MICROWAVE ENERGY ASSISTED TRANSESTERIFICATION REACTION

by

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13752

Dissertation submitted in partial fulfilment of

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Bachelor of Engineering (Hons)

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CERTIFICATIONOF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirements for the
Bachelor of Engineering (Hons)
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Approved by,

_____

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UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK

August 2014

CERTIFICATION OF ORIGINALITY

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

_____

(MUHAMMAD YUSRI BIN GAZALI)

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ABSTRACT

Biodiesel is gaining increasing attention due to the versatility of raw material available for its production. However, currently more than 95% of biodiesel is made from edible oil sources affecting the cost of food as well as biodiesel industries as both industries compete for edible oil sources. Use of non-edible oil source such as jatropha and neem trees for the production of biodiesel can potentially reduce the high cost of biodiesel produced from edible oil sources. Long reaction time due to the low solubility of oils and alcohol also increased the cost of biodiesel processing. However, the use of microwave energy can increase the rate of reaction and yield of biodiesel. In the present work, these two concepts were utilized together to investigate transesterification of pre-treated neem oil with microwave energy. A two-step reaction was carried out on neem oil due to high free fatty acid content. It was observed that the use of neem oil pre-treated with microwave have substantially increased the reaction rate of transesterification reaction. Optimum conditions for the reaction were established using Response Surface Methodology (RSM). With microwave energy pre-treatment, the maximum yield was observed to be 99.1% in 15 minutes at 50 ^{o}C while without microwave energy treatment, the maximum yield achieved was 95.2% in 30 minutes at 50 ^{o}C reaction temperature.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1: INTRODUCTION

1.1 Background of the Study

Energy dependence on fossil fuels and the rising global energy demand are becoming the concern of every nation as petroleum based energy are getting depleted. It was reported that the existing fossil fuels are expected to be depleted in less than half century [1]. About 88% of the global energy demand is supplied from fossil fuel sources. The consumption of fossil fuel sources was also estimated to rise from 85.7 million barrels per day in 2008 to 112.2 million barrels per day in 2035 [1]. On the other hand, the emission of greenhouse gases from use of fossil fuel such as carbon dioxide is polluting the environment and its ecosystems.

Renewable and environmentally friendly alternative energy and feedstock with zero net carbon dioxide emission are necessary for sustainable development. One such option is biofuel which encompasses bioethanol, biodiesel and bio-hydrogen. Biodiesel is getting global attraction due to its versatile source of raw material, use of the fuel by mixing at any proportion with petrol based diesel or directly to the existing fossil fuel based engine without modification.

Biodiesel is produced by transesterification of vegetable oil or animal fats. Transesterification is a chemical reaction between triglycerides present in the oils and methanol or ethanol to form esters and glycerol in the presence of a catalyst or at high pressure and temperature. The biodiesel produced will have physical characteristic very similar to petroleum diesel. Primarily, vegetable oils and animal fats are esters of saturated and unsaturated mono-carboxylic acids with trihydric alcohol glycerides. All three OH group present in them can be esterified with alcohol [16]. Stoichiometrically, one mole of triglycerides will react with three moles of alcohol to produce three moles of biodiesel and one mole of glycerol as by product as shown below

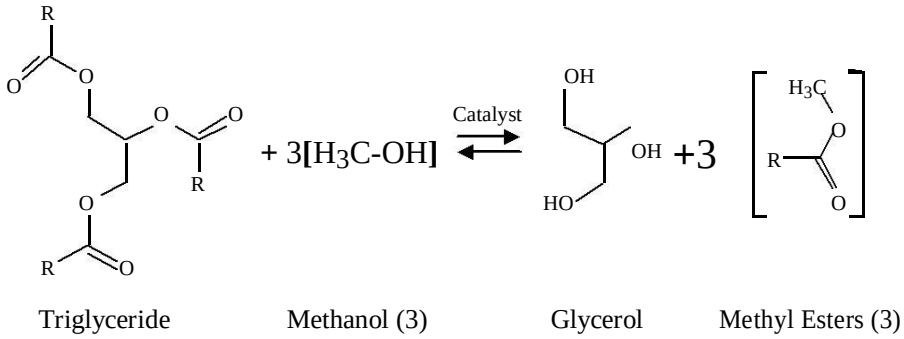


Figure 1: Schematic representation of transesterification reaction

Currently, most of the biodiesel produced is from edible oil sources such as palm tree, soybean, sunflower seeds, and others. Resulting in high cost of biodiesel as it competes for its main feedstock with food processing industries which in turn increases the cost for edible oil. It was reported that 75% of the cost of production of biodiesel comes from edible oil feedstock demanding for the search of non-edible and cheaper alternative sources [1]. Use of non-edible oil sources are currently under extensive investigation by various researches at global level. Non-edible oil sources such as jatropha curcas, neem oil, castor oil are believed to significantly reduce the cost of biodiesel feedstock's as it does not compete with food processing industries.

However, there are also some disadvantages in using biodiesel from plant oil and animal fats as a source because the performance of this oil is poor compared to petroleum diesel due to the high viscosity of the oil. Thus, a method is needed in order to decrease its viscosity so that it can burn as properly as the petroleum diesel.

Few methods have been proposed to reduce its viscosity such as blending with solvents, pyrolysis and transesterification. Transesterification is a chemical reaction where the oil is reacted with alcohol to produce fatty acid ethyl esters which produces biodiesel which has similar properties as petroleum based diesel and thus can be used in a diesel engine without any modifications requires on the engine.

Nevertheless, transesterification reaction also has some drawbacks. The alcohol that is usually used for the reaction are methanol and ethanol because they are the cheapest of alcohol [4]. As vegetable oil has a sparingly lower solubility in lower alcohols, the transesterification reaction has a slow rate due to limited mass transfer rate between the oil and alcohol phase [5]. Several techniques to enhance the reaction

rate of transesterification has been investigated which include technique such as mixing, co-solvent addition, higher temperature and pressure, super critical alcohol, ultrasonication, and also microwave irradiation [22].

In the present project work, neem oil extracted from neem tree is used as a source of non-edible oil to replace the production of biodiesel from edible oil sources such as palm oil. To enhance the limited solubility of the oil in methanol and increase the mass transfer rate between the two reactants in order to increase the rate of transesterification reaction, neem oil will be preheated with microwave energy before transesterification reaction takes place.

1.2 Problem Statement

Biodiesel is a new attractive source of energy that has the potential to reduce the dependence on petroleum based diesel. It can be produced by transesterification of vegetable oils or animal fats with methanol in the presence of suitable catalysts. Currently, over 90% of biodiesel is made from high cost edible oil such as rapeseed oil, soybeans, sunflower oil, and many others. The high cost is due to the edible oil sources are also being used in the food processing industries. Moreover, transesterification reaction also has a slow reaction rate due to the low solubility of vegetable oil in alcohol. Thus, it is necessary to use cheap feedstock for the production of biodiesel and also speed up the reaction rate to keep the cost of production of biodiesel under control. In the present work, neem oil which is a non-edible oil is proposed to be used as the raw material for transesterification reaction. To enhance the rate of reaction, it is proposed that the feed to be preheated with microwave energy before the transesterification reaction.

1.3 Objectives

The objectives to be achieved for this study include:

To investigate alkaline transesterification of neem oil with methanol that is preheated with microwave energy; this includes:

i) Investigation of the effect of preheating of the neem oil using microwave energy on the rate of transesterification reaction.

ii) To study the individual and interaction effect of reaction variables on transesterification reaction of neem oil.

iii) Optimization of reaction parameters by statistical experimental design technique of response surface methodology (RSM).

