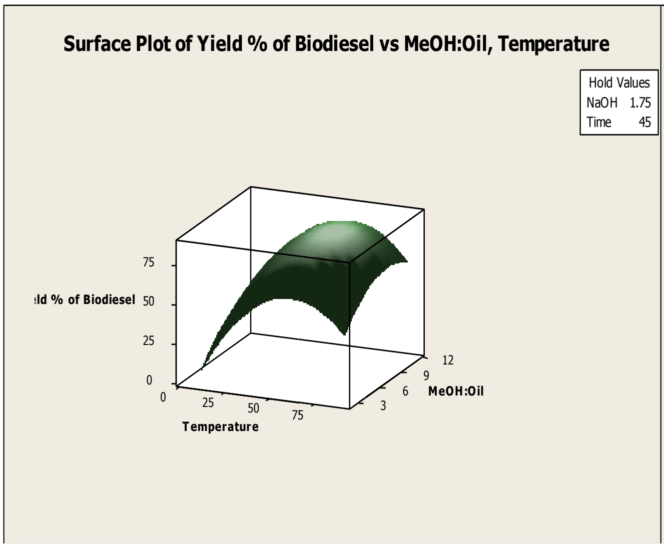


FIGURE 4.6 Surface Plot Yield % of Biodiesel vs MeOH:Oil, Temperature

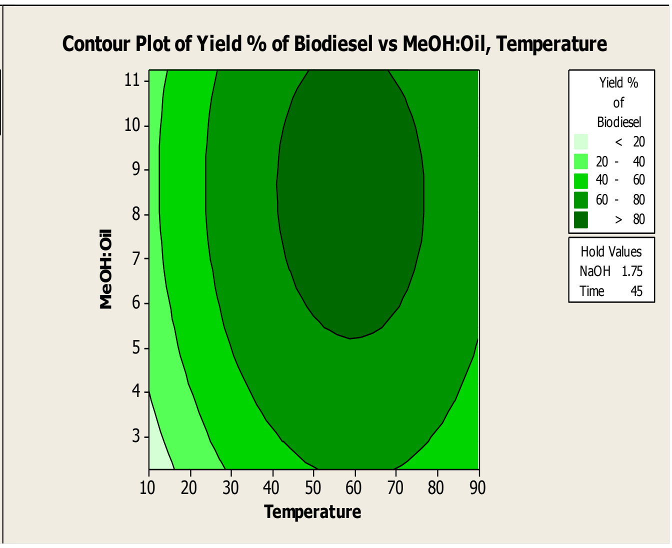


FIGURE 4.7: Contour Plot Yield % of Biodiesel vs MeOH:Oil, Temperature

Figure above show the interaction effect of methanol to oil ratio and catalyst concentration (NaOH w/wt %) on yield of FAME. From the contour plot, it was observed that the increasing volume of methanol can increase the FAME yield. However, the FAME yield started to decrease when methanol volume reaches to a certain marginal level which is about 8.0 methanol to oil ratio. Overloading of methanol reduced the concentration of the catalyst thus it effect the catalytic reaction Apart from that, it is also lead to the solubility problem where the product FAME easily dissolved in glycerol phase thus reduced the biodiesel recovery process. It was also observed that increasing of NaOH concentration can also increase the FAME yield up to certain level. However, further increased the NaOH concentration also favors the saponification reaction this it reduced the FAME yield. From the response surface, the maximum yield was gained with 6.5 methanol to oil molar ratio and 1.5% w/wt of NaOH concentration. Meanwhile for the reaction temperature, it was observed that increasing the temperature up to certain point will also increase the yield of biodiesel. However, further increase in temperature does caused the reduction of FAME yield. This is because, transesterification under high temperature promotes saponification reactions.