1.4 Scope of Study

To achieve the above mentioned objectives, neem oil will be used and characterized to determine their physical and chemical properties. Effects of preheating of the neem oil prior of the reaction, parametric effect of reactant ratios (methanol to neem oil), mixing speed, reaction temperature on transesterification of neem oil as well as the rate of reaction will be investigated in a batch reactor. Optimum operating conditions will be established using response surface methodology (RSM). Conversions of triglycerides with time at different reaction conditions will be measured to investigate the rate of reaction and order of reaction equations. The scope of study is restricted to the use of non-edible oil as the feedstock of the transesterification reaction, specifically neem oil.

CHAPTER 2: LITERATURE REVIEW

2.1 Biodiesel

Biodiesel is generally a renewable source of energy that has almost the same properties of the diesel fuel derived from plants and animals. Extensive studies and researches have currently been conducted to promote the use of biodiesel as the potential replacement of diesel because of its many advantages over petroleum diesel. Biodiesel is renewable, non-explosive, biodegradable, non-flammable, and non-toxic [7-9]. It has almost the same properties as petroleum diesel which allows it to be blended with diesel fuel at any proportion and allows it to be used in a diesel engine without any modification [10]. Moreover, it is free from harmful substances and more environmental friendly than diesel fuel.

2.2 Properties of Biodiesel

ASTM defined biodiesel as "a fuel comprised of monoalkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100" [2]. Its properties are determined by the compositional profiles and may vary significantly from one type to another. When compared to diesel fuel, biodiesel has lower hydrogen content, higher density, viscosity, and distillation temperatures. All these properties show that biodiesel has slightly lower energy content than diesel fuel but it has excellent cetane numbers [2]. The high density of the biodiesel makes it less desirable than petroleum diesel.

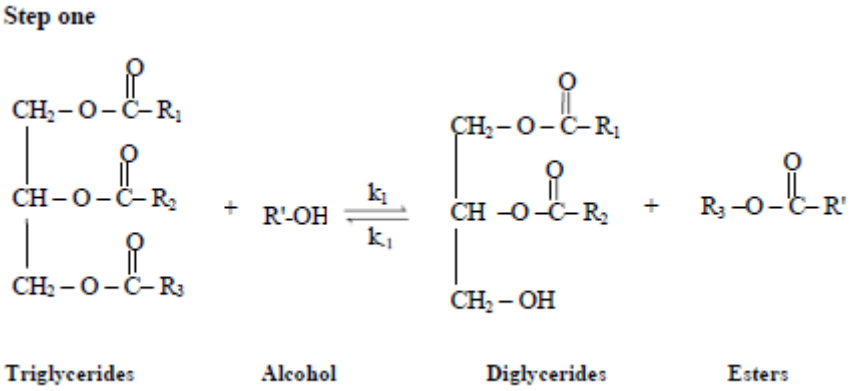
2.3 Transesterification Reaction

Biodiesel is commonly produced by a chemical process known as transesterification reaction, where the triglycerides of the vegetable oils are reacted with alcohols in the presence of catalyst at high pressure and temperature, to produce fatty acid alkyl esters and glycerol as a by-product [1, 3]. Because methanol is the cheapest alcohol, most of the esters from the transesterification reaction are methyl esters which are why sometimes biodiesel is also called fatty acid methyl esters (FAME).

Due to the high viscosity of the biodiesel taken directly from plants and animals, this

reaction is needed to reduce the value in order to enable their use in common diesel engines without any operational difficulties such as deposits in the engine. Currently, there are four methods that are used explored to reduce the viscosity of biodiesel which include diluting with petrodiesel, pyrolysis, microemulsification, and transesterification [4]. However, only the transesterification reaction leads to the production of biodiesel [5]. After the reaction, the viscosity of the esters reduces from around twice to very close to petro-diesel's viscosity.

Stoichiometrically, biodiesel is produced when one mole of triglycerides reacts with three moles of alcohol to produce three moles of esters and one mole of glycerol. The transesterification reaction consists of three consecutive reaction that is reversible. The first step is where the triglyceride molecules remove one chain of the fatty acid to become diglycerides molecules. Next, another chain of fatty acid is broken from the diglycerides to form monoglyceride. Lastly, the monoglyceride molecule is converted into glycerol by the breaking of the final chain. It is an equilibrium reaction, thus large excess of alcohol is used to shift the reaction to form glycerol and esters. The figure below shows the formation of biodiesel through transesterification process:



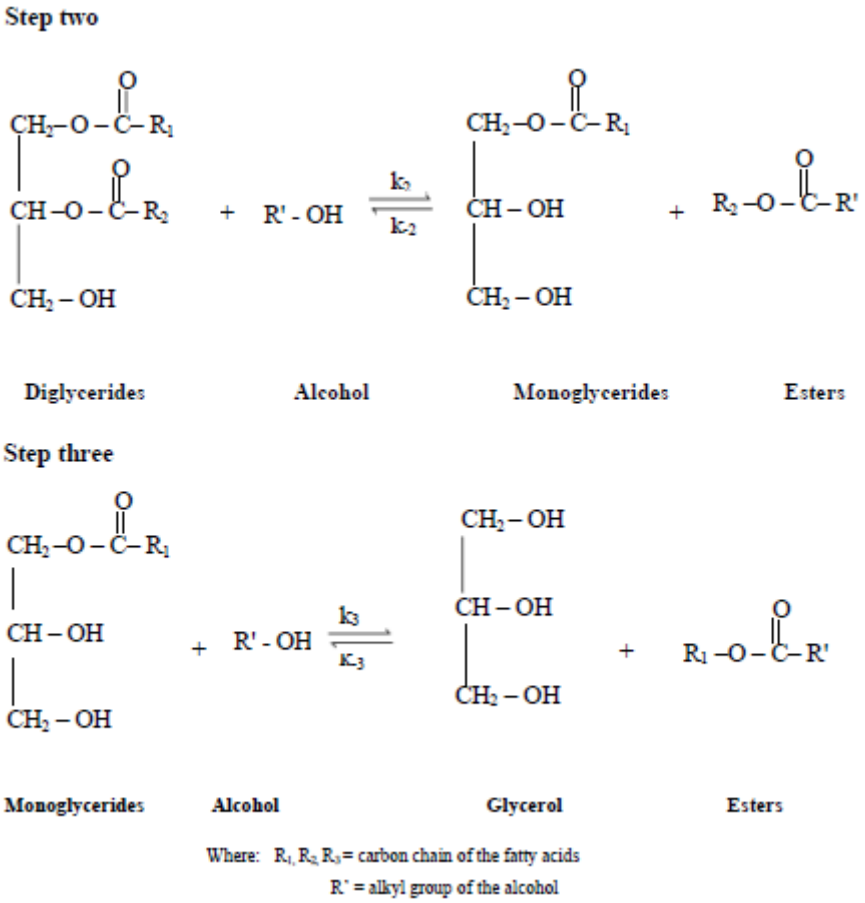


Figure 2: Formation of Biodiesel by Transesterification Process

2.4 Microwave Energy Assisted Transesterification Reaction

Microwave irradiation is one of the methods of enhancing transesterification reaction. When the reaction is carried out under microwaves, transesterification is efficiently accelerated in a short reaction time [11]. As a result, the formation of byproducts of the reaction is greatly reduced while the separation time of the glycerides is shortening [12, 13]. This is because microwave radiation increases the solubility of oil and alcohol that results in increased rate transesterification reaction and conversion of glycerides. As a result, higher reaction rate and yield are obtained.

2.5 Feedstock for Transesterification Reaction

The feedstocks for the transesterification reaction are usually from vegetable oil and animal fat. This variety of feedstock available for biodiesel production makes

biodiesel a potential new alternative source of energy. Oil and fats may be edible or non-edible. The use of edible feedstock for biodiesel production has a few challenges such as high cost of the feedstock which accounts for 75% of the biodiesel production cost [1] due to its need for the food industry. Thus, the use of non-edible sources such as neem oil, castor oil, and jathropa oil can make the technology economically viable. These oils contains compounds which are unsuitable for human consumption and is cheaper than edible oil while still maintaining a high percentage of biodiesel yield.

2.6 Neem Oil

Neem oil is one of the sources of non-edible oil. It is extracted from the seed of the neem tree which belongs to the mahogany family Meliaceae and grows in most parts in India and Burma. The seeds have an oil content value of 45 %wt which has a high potential for the production of biodiesel [16]. The colour of neem oil is usually light to dark brown, bitter, and has a strong odour. It consists mainly of triglycerides and large amounts of triterpenoid compounds which made up the bitter taste [17]. The oil is hydrophobic in nature and it needs to be formulated with appropriate surfactants in order to emulsify it. Neem oil has been identified to have the potential of becoming the supplier of biodiesel in the future [17] and thus this study will use neem oil as the feedstock for transesterification reaction.

Olugbenga Olufemi Awolu proved in his study that neem biodiesel showed a general compliance with known standards judging from its physicochemical properties and the engine test. These, coupled with its high yield, attested to the production viability and efficiency of neem biodiesel using two-step transesterification process [23].

CHAPTER 3: METHODOLOGY

3.1 Introduction

Overall process flow diagram of the research methodology to investigate transesterification of neem oil with preheating using microwave energy followed in the present study is presented in Figure 3.1. Materials used were presented in section 3.2. Experimental methodology is presented in section 3.3. Statistical design of the experiment for transesterification of neem oil is discussed in section 3.4. Standard methods used to analyze the quality of biodiesel and quantification of the results is presented in sections 3.5.

3.2 Materials and Apparatus

The biodiesel that was used in this study was neem oil or also called margosa oil. The neem oil was purchased from a supplier in Ipoh, Malaysia. This study consisted of three main parts which are oil characterization part, transesterification reaction, and analysis of the produced biodiesel using gas chromatography. The chemicals that were used for the transesterification reaction, for pro-analysis, alkaline and acidic catalyst, and standard chemicals for biodiesel analysis in gas chromatograph are presented in Table 1.

Table 1: Chemicals used in the present research work

Description	Purity
Alcohol	
Methanol	≥ 99.7%
Catalyst	
Sodium hydroxide (alkaline catalyst)	≥ 99%
Pro-analysis chemicals	
Iso-propanol	>99.8%
Toluene	>99%

N-hexane	≥ 99%
N-heptanes	≥ 99.5%
Potassium hydroxide	0.1 N
Iodine	≥ 99.99%
Sodium sulphate	≥ 99%
Phenolphthalein	Reagent Grade
Acetic acid	Reagent grade
Diethyl ether	Reagent grade
Reference standards for GC	
1,2,4 butanetriol	GC grade
Tricaprin	GC grade
Glycerin	GC grade
Monoolein, Diolein, Triolein	GC grade
N-Methyl-N-trimethylsilyltriflouroacetamide (MSTFA)	GC grade
Pyridine	≥99%

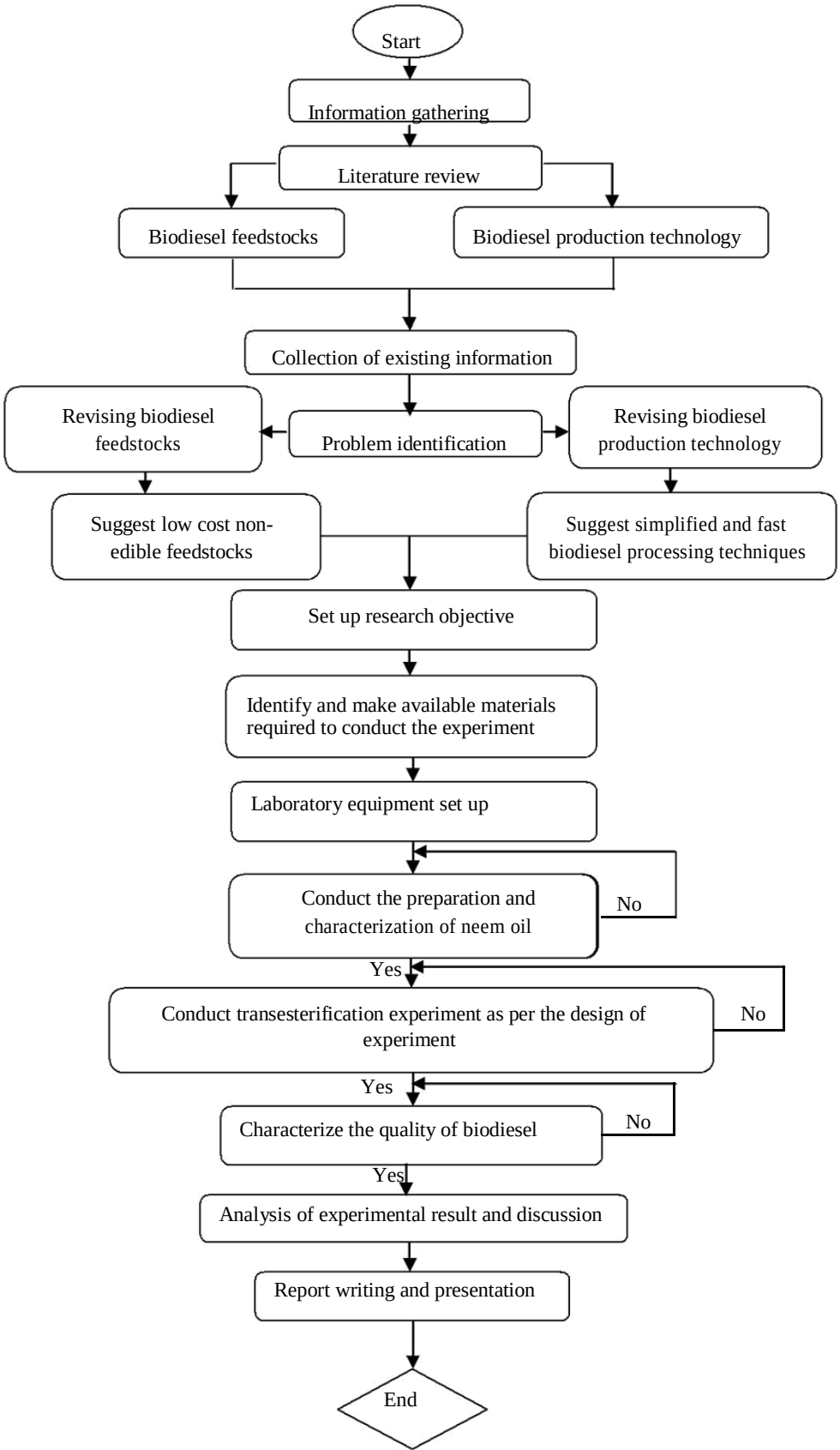


Figure 3: Flow Chart of The study

3.3 Experimental Methodology

3.3.1 Characterization of Neem Oil

Vegetable oils contain free fatty acids (FFA), saturated and unsaturated fatty acid glycerides. Acid Value provides a measure of FFA. Saponification Value provides a measure of fatty acid glycerides and Iodine Value gives a measure of level of unsaturation. Calorific value of the oil is an indicator of its fuel value; viscosity and density of the oil provide an indication of its usability as a fuel. Methods used to measure these properties and the importance of determining each of them is presented in details in the following sections.