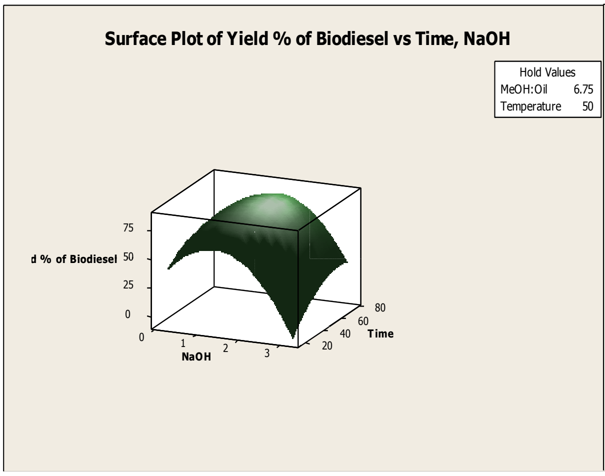


FIGURE 4.8 Surface Plot Yield % of Biodiesel vs Time, NaOH

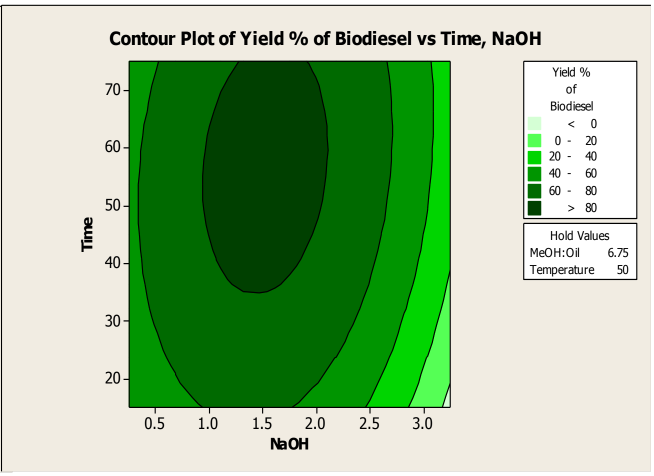


FIGURE 4.9 Contour Plot Yield % of Biodiesel vs Time, NaOH

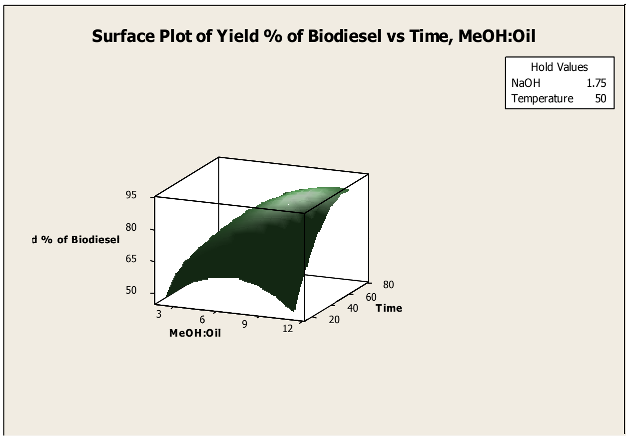


FIGURE 4.10 Surface Plot Yield % of Biodiesel vs Time, MeOH:Oil

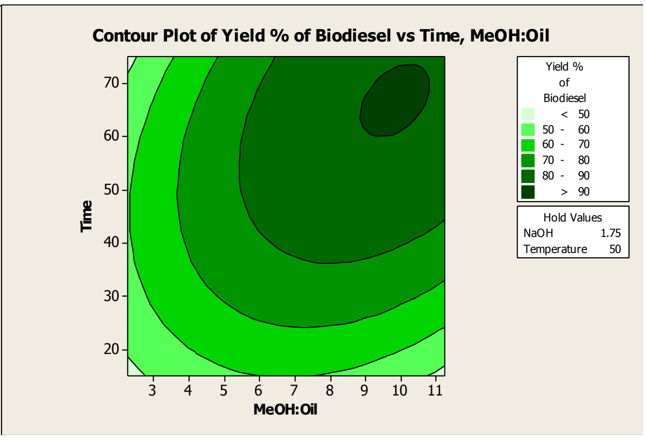


FIGURE 4.11 Contour Plot Yield % of Biodiesel vs Time, MeOH:Oil

Figure 4.8, 4.9, 4.10 and 4.11 shows interaction of reaction variables with constant temperature at 50°C. It is expected that increasing the reaction time can increase the FAME yield. However further increase reaction time beyond its optimum value could reduce the FAME recovery process. This is because saponification will likely to happen at longer period. The optimum reaction time to produce high yield of FAME is determined to be around 45 min for reaction without microwave pre-treatment. Meanwhile, it can be observed that the methanol: oil ratio still give the optimum value within range 6.0 to 9.0 and the yield also starts to increasing starting at about 1.0 wt% catalyst concentration. As mentioned earlier, increasing the molar ratio of methanol: oil ratio and catalyst concentration could promote saponification to occur. The formation of soap is the undesirable product in transesterification reaction as more catalyst is required to replace the catalyst lost due to soap formation. The presence of soap increases the viscosity that lead to formation of gel and emulsification resulting in difficulties in separation of biodiesel from glycerol resulting in excessive washing and low yield of biodiesel.

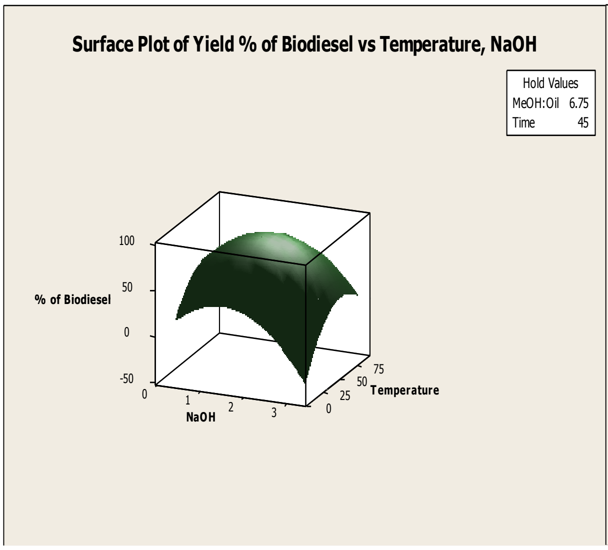


FIGURE 4.12 Surface Plot Yield % of Biodiesel vs Temperature, NaOH

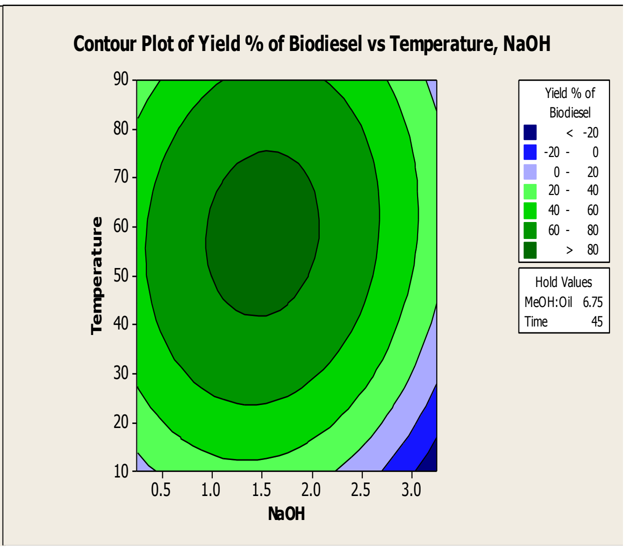


FIGURE 4.13 Contour Plot Yield % of Biodiesel vs Temperature, NaOH

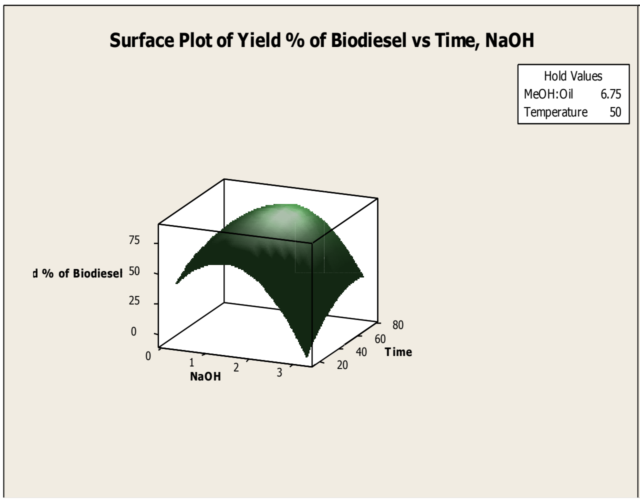


FIGURE 4.14 Surface Plot Yield % of Biodiesel vs Time, NaOH

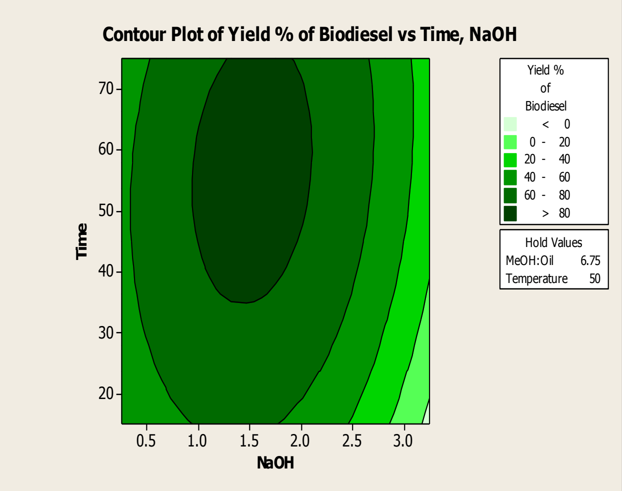


FIGURE 4.15 Contour Plot Yield % of Biodiesel vs Time, NaOH

Figure 4.12, 4.13, 4.14, and 4.15 shows the interaction of variables with volume of methanol. From the observation, we could see that maximum yield of FAME is around 89%. The optimum concentration of NaOH was observed to be at 1.5 wt% and the optimum reaction temperature was found to be at 45°C. Increasing the volume of methanol up to a certain level also give optimum FAME yield. However, if the reaction temperature is very high it will promotes the saponification reaction.

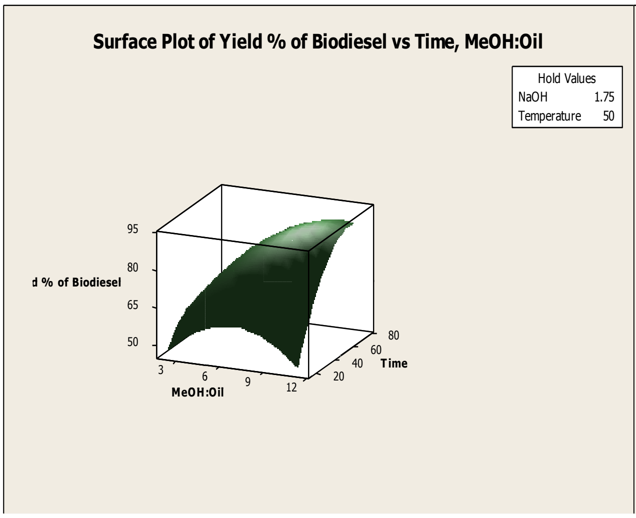


FIGURE 4.16 Surface Plot Yield % of Biodiesel vs Time, MeOH:Oil

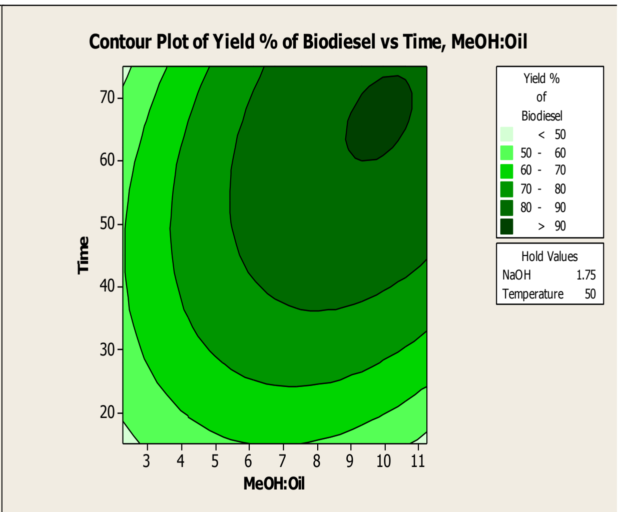
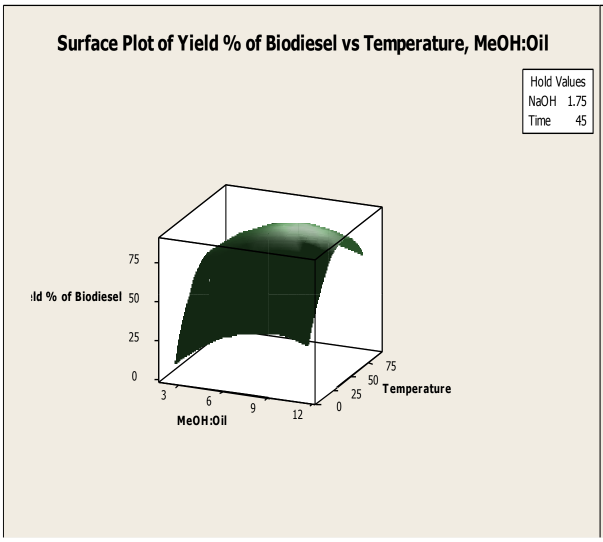


FIGURE 4.17 Contour Plot Yield % of Biodiesel vs Time, MeOH:Oil



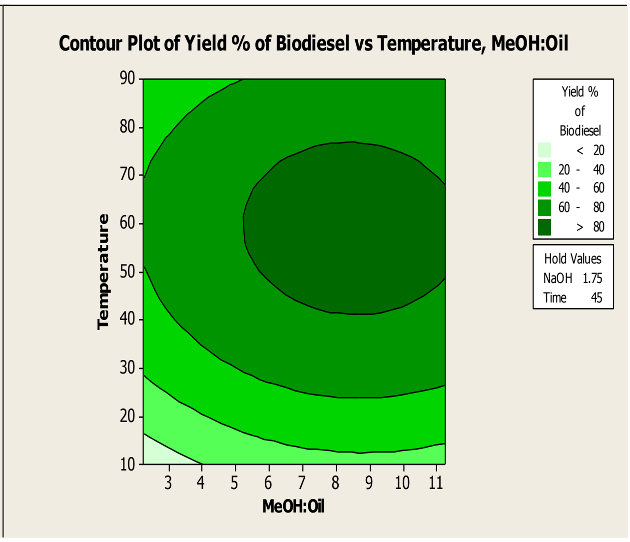


FIGURE 4.18 Surface Plot Yield % of Biodiesel vs Temperature, MeOH:Oil

FIGURE 4.19 Contour Plot Yield % of Biodiesel vs Temperature, MeOH:Oil

### 4.3.3 Optimum reaction conditions for base catalyzed transesterification

From the design expert, RSM analyzation, it was observed that the maximum optimum FAME yield is 88.63% for base catalyzed transesterification of castor oil without undergoing microwave pre-treatment.

TABLE 4.12 Optimum condition of Base Catalyzed Transesterification of Castor Oil

| Factor | Low | High | Optimum |
|---|---|---|---|
| Methanol: Oil Ratio | 4.5 | 9 | 6.75 |
| NaOH conc (wt%) | 1.0 | 2.5 | 1.75 |
| Temperature (°C) | 30 | 70 | 50 |
| Reaction Time (min) | 30 | 90 | 45 |

## 4.4 Microwave Energy Pre-treatment Transesterification of Castor Oil with Alkali Catalyst

In this section, the reaction of base catalyzed transesterification of castor oil was enhance by pre-treated the oil with microwave energy at the beginning experiment.