3.3.1.1 Determination of Acid Value and Acid Number

Acid value is the measure of the free fatty acid (FFA) present in the oil. According to ASTM D 974-06, acid number is defined as the quantity of base expressed in milligrams of potassium hydroxide per gram of sample to a specified end point and it affects the quality of the biodiesel as a fuel. The determination of acid value is important for the design of the transesterification reaction experiments. Fuels with high acid value require acid catalyst while low acid value fuels require base catalyst. This is very essential to produce biodiesel that meets international requirements. The acid value of neem oil and the corresponding biodiesel produced were determined using titration method and procedures of American Oil Chemists Society, AOCS Official Methods cd 3d-63, revised 2003.

The procedure of the experiment is as follows:

1. A solvent mixture consisting of equal parts by volume of isopropyl alcohol and toluene was prepared.
2. A 0.1 N KOH was prepared
3. Phenolphthalein solution was added to the required amount of solvent in ratio of 2 mL to 125 mL and neutralize with KOH to a faint pink colour.
4. The sample size was determined from the following table:

Table 2: Acid Value Sample Size

Acid Value	Mass 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

5. The sample was shaken vigorously while titrating with standard alkali to the first permanent pink colour of the same intensity as that of the neutralized solvent before the latter was added to the sample. The colour must persist for 30 s.

6. A blank titration using 125 mL of the neutralized solvent mixture was performed.

7. The acid value using the formula was calculated

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

Where,

A is volume, mL of standard alkali used in titration

B is volume, mL of standard alkali used in titrating the blank

N is normality of standard alkali

W mass, g of sample

3.3.1.2 Determination of viscosity, specific gravity and calorific value

The viscosity, density and calorific value of neem oil and the corresponding alkyl esters synthesized weree measured using BROOKFIELD (model cap 2000+, USA) programmable digital viscometer, a calibrated pycnometer (Jayteck, UK) and bomb calorimeter, respectively.

For viscosity, the procedure is as follows:

1. The viscometer was switched on.
2. A spindle was selected and attached. The spindle number, temperature, and speed control were set.
3. The handle placing the cone was lowered onto the plate. The handle was locked into its lowest position. Allow around ten minutes for the cone to come to equilibrium temperature with the plate.
4. Raise the plate. Place sample onto the plate. Lower the spinde on the sample. The sample must completely cover the face of the spindle.
5. Allow the spindle, plate, and sample to equilibrate to the temperature control setting.
6. Set the RUN TIME for rotating the spindle. Press RUN key and execute the viscosity measurement. Read the result of the sample test.

For specific gravity, the procedure is as follows:

1. An empty beaker was weighed
2. 10 mL of neem oil was measured using a measuring cylinder and pour into the empty beaker.
3. The beaker with neem oil was weighed.
4. The weight of beaker with neem oil was subtracted with the weight of empty beaker.
5. The density of neem oil was determined
6. Specific gravity of neem oil was determined

For calorific value determination, a sample of neem oil is sent to the required personnel in UTP to undergo the bomb calorimeter experiment.

3.3.2 Transesterification Reaction Experimental Approach

A two neck round bottom flask was equipped with a reflux condenser, a magnetic stirrer, and a thermometer will be used. Predetermined and measured amount of neem oil were prepared and placed in a round bottom flask reactor. Required amount of methanol was added to the neem oil in the reactor. The flask was inserted in a microwave to be heated with microwave energy for the required time under investigation for pre-treatment. The flask was then be taken out and heated to the reaction temperature and then immediately immersed in a silicon oil thermostat to maintain the reaction temperature.

After a specified reaction time, the reactor was taken out of the thermostat. The mixtures were transferred to a separation funnel and diluted with distilled water to prevent further reaction. Then, the upper layer was recovered and washed with warm water (50-60 ^{o}C) and then passed through sodium sulphate particles to remove impurities. The recovered alkyl ester will be weighed and stored in a screw capped bottle for further analysis.

3.3.3 Statistical Experimental Design

Determining and identifying the optimum operating condition for transesterification reaction conventionally is very difficult due to the interaction effect of different parameters. The use of statistical methods of experimental design will help in determining the optimal condition of the reaction with a minimum number of experiments and thus increase the yield biodiesel. Response Surface Methodology (RSM) is one of the widely used tool for the identification of optimum experiment design. In this study, the Central Composite Design (CCD) technique of RSM was used for designing and finding the optimum operating condition of transesterification reaction of neem oil.

3.3.4 Analysis of Biodiesel Samples

The biodiesel that was produced from the transesterification reaction need to meet the international standards established to maintain the quality of biodiesel as a fuel to increase the credibility of biodiesel consumers. ASTM D6751 and EN 14214 are two well established standards for testing the quality of biodiesel as motor fuel. The

standards define the quality of biodiesel in terms of its physical and chemical properties such as glycerides (G), monoglycerides (MG), diglycerides (DG) and triglycerides (TG), acid numbers, viscosity, specific gravity, and others. Quality of biodiesel produced was analyzed using gas chromatography (GC) technique to verify its quality with international requirements.

For the analysis, a sample of neem oil diluted with hexane was sent to the UTP's Central Analytical Centre in Block P for gas chromatography mass spectrometer (GCMS) analysis.

3.4 Gantt Chart and Key Milestones

Table 3: Gantt Chart and Key Milestones

No	Detail Work	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Neem oil characterization														
2	Preliminary experiment														
3	Design of experiment														
4	Main experiment														
5	Acid Value, Viscosity, Specific gravity														
6	GCMS result														
7	Submission progress report														
8	Pre-EDX														
9	Submission draft report														
10	Submission of dissertation (soft bound)														
11	Submission of technical paper														
12	Oral Presentation														
13	Submission of dissertation (hard bound)														

CHAPTER 4: RESULT AND DISCUSSIONS

4.1 Acid Number Determination

The result for the determination of acid value is as follows:

Table 4: Acid Number Result

	1st Trial	2nd Trial
Mass of KOH (g)	2.8005	2.8155
Mass of neem oil (g)	20.0966	10.0994
Titration starting point	0	0.10
Blank titration end point	0.25	0.35
Volume KOH used (mL)	0.25	0.25
Neem oil titration start point	0.25	0.35
Neem oil titration end point	18.25	9.25
Volume KOH used (mL)	18	8.90
Acid Value (mg KOH/g)	4.8852	4.85265
Average (mg KOH/g)	4.868925	

From the above table, it is determined that the free fatty acid (FFA) content of neem oil is average about 4.868925. The presence of high FFA in a vegetable oil can cause the formation of soap when alkaline catalysed transesterification is carried out. The alkaline catalyst will partially neutralize the FFA in the oil producing soap and decreasing the biodiesel yield [18]. Studies had shown that oils that containing FFA above 5% is not suitable for alkaline catalysed transesterification due to the soap formation. In order to prevent soap formation, the FFA content must be below 2% [19, 20, 21].

Since the acid value of neem oil is above 2%, the tendency for formation of soap during transesterification reaction is high, thus it can be predetermined that the design of the experiment will require a two-step transesterification reaction, first using acid as the catalyst to reduce the FFA content in the oil and next with alkaline catalyst.

4.2 Viscosity Determination

The result obtained from the viscosity experiment is as follows:

Temperature = 50 ^{o}C

Speed = 250 rpm

Shear Rate = 3333 s^{-1}

	Spindle 1	Spindle 2	Spindle 3
cP	51.8	26	-
%	6.9	1.7	-2.9

Temperature = 50 ^{o}C

Speed = 250 rpm

Shear Rate = 833 s^{-1}

	Spindle 4	Spindle 5	Spindle 6
cP	54	36	60
%	0.9	0.3	0.2

From the result above, according to the procedure of the experiment, the value for the viscosity is taken when the percentage value is the highest. According to the above table, the viscosity of neem oil is 51.8 cP which is equivalent to 5.18 Pa.s which is higher than petroleum based diesel. Thus, neem oil will need to undergo transesterification reaction to reduce its viscosity to a range similar with petroleum oil so that it can be used as a diesel fuel.

4.3 Specific Gravity Determination

For specific gravity determination, the result is as follows:

Table 5: Specific Gravity Result

Mass of measuring cylinder (g)	29.0705
Mass of measuring cylinder with neem oil (g)	31.1718
Mass of neem oil (g)	2.1013
Volume of neem oil (mL)	2.2
Density of neem oil (g/mL)	0.9551
Density of water (g/mL)	1
Specific gravity of neem oil	0.9551

From the above table, the specific gravity obtained from the experiment is 0.9551.

4.4 Calorific Value Determination

The calorific value of neem oil obtained from bomb calorimeter experiment is 39.14 MJ/kg. This is comparable when considering the energy content of diesel which is at 43.1 MJ/kg. The heating energy of neem oil is high enough for it to be considered as a feasible fuel.

4.5 GCMS Result

The result from the GCMS will be attached in the appendix section.

4.6 Preliminary Experiment Result

When a single step transesterification reaction using alkaline catalyst is performed on neem oil, most of the product formed is soap and very little biodiesel is produced. This is because of the high FFA content of neem oil. So, the neem oil needs to undergo a two-step transesterification reaction.

The result of the preliminary two-steps transesterification reaction of neem oil:

Neem oil : 10 g

Reaction temperature : 50 ^{o}C

Stirring speed : 300 rpm

Weight percent of NaOH : 1% of neem oil sample

Reaction time : 45 minutes

Oil to methanol ratio : 1:9

Table 6: Preliminary Experiment Result

Weight percent of H_2SO_4 (%)	Biodiesel Yield
0.3	89.6
0.5	85.2
1.5	80.2
2	80.0
10	76.8
25	72.6
40	69.4

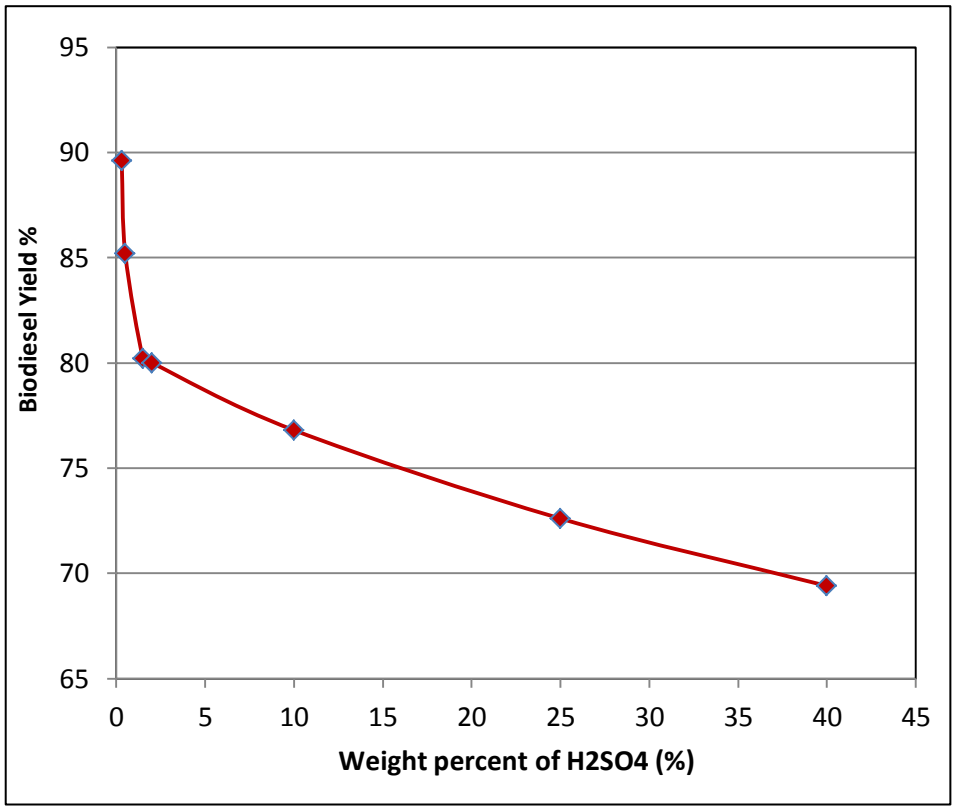


Figure 4: Yield with Varying amount of H_2SO_4

From the results obtained, it is determined that the amount of H_2SO_4 that produces the highest biodiesel is 0.3 wt%. Thus, for the design of the experiment, it is

proposed that for the acid esterification part the amount of H_2SO_4 should be 0.3 wt% of the weight of oil because this will produce highest biodiesel yield.

4.7 Result of Transesterification of Neem Oil

Two steps transesterification of (i) preheated neem oil with microwave energy and (ii) non treated neem oil with methanol was carried out to investigate the effect of microwave energy on the rate of transesterification of neem oil. For all experiments, all process parameters for acid esterification of neem oil are kept constant. Only transesterification process parameters are varied in order to investigate the effect for each parameter on the rate of transesterification of neem oil. The results for the transesterification experiment are shown in the next section.

4.7.1 Transesterification of Neem Oil

The result of transesterification of neem oil is shown in the table below:

Table 7: Yield of Neem Oil Transesterification

Reaction Temperature	NaOH	Oil to Methanol	Reaction Time	Yield
^{o}C	wt%	Molar Ratio	min	wt%
50	0.5	9.0	30.0	85.1
30	1.5	9.0	15.0	92.7
50	0.5	6.0	15.0	83.5
40	1.0	7.5	37.5	88.6
50	1.5	9.0	15.0	91.0
60	1.0	7.5	22.5	90.1
40	1.0	10.5	22.5	83.5
50	1.5	9.0	30.0	95.2
30	1.5	6.0	15.0	72.6
40	1.0	7.5	22.5	89.6
30	1.5	9.0	30.0	83.1
40	1.0	7.5	7.5	93.0
50	0.5	6.0	30.0	87.4
20	1.0	7.5	22.5	86.0
50	0.5	9.0	15.0	74.9
30	1.5	6.0	30.0	81.1
40	0.0	7.5	22.5	865
40	2.0	7.5	22.5	73.8
40	1.0	7.5	22.5	89.6
50	1.5	6.0	15.0	801
30	0.5	6.0	30.0	79.0
30	0.5	9.0	30.0	83.5
30	0.5	9.0	15.0	76.8
40	1.0	4.5	22.5	94.8
30	0.5	6.0	15.0	75.5
50	1.5	6.0	30.0	88.4

From the table above, it can be seen that the maximum yield of biodiesel is 95.2%.