### 4.4.1 Optimization of Microwave Energy Pre-treatment Transesterification with Alkali Catalyst.

FAME yield produced is mainly depends on four independent variables: Microwave heating time (A), methanol to oil molar ratio (B), NaOH concentration (C), and reaction time (D). In all the experiment, 10 g of castor oil, 300 rpm stirrer speed and reaction temperature at 30-40℃ were kept constant. The individual and interaction effect of process variables and the optimal conditions to get the maximum FAME yield were investigated by using central composite design (CCD) technique of response surface methodology (RSM) for microwave pre-treatment transesterification with alkali catalyst (NaOH). According to three different level from low (-1), (0) and to high (1). The experiment range and level of the independent variable is shown in the Table 4.13:

TABLE 4.13 Experimental Range and Level of Independent Variables

| Variables | Coded Symbol | Range & Levels | | |
|---|---|---|---|---|
| | | -1 | 0 | 1 |
| MWHT | *A* | 2 | 3 | 4 |
| Methanol: Oil | *B* | 4.5 | 6.75 | 9.00 |
| NaOH conc | *C* | 1.00 | 1.75 | 2.50 |
| Reaction time | *D* | 20 | 40 | 60 |

The experiment carried out as a function of the un-coded variables prompted by central composite design technique along with observed biodiesel yield for microwave energy pre-treatment base transesterification are presented in Table 4.14:

TABLE 4.14 Experimental design matrix by CCD technique for microwave energy pre-treatment transesterification along with the experimental and model predicted yields

| No of Exp | Micrwave Time | NaOH | MeOH:Oil | Reaction Time | Mass of Biodiesel | % Yield of Biodiesel | Predicted Yield |
|---|---|---|---|---|---|---|---|
| 1 | 4 | 1 | 9 | 20 | 7.4007 | 74.007 | 73.366 |
| 2 | 2 | 1 | 4.5 | 20 | 7.6163 | 76.163 | 74.0925 |
| 3 | 3 | 1.75 | 11.25 | 40 | 8.9074 | 89.074 | 89.2457 |
| 4 | 2 | 2.5 | 9 | 20 | 7.1347 | 71.347 | 68.1913 |
| 5 | 4 | 2.5 | 4.5 | 20 | 6.0813 | 60.813 | 48.3388 |
| 6 | 3 | 1.75 | 6.75 | 40 | 9.2093 | 92.093 | 89.1291 |
| 7 | 3 | 1.75 | 6.75 | 0 | 6.371 | 63.71 | 71.8882 |
| 8 | 4 | 1 | 4.5 | 20 | 6.9237 | 69.237 | 72.977 |
| 9 | 3 | 1.75 | 6.75 | 80 | 8.5431 | 85.431 | 84.9902 |
| 10 | 3 | 1.75 | 6.75 | 40 | 9.7837 | 97.837 | 89.1291 |
| 11 | 4 | 2.5 | 4.5 | 60 | 6.3791 | 63.791 | 53.7128 |
| 12 | 3 | 1.75 | 6.75 | 40 | 8.9379 | 89.379 | 89.1291 |
| 13 | 4 | 2.5 | 9 | 20 | 7.9472 | 79.472 | 67.8183 |
| 14 | 3 | 1.75 | 6.75 | 40 | 8.7814 | 87.814 | 89.1291 |
| 15 | 2 | 1 | 9 | 60 | 7.1843 | 71.843 | 79.5575 |
| 16 | 2 | 1 | 9 | 20 | 6.4729 | 64.729 | 71.8295 |
| 17 | 4 | 2.5 | 9 | 60 | 7.7926 | 77.926 | 75.2368 |
| 18 | 3 | 0.25 | 6.75 | 40 | 7.0169 | 70.169 | 53.8618 |
| 19 | 1 | 1.75 | 6.75 | 40 | 8.5325 | 85.325 | 80.2117 |
| 20 | 2 | 2.5 | 9 | 60 | 8.1096 | 81.096 | 74.3783 |
| 21 | 3 | 3.25 | 6.75 | 40 | 0 | 0 | 24.0445 |
| 22 | 4 | 1 | 9 | 60 | 8.0364 | 80.364 | 82.3255 |
| 23 | 2 | 2.5 | 4.5 | 60 | 5.9625 | 59.625 | 55.5063 |
| 24 | 3 | 1.75 | 6.75 | 40 | 8.5724 | 85.724 | 89.1291 |
| 25 | 3 | 1.75 | 2.25 | 40 | 6.2419 | 62.419 | 69.9847 |
| 26 | 5 | 1.75 | 6.75 | 40 | 6.7104 | 67.104 | 79.9547 |
| 27 | 2 | 1 | 4.5 | 60 | 7.11 | 71.1 | 79.776 |
| 28 | 3 | 1.75 | 6.75 | 40 | 8.8319 | 88.319 | 89.1291 |
| 29 | 4 | 1 | 4.5 | 60 | 8.1496 | 81.496 | 79.892 |
| 30 | 2 | 2.5 | 4.5 | 20 | 5.6303 | 56.303 | 51.3638 |
| 31 | 3 | 1.75 | 6.75 | 40 | 8.2738 | 82.738 | 89.1291 |

TABLE 4.15 T and P Values for The Regression Coefficient in The Second Order Model Equation

| **Coefficient** | **Estimate** | **T-Value** | **P-Value** |
|---|---|---|---|
| *Constant* | 4.1236 | 0.073 | 0.943 |
| *A:MWHT* | 12.0138 | 0.685 | 0.503 |
| *B: Methanol: Oil Ratio* | 2.1950 | 0.282 | 0.031 |
| *C: NaOH Concentration* | 51.9587 | 2.358 | 0.031 |
| *D: Reaction Time* | 0.6204 | 0.771 | 0.452 |
| *AA* | -2.2615 | -1.080 | 0.296 |
| *AB* | 0.2947 | 0.237 | 0.816 |
| *AC* | -0.6365 | -0.171 | 0.867 |
| *AD* | 0.0154 | 0.110 | 0.914 |
| *BB* | -0.4698 | -1.136 | 0.273 |
| *BC* | 2.8282 | 1.705 | 0.108 |
| *BD* | 0.0114 | 0.183 | 0.857 |
| *CC* | -22.3004 | -5.991 | 0.000 |
| *CD* | -0.0257 | -0.138 | 0.892 |
| *DD* | -0.0067 | -1.276 | 0.220 |

The regression analysis fitted output response with the input process variables. Second order polynomial model equations in terms of coded and actual factors are result of regression analysis. The second order model equation is shown below;

$$\text{FAME yield} = 4.1236 + 12.0138A + 2.1950B + 51.9587C + 0.62064D - 2.2615A^2 + 0.294AB - 0.6364AC + 0.0154AD - 0.4698B^2 + 2.8282BC + 0.0114BD - 22.3004C^2 - 0.0257CD - 0.0067D^2 \qquad (12)$$

FAME yields predicted by this second order model equations were tabulated in the table above together with the experimental observation. The second order model equations were evaluated statistically in order to study the significance of the model term. In microwave pre-treatment transesterification with alkali catalyst indicating they are significantly different from zero at 95% confidence level. Thus, in this experiment, we can conclude that the reaction time has most influence on the FAME yields as it has the low P-value and high T-value as compared to other variables.

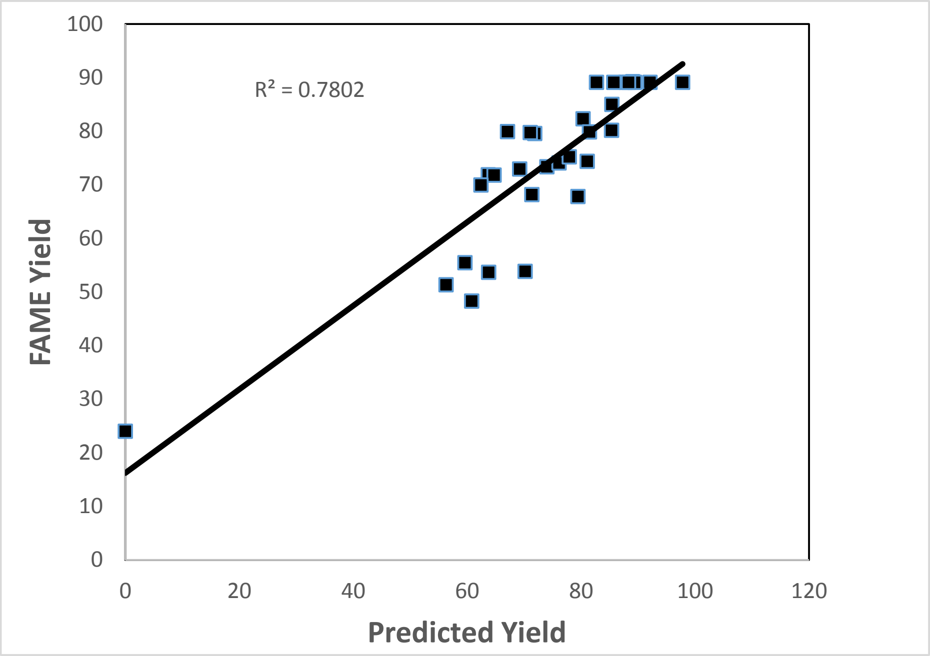


FIGURE 4.20 The Diagnostic Plot of Experimental FAME Yield versus Predicted FAME Yield for Base Catalyzed Transesterification

Figure 4.20 shows the diagnostic plot of experimental FAME yield versus the predicted FAME yield which have undergo microwave pre-treatment of castor oil. Linear trend are shown between the experimental values versus predicted values of the FAME yield. This indicate that the experimental values are nearly same to the predicted values. A part from that, the R-square statistic ($R^2 = 0.7802$) indicate that the model as fitted explains 78.02% of the variability in FAME yield. This implies that, 78.02% of the experiment values for microwave energy pre-treatment transesterification is reliable.

### 4.4.2 The individual and interaction effect of the reaction variables on FAME yield

The response surface plots for the yield of FAME yield as a function of two factors at a time while keeping the other two factors at their center level point were plotted in a two dimensional surface with the contour plot at the bottom as shown in figure below. Good interaction between two variables on the response are indicated by elliptical shape of the contour plot. Meanwhile, if the contour plot is circle shape, this indicate that less interaction effect between the variables to affect the response. From the surface contour plot, it was also determined that the FAME yield was at highest for all experiment with microwave pre-treatment of castor oil. In this experiment also, the reaction temperature were kept constant at 30-40°C in order to study the effect of MWHT and transesterification reaction time towards yield of FAME.

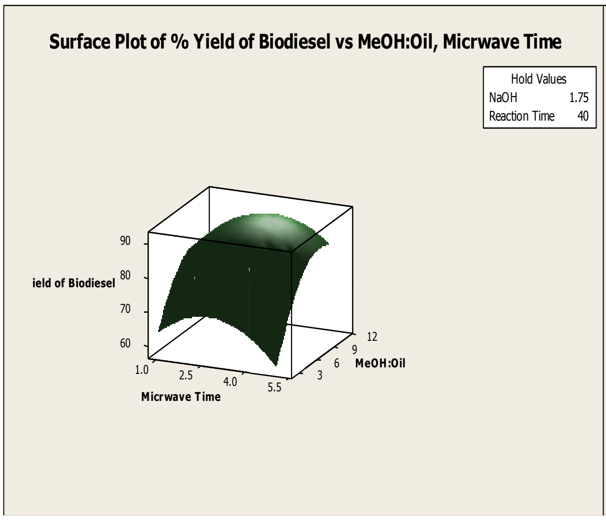


FIGURE 4.21 Surface Plot Yield % of Biodiesel vs MeOH, MWHT

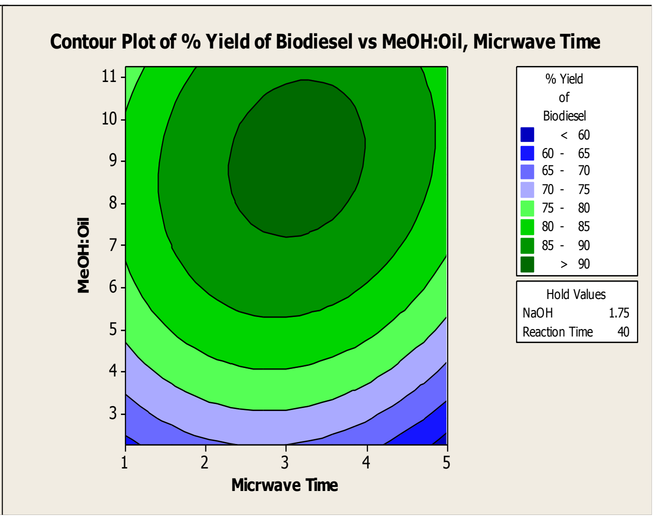
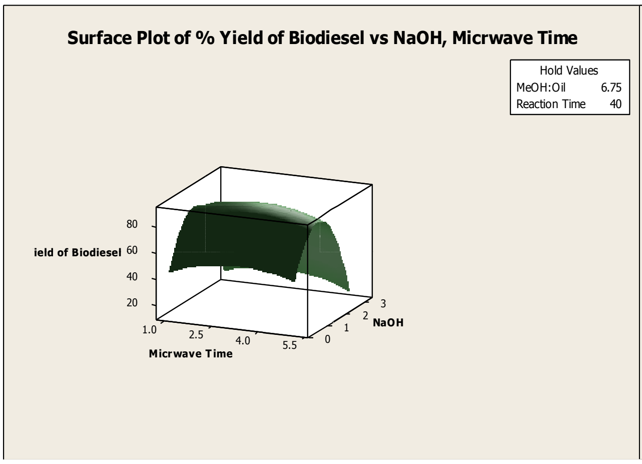