Table 8: Regression Coefficient of Yield Without Microwave Heating

Coefficient	*Estimate*
constant	0.259625
W:Temperature	0.0125625
X:NaOH	-0.0255833
Y:Oil to Methanol	0.0680278
Z:Reaction Time	0.00592778
WW	-0.000104062
WX	0.0011375
WY	-0.000879167
WZ	0.000145833
XX	-0.120625
XY	0.0374167
XZ	-0.00215
YY	-0.00340278
YZ	-0.000705556
ZZ	-0.0000627778

The estimated regression equation is given by the following formula:

Yield = 0.259625 + 0.0125625*W - 0.0255833*X + 0.0680278*Y + 0.00592778*Z - 0.000104062*W^2 + 0.0011375*W*X - 0.000879167*W*Y + 0.000145833*W*Z - 0.120625*X^2 + 0.0374167*X*Y - 0.00215*X*Z - 0.00340278*Y^2 - 0.000705556*Y*Z - 0.0000627778*Z^2

This formula can be used to estimate the biodiesel yield. The comparison of the experimental result and estimated result is shown in the following table:

Table 9: Experimental Yield vs Calculated Yield Without Microwave Heating

Reaction Temperature	NaOH	Oil to Methanol	Reaction Time	Yield (experimental)	Yield (estimated)
^{o}C	wt%	Molar Ratio	min	wt%	wt%
50	0.5	9.0	30.0	85.1	84.0
30	1.5	9.0	15.0	92.7	88.5
50	0.5	6.0	15.0	83.5	85.2
40	1.0	7.5	37.5	88.6	90.4
50	1.5	9.0	15.0	91.0	89.0
60	1.0	7.5	22.5	90.1	89.6
40	1.0	10.5	22.5	83.5	87.5
50	1.5	9.0	30.0	95.2	90.2
30	1.5	6.0	15.0	72.6	77.7
40	1.0	7.5	22.5	89.6	89.6
30	1.5	9.0	30.0	83.1	85.4
40	1.0	7.5	7.5	93.0	85.9
50	0.5	6.0	30.0	87.4	92.8
20	1.0	7.5	22.5	86.0	81.3
50	0.5	9.0	15.0	74.9	79.5
30	1.5	6.0	30.0	81.1	77.7
40	0.0	7.5	22.5	865	76.4
40	2.0	7.5	22.5	73.8	78.6
40	1.0	7.5	22.5	89.6	89.6
50	1.5	6.0	15.0	801	83.4
30	0.5	6.0	30.0	79.0	85.0
30	0.5	9.0	30.0	83.5	81.4
30	0.5	9.0	15.0	76.8	81.4
40	1.0	4.5	22.5	94.8	85.5
30	0.5	6.0	15.0	75.5	081.7
50	1.5	6.0	30.0	88.4	87.8

From the table of biodiesel yield above, it can be seen that the regression equation

can be used to estimate the biodiesel yield with the lowest deviation from the experimental value is 0.13%.

The effect of process parameters interaction on the transesterification rate are shown using response surface plots. The response surface plots for the yield of biodiesel as a function of two factors at a time while keeping the other factors at their centre point level were plotted in a three dimensional surface with contour plot at the bottom. The elliptical of the contour plot indicates a good interaction of the two parameters on the response while circular shape indicates less interaction effects between the parameters affecting the response. The response surface plots are shown below:

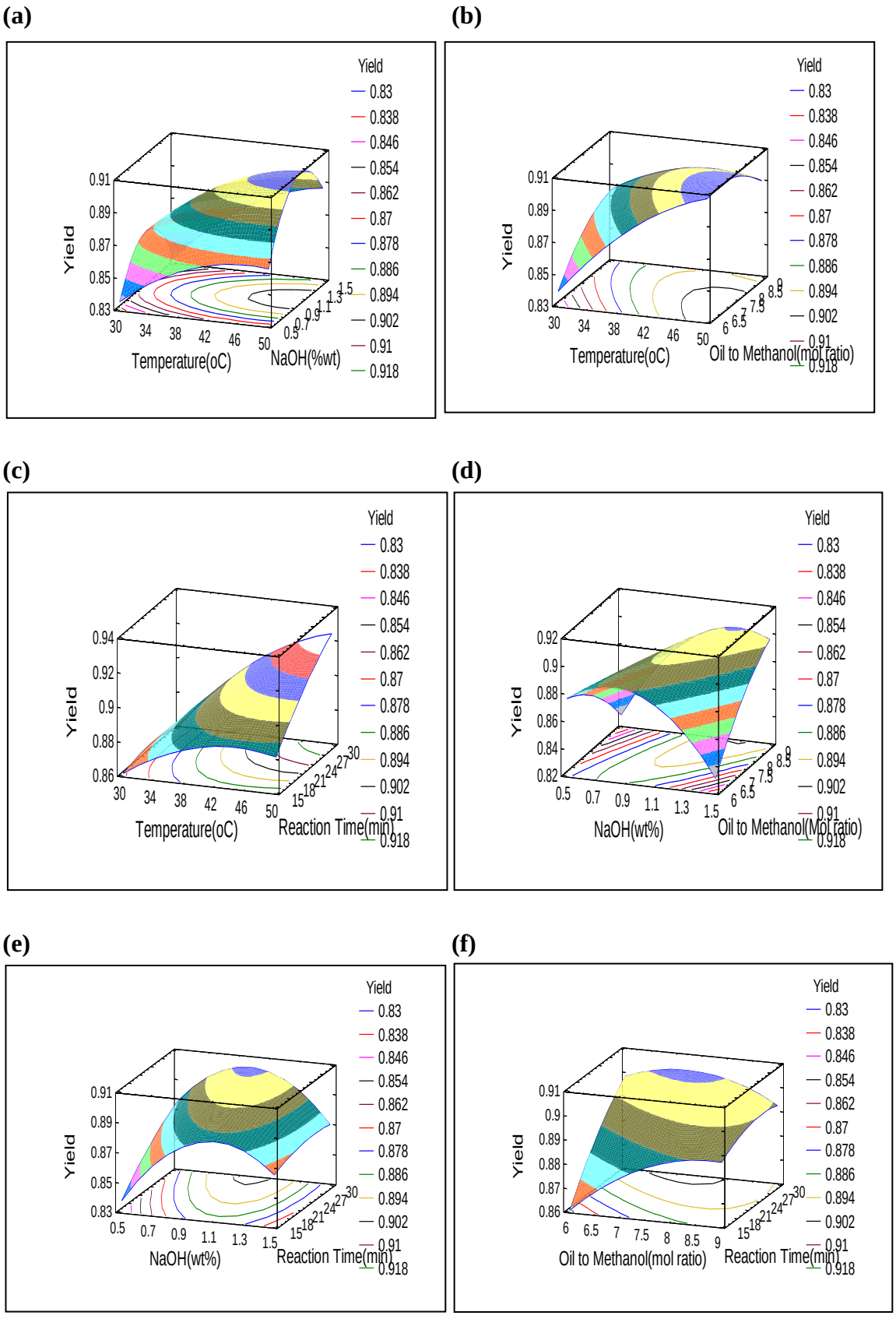


Figure 5: Response Surface Plot of Combined Variables for Transesterification of Neem Oil

Figure 5(a) presents biodiesel yield as a function of reaction temperature and wt% NaOH. Maximum yield is observed at 50^{o}C and 1.1 wt% NaOH loading. Higher temperature increases reaction rate by increasing the solubility of methanol and oil. NaOH promotes transesterification reaction until an optimal value of about 1.1% after which addition of extra NaOH will promote saponification reaction and reduce biodiesel yield.

Figure 5(b) presents biodiesel yield as a function of reaction temperature and oil to methanol ratio. The maximum yield is observed when oil to methanol ratio is 1:6. Addition of methanol will increase solubility of oil into methanol, thus increases rate of transesterification reaction. However, if too much methanol is used, product biodiesel will dissolve in the glycerol phase and affect the biodiesel recovery process.