FIGURE 4.22 Contour Plot Yield % of Biodiesel vs MeOH, MWHT



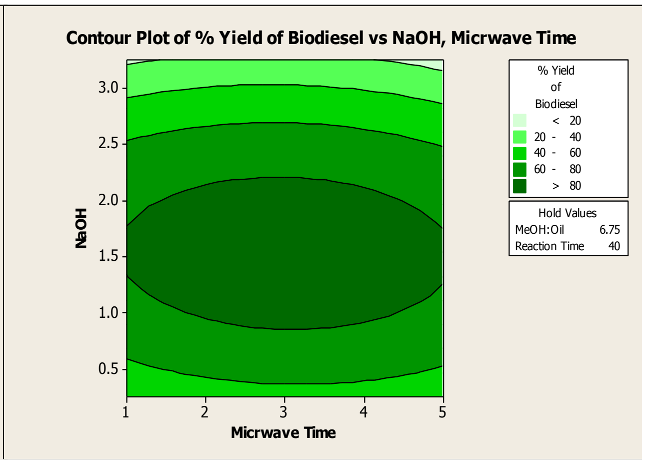
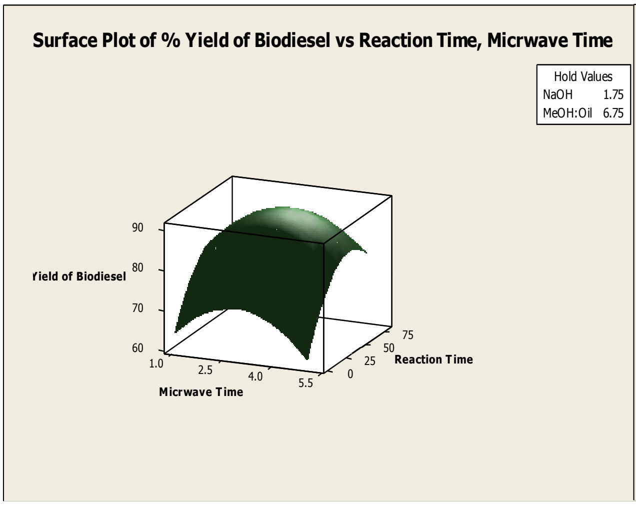


FIGURE 4.23 Surface Plot Yield % of Biodiesel vs NaOH, MWHT

FIGURE 4.24 Contour Plot Yield % of Biodiesel vs NaOH, MWHT



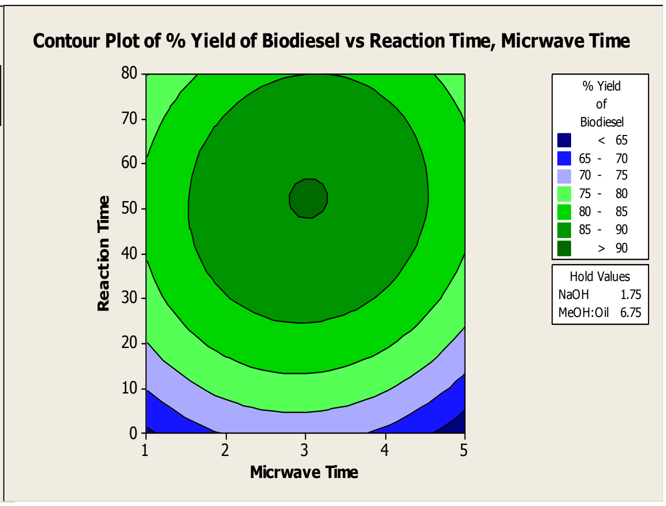


FIGURE 4.25 Surface Plot Yield % of Biodiesel vs Reaction Time, MWHT

FIGURE 4.26 Contour Plot Yield % of Biodiesel vs Reaction Time, MWHT

Figure 4.21, 4.22, 4.23, 4.24, 4.25, and 4.26 shows the effects of methanol to oil molar ratio to FAME yield with the microwave energy pre-treated (min) transesterification. Maximum yield was observed at volume of methanol at 6.75 molar ratios of methanol to castor oil. Increasing amount of methanol can increase the FAME yield. However, further increase of the volume of methanol beyond the optimum value can decreased the FAME yield. This is due to the solubility problem where the product biodiesel can easily dissolve into the glycerol phase that affect the biodiesel recovery process thus reducing the FAME yield.

From previous analysis, increasing the NaOH concentration can increase the FAME yield up to a certain marginal value (1.75 w/wt %). However, overloading the NaOH concentration can decreased the FAME yield. Therefore, in this experiment the interaction effect of microwave heating time with the FAME yield could be studied more clearly. From observations, it is found that the optimum time for the castor oil to undergo microwave heating is around 3 min.

From the reaction time versus microwave time, depicts the interaction between reaction time and FAME yield on microwave energy pre-treated transesterification on castor oil. In this plot, we could observe the relationship between reaction time and FAME yield. In this case, it is predicted that the reaction time for base transesterification reaction with presence of microwave pre- treatment of castor oil should be lower than without microwave pre-heating due to rapid heating & cooling and also selective heating of microwave. From the observation, increasing the reaction time will increase the FAME yield. Further increase the reaction time can lead into saponification reaction thus reduced the FAME yield. At this figure, the maximum biodiesel yield is about 40 minutes of reaction time which is shorter than reaction without microwave heating.

### 4.4.3 Optimum reaction conditions for Microwave Energy Pre-treated Transesterification with alkali catalyst (NaOH)

TABLE 4.16 Optimum Condition of Microwave Energy Pre-Treatment Transesterification

| Factor | Low | High | Optimum |
|---|---|---|---|
| Methanol: Oil Ratio | 4.5 | 11.25 | 6.75 |
| NaOH Conc. (w/wt%) | 0.25 | 3.25 | 1.75 |
| MWHT (min) | 1 | 5 | 3 |
| Reaction Time (min) | 20 | 80 | 40 |

From the RSM analyzation, it was observed that the maximum optimum FAME yield is 97.84% for microwave energy pre-treatment transesterification of castor oil.

## 4.5 Summary for optimization of FAME yield

In the present studies, optimization on the FAME yield has been investigated with three different conditions which are;

| | |
|---|---|
| Optimization 1: | Base catalyzed transesterification (without Microwave Heating) |
| Optimization 2: | Microwave energy pre-treated transesterification with alkali catalyst |

In each experiment there are an enhancement towards the transesterification reaction to produce high FAME yield. Table 4.17 shows the summary of the optimum condition to achieve the maximum of FAEE yield as presented by design expert software MINITAB 14 RSM technique and optimum condition from experiment results.

TABLE 4.17 Optimization Summary

| **Parameters/Condition** | **Optimization 1** | **Optimization 2** |
|---|---|---|
| MWHT (min) | - | 3.0 |
| Methanol to oil molar | 6.75 | 6.75 |
| NaOH Concentration (w/wt %) | 1.75 | 1.75 |
| Reaction Temperature (℃) | 45 | 30-4 (constant) |
| Reaction Time (min) | 45 | 40 |
| FAEE yield (w/wt%) | 88.63 | 97.84 |

From Table 4.17, it can be seen that optimization transesterification of castor oil with microwave pre-treatment gives the highest FAME yield. Base transesterification has the least FAME yield. Results shows that 97.84% w/wt of FAME yield can be obtained within 40 minutes reaction time for transesterification reaction pre-treated with microwave irradiation. As compared to the base transesterification with the absence of microwave heating the highest FAME yield obtained was only 88.63 wt%. This shows that in the presence of microwave heating, there was a significant increment of FAME yield which is around 9.21wt%.

Besides that, it was also observed that the reaction time of transesterification with microwave pre-heating of castor oil was lower than the reaction time for the reaction conducted in the absence of microwave pre-treatment by 5 minutes. Thus, it can be conclude that microwave energy pre-treatment of castor oil can improve the yield of FAME in a transesterification reaction and speed up the reaction at lower mild condition.

# CHAPTER 5

# CONCLUSIONS AND RECOMMENDATIONS

## 5.1 Conclusion

Microwave pre-treatment enhanced organic or inorganic synthesis was consider as green chemistry and it was one of preferred method due to several advantages such as substantial reduction in reaction times and solvent requirements, lower energy consumption, enhanced selectivity and improved conversions with less by-product formation. By using microwave irradiation, many reaction that do not occur under classical methods of heating can be carried out with high yields of biodiesel. Microwave pre-treatment technique have the potential for large scale applications specifically in biodiesel production, this is because due to microwave ability to interact with variety of reagents.

In this present studies, the non-edible oil source that were used in this project was castor oil as the raw material for transesterification reaction to produce biodiesel. Homogeneous base catalyzed transesterification and microwave energy pre-treatment transesterification were investigated. Results show that at optimum condition, 97.84 w/wt % within 40 minutes reaction time of Fatty Acid Methyl Ester (FAME) yield was observed when the reaction was conducted with microwave energy pre-treatment of castor oil. It was also demonstrated that a gain of 9.21 w/wt % of FAME yield for a reaction conducted using microwave energy pre-treatment castor oil transesterification reaction as compared to transesterification reaction in the absence of microwave pre-heating (FAME = 88.63 w/wt %)

As compared to alkaline catalyzed transesterification, the reaction that conducted by using microwave energy pre-treatment of castor oil, the transesterification reaction is assisted and also has a reduction of 5 minutes of reaction time. Thus, this can conclude that the microwave energy can be improve the transesterification reaction and prove that this method was efficiently and economically feasible for operation.

Hence, by using microwave pre-treatment of castor oil has a promising future in terms of enhancing the transesterification reaction time and also increasing the yield of biodiesel.

## 5.2 Recommendation for future work

As for the future work and recommendation for this project, the microwave energy pre-treatment transesterification should also be done in the presence of phase transfer catalyst (PTC). By using PTC process, this can achieve a faster reactions, and also it can obtain a higher conversion or yield of biodiesel. This PTC also can minimize the by-product for the reaction and eliminate the need for expensive or dangerous solvents that will dissolve all the reactant in one phase. PTC also can eliminate the need for expensive raw materials and reduce the waste problems. PTC are especially useful in green chemistry by allowing the use of water so that the need for organic solvents is reduced. Furthermore, research should be done with other non-edible oil such as waste cooking oil, Karanja oil, Margosa oil, Neem oil and etc. in order to find new alternative in production of biodiesel using non-edible oil.

Moreover, by using different type of PTC can also be used as a rate enhancement agent in transesterification reaction such as crown ether and benzyltrimethylammonium hydroxide. For addition, higher quality of biodiesel can be achieve by using good and reliable equipment such as cleaner biodiesel can be achieved if using the rotary evaporator equipment. The physical separation using filtration funnel of castor oil such as removal of impurities should be carried out with a proper filtration technique in order to obtain a good purity of biodiesel. Therefore, action need to be taken by the personnel in charge with the laboratory equipment to bring in new and more advance equipment for biodiesel synthesis.

# REFERENCES

Atabani, A. E., Silitonga, A. S., Badruddin, I. A., Mahlia, T. M. I., Masjuki, H. H., & Mekhilef, S.,2012. A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *Renewable and Sustainable Energy Reviews*, ***16*****(4)**, 2070-2093.

Atadashi, I., Aroua, M., & Aziz, A. A., 2010. High quality biodiesel and its diesel engine application: a review. *Renewable and Sustainable Energy Reviews,* ***14*****(7)**, 1999-2008.

Atadashi, I. M., Aroua, M. K., & Aziz, A. A., 2010. High quality biodiesel and its diesel engine application: A review. *Renewable and Sustainable Energy Reviews*, ***14*****(7)**, 1999-2008.

Azcan, N., & Danisman, A., 2008. Microwave assisted transesterification of rapeseed oil. *Fuel,* ***87*****(10–11)**, 1781-1788.

Banković-Ilić, I. B., Stamenković, O. S., & Veljković, V. B., 2012. Biodiesel production from non-edible plant oils. *Renewable and Sustainable Energy Reviews,* ***16*****(6)**, 3621-3647.

Bean, C., 2010. Fatty Acid Composition and Physicochemical Properties of Malaysian. *Sains Malaysiana,* ***39*****(5)**, 761-764.