Figure 5(c) presents biodiesel yield as a function of reaction temperature and reaction time. The maximum yield is observed at highest temperature and highest reaction time. Longer reaction time will produce more biodiesel thus, increases the yield.

Figure 5(d) presents biodiesel yield as a function of wt% of NaOH and oil to methanol ratio. Maximum yield is observed at 1.1 wt% NaOH and ratio of oil to methanol of 1:6.

The optimization of process parameters for transesterification of treated neem oil is done using CENTRIO STATGRAPHICS software. The optimum value for the process parameters are given in the table below:

Table 10:Optimum of Process Parameters Without Microwave Heating

Factor	*Low*	*High*	*Optimum*
Temperature	20.0	60.0	60.0
NaOH	0.0	2.0	0.7
Oil to Methanol	4.5	10.5	4.5
Reaction Time	7.5	37.5	37.5

4.7.2 Transesterification of Microwave Energy Pre-treated Neem Oil

The result of transesterification of microwave energy pre-treated neem oil is shown below:

Table 11: Yield of Pretreated Neem Oil Transesterification

MHWT	NaOH	Oil to Methanol	Reaction Time	Yield
min	wt%	Molar ratio	min	wt%
4	0.5	9.0	30.0	84.8
4	0.5	6.0	30.0	83.3
2	0.5	6.0	30.0	87.6
2	1.5	6.0	15.0	86.4
3	1.0	7.5	22.5	87.4
4	1.5	6.0	15.0	78.0
3	2.0	7.5	22.5	74.6
4	1.5	9.0	30.0	86.9
4	1.5	9.0	15.0	86.2
4	0.5	6.0	15.0	99.1
2	0.5	9.0	15.0	76.9
3	1.0	7.5	22.5	94.2
5	1.0	7.5	22.5	87.0
2	0.5	6.0	15.0	81.0
3	0.0	7.5	22.5	86.9
2	1.5	9.0	30.0	95.9
4	1.5	6.0	30.0	95.7
2	0.5	9.0	30.0	96.2
1	1.0	7.5	22.5	88.7
3	1.0	7.5	37.5	91.1
2	1.5	6.0	30.0	93.5
4	0.5	9.0	15.0	93.1
3	1.0	4.5	22.5	98.6
3	1.0	10.5	22.5	93.3
2	1.5	9.0	15.0	94.6
3	1.0	7.5	7.5	87.9

From the table above, it can be seen that the maximum yield of transesterification of treated neem oil is 99.1%.

Table 12: Regression Coefficient of Yield With Microwave Heating

Coefficient	*Estimate*
constant	0.583521
A:MWHT	0.22975
B:NaOH	0.192667
C:Oil toMethanol	-0.0679167
D:Reaction time	0.0112111
AA	-0.0070625
AB	-0.05275
AC	-0.00841667
AD	-0.00333333
BB	-0.09925
BC	0.00833333
BD	0.00416667
CC	0.00586111
CD	-0.000144444
DD	-0.0000522222

The estimated regression equation is given by the following formula:

Yield = 0.583521 + 0.22975*A + 0.192667*B - 0.0679167*C + 0.0112111*D - 0.0070625*A^2 - 0.05275*A*B - 0.00841667*A*C - 0.00333333*A*D- 0.09925*B^2 + 0.00833333*B*C + 0.00416667*B*D + 0.00586111*C^2 - 0.000144444*C*D - 0.0000522222*D^2

This formula can be used to estimate the biodiesel yield. The comparison of the experimental result and estimated result is shown in the table below:

Table 13: Experimental Yield vs Calculated Yield With Microwave Heating

MHWT	NaOH	Oil to Methanol	Reaction Time	Yield (experimental)	Yield (calculated)
min	wt%	Molar ratio	min	wt%	wt%
4	0.5	9.0	30.0	84.8	86.6
4	0.5	6.0	30.0	83.3	90.8
2	0.5	6.0	30.0	87.6	88.7
2	1.5	6.0	15.0	86.4	83.7
3	1.0	7.5	22.5	87.4	90.8
4	1.5	6.0	15.0	78.0	85.2
3	2.0	7.5	22.5	74.6	80.1
4	1.5	9.0	30.0	86.9	85.0
4	1.5	9.0	15.0	86.2	84.2
4	0.5	6.0	15.0	99.1	95.7
2	0.5	9.0	15.0	76.9	85.1
3	1.0	7.5	22.5	94.2	90.8
5	1.0	7.5	22.5	87.0	87.3
2	0.5	6.0	15.0	81.0	83.6
3	0.0	7.5	22.5	86.9	81.7
2	1.5	9.0	30.0	95.9	98.5
4	1.5	6.0	30.0	95.7	86.6
2	0.5	9.0	30.0	96.2	89.6
1	1.0	7.5	22.5	88.7	88.7
3	1.0	7.5	37.5	91.1	92.5
2	1.5	6.0	30.0	93.5	95.1
4	0.5	9.0	15.0	93.1	92.2
3	1.0	4.5	22.5	98.6	96.1
3	1.0	10.5	22.5	93.3	96.0
2	1.5	9.0	15.0	94.6	87.
3	1.0	7.5	7.5	87.9	86.7

From the table of biodiesel yield above, it can be seen that the regression equation can be used to estimate the biodiesel yield with the highest deviation from the

experimental value is 0.1%.

The effect of process parameters interaction on the transesterification rate are shown using response surface plots. The response surface plots for the yield of biodiesel as a function of two factors at a time while keeping the other factors at their centre point level were plotted in a three dimensional surface with contour plot at the bottom. The elliptical of the contour plot indicates a good interaction of the two parameters on the response while circular shape indicates less interaction effects between the parameters affecting the response. The response surface plots are shown below:

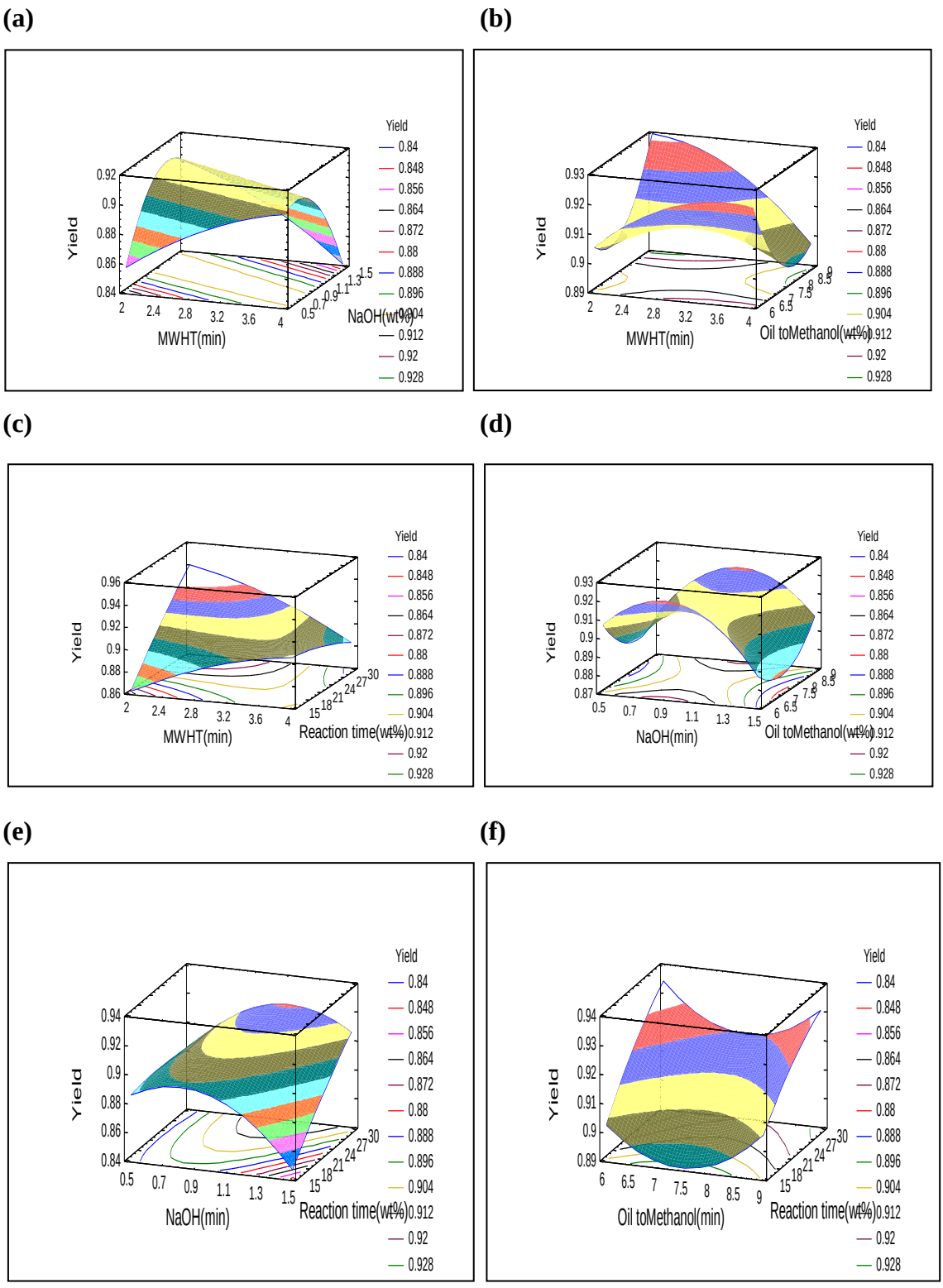


Figure 6: Response Surface Plot of Combined Variables for Transesterification of Pretreated Neem Oil

Figure 6(a) presents biodiesel yield as a function of microwave heating time and wt%

NaOH. Maximum yield was observed at 0.9 wt% NaOH. Increase of NaOH promotes transesterification. However, further overloading of NaOH decreases the yield due to the reaction favouring saponification. Figure 6 (b) presents biodiesel yield as a function of microwave heating time and oil to methanol ratio. Maximum yield was observed at 9 molar ratio of oil to methanol. This is because methanol increases rate of reaction. However, further addition of methanol may dissolve the product biodiesel into the glycerol phase and affect the biodiesel recovery process.

Figure 6(c) presents biodiesel yield as a function of microwave heating time and reaction time. Maximum yield was observed at the longest reaction time. This is because more biodiesel is produced as the reaction time increases. Figure 6(d) presents biodiesel yield as a function of wt% NaOH and oil to methanol ratio. Maximum yield was observed at 0.8 wt% NaOH. This is because above the maximum amount, NaOH will promote saponification process.

Figure 6(e) presents biodiesel yield as a function of wt% NaOH and Reaction time. Maximum yield is observed at 30 minutes reaction time. This is because the longer time of reaction, more biodiesel will be produced. Figure 6(f) presents biodiesel yield as a function of oil to methanol ratio and reaction time. Maximum yield was observed at highest oil to methanol ratio and longest reaction time. This is because methanol promotes transesterification until a certain limit where it will promote saponification reaction while longer reaction time produces higher amount of biodiesel.

The optimization of process parameters for transesterification of treated neem oil is done using STATGRAPHICS software. The optimum value for the process parameters are given in the table below:

Table 14 :Optimum of Process Parameters With Microwave Heating

Factor	*Low*	*High*	*Optimum*
MWHT	1.0	5.0	1.0
NaOH	0.0	2.0	1.5
Oil toMethanol	4.5	10.5	10.5
Reaction time	7.5	37.5	37.5

CHAPTER 5: CONCLUSION

5.1 Conclusion

In the present work, non-edible oil source, neem oil is used to investigate the effect of pre-treated neem oil with microwave energy on the rate of transesterification in order to enhance the rate of reaction. A two-step reaction was carried out on neem oil due to high free fatty acid content. It was observed that use of microwave pre-treated neem oil have substantially increased the reaction rate of transesterification reaction. Optimum conditions for the reaction were established using response surface methodology (RSM). With microwave energy pre-treatment, the maximum yield was found to be 99.1% in 15 minutes at 50 ^{o}C while without microwave energy treatment, the maximum yield achieved was 95.2% in 30 minutes at 50 ^{o}C reaction temperature.

5.2 Recommendation for Future Work

For future work, it is recommended that the study is expanded to investigate the effect of different power of microwave energy on the rate of transesterification. The parameters to be investigated such as temperature and time can also be used in a higher range to determine the optimum value for each variable.

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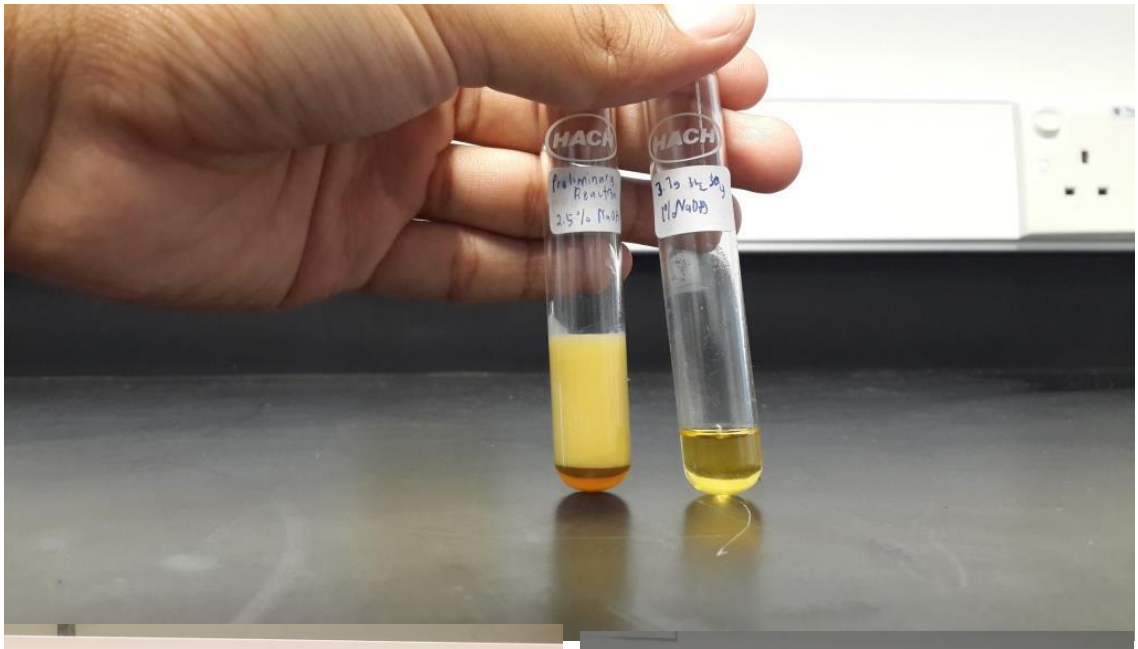