Budau, G., Campean, M., Cosereanu, C., & Lica, D., 2011. REED - PLANT BIOMASS - AS RENEWABLE AND LOW-POLLUTING ENERGY RESOURCE. *Environmental Engineering and Management Journal,* ***10*****(8)**, 1053-1057.

Chang, Y., Lee, J., & Yoon, H., 2012. Alternative projection of the world energy consumption-in comparison with the 2010 international energy outlook. *Energy Policy, 50*, 154-160.

Danlami, J. M., Arsad, A., & Zaini, M. A. A., 2015. Characterization and process optimization of castor oil (Ricinus communis L.) extracted by the soxhlet method using polar and non-polar solvents. *Journal of the Taiwan Institute of Chemical Engineers, **47*****(0)**, 99-104.

Gude, V. G., Patil, P., Martinez-Guerra, E., Deng, S., & Nirmalakhandan, N., 2013. Microwave energy potential for biodiesel production. *Sustainable Chemical Processes, **1*****(1)**, 5.

Gui, M. M., Lee, K. T., & Bhatia, S., 2008. Feasibility of edible oil vs. non-edible oil vs. waste edible oil as biodiesel feedstock. *Energy, **33*****(11)**, 1646-1653.

Hailegiorgis, S. M., Mahadzir, S., & Subbarao, D., 2013. Parametric study and optimization of in situ transesterification of Jatropha curcas L assisted by benzyltrimethylammonium hydroxide as a phase transfer catalyst via response surface methodology. *Biomass and Bioenergy, **49*****(0)**, 63-73. He, J., 2015. A review of Chinese fish trade involving the development and limitations of food safety strategy. *Ocean & Coastal Management, 116*, 150-161.

Hernando, J., Leton, P., Matia, M. P., Novella, J. L., & Alvarez-Builla, J., 2007. Biodiesel and FAME synthesis assisted by microwaves: Homogeneous batch and flow processes. *Fuel, **86*****(10–11)**, 1641-1644.

Knothe, G. (2012). 5.02 - Historical Perspectives on Biofuels. In A. Sayigh (Ed.), *Comprehensive Renewable Energy* (pp. 11-14). Oxford: Elsevier.

Kumar, A., & Sharma, S., 2011. Potential non-edible oil resources as biodiesel feedstock: An Indian perspective. *Renewable and Sustainable Energy Reviews, **15*****(4)**, 1791-1800.

Kumar, R., Kumar, G. R., & Chandrashekar, N., 2011. Microwave assisted alkali-catalyzed transesterification of Pongamia pinnata seed oil for biodiesel production. *Bioresource Technology, 102*(11), 6617-6620.

Lam, M. K., Lee, K. T., & Mohamed, A. R., 2010. Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: a review. *Biotechnology advances, **28*****(4)**, 500-518.

Larhed, M., Moberg, C., & Hallberg, A., 2002. Microwave-accelerated homogeneous catalysis in organic chemistry. *Accounts of chemical research, **35*****(9)**, 717-727.

Leung, D. Y. C., Wu, X., & Leung, M. K. H., 2010. A review on biodiesel production using catalyzed transesterification. *Applied Energy, **87*****(4)**, 1083-1095.

Lidström, P., Tierney, J., Wathey, B., & Westman, J., 2001. Microwave assisted organic synthesis—a review. *Tetrahedron, **57*****(45)**, 9225-9283. Lim, S., & Teong, L. K., 2010. Recent trends, opportunities and challenges of biodiesel in

Malaysia: An overview. *Renewable and Sustainable Energy Reviews,* ***14*****(3)**, 938-954.

Lin, L., Cunshan, Z., Vittayapadung, S., Xiangqian, S., & Mingdong, D., 2011. Opportunities and challenges for biodiesel fuel. *Applied Energy,* ***88*****(4)**, 1020-1031.

Lotero, E., Liu, Y., Lopez, D. E., Suwannakarn, K., Bruce, D. A., & Goodwin, J. G., 2005. Synthesis of biodiesel via acid catalysis. *Industrial & engineering chemistry research,* ***44*****(14)**, 5353-5363.

Ma, F., & Hanna, M. A., 1999. Biodiesel production: a review1. *Bioresource Technology,* ***70*****(1)**, 1-15.

Nagariya, A., Meena, A., Yadav, A., Niranjan, U., Pathak, A., Singh, B., & Rao, M., 2010. Microwave assisted organic reaction as new tool in organic synthesis. *Journal of pharmacy Research,* ***3*****(3)**.

Ong, H., Mahlia, T., & Masjuki, H., 2011. A review on energy scenario and sustainable energy in Malaysia. *Renewable and Sustainable Energy Reviews,* ***15*****(1)**, 639-647.

Patil, P., Gude, V. G., Pinappu, S., & Deng, S., 2011. Transesterification kinetics of Camelina sativa oil on metal oxide catalysts under conventional and microwave heating conditions. *Chemical Engineering Journal,* ***168*****(3)**, 1296-1300.

Scholz, V., & da Silva, J. N.,(200). Prospects and risks of the use of castor oil as a fuel. *Biomass and Bioenergy,* ***32*****(2)**, 95-100.

Sharma, Y. C., & Singh, B., 2008. Development of biodiesel from karanja, a tree found in rural India. *Fuel,* ***87*****(8–9)**, 1740-1742.

Silitonga, A. S., Atabani, A. E., Mahlia, T. M. I., Masjuki, H. H., Badruddin, I. A., & Mekhilef, S., 2011. A review on prospect of Jatropha curcas for biodiesel in Indonesia. *Renewable and Sustainable Energy Reviews,* ***15*****(8)**, 3733-3756.

Srivastava, A., & Prasad, R., 2000. Triglycerides-based diesel fuels. *Renewable and Sustainable Energy Reviews,* ***4*****(2)**, 111-133.

Taylor, M., Atri, B. S., Minhas, S., & Bisht, P., 2005. Developments in microwave chemistry. *Evaluserve special report*, 1-50.

Yadav, G. D., & Bisht, P. M., 2004. Novelties of microwave assisted liquid–liquid phase transfer catalysis in enhancement of rates and selectivities in alkylation of phenols under mild conditions. *Catalysis Communications,* ***5*****(5)**, 259-263.

Yusuf, N., Kamarudin, S., & Yaakub, Z., 2011. Overview on the current trends in biodiesel production. *Energy Conversion and Management,* ***52*****(7)**, 2741-2751.

Yusuf, N. N. A. N., Kamarudin, S. K., & Yaakub, Z., 2011. Overview on the current trends in biodiesel production. *Energy Conversion and Management,* ***52*****(7)**, 2741-2751.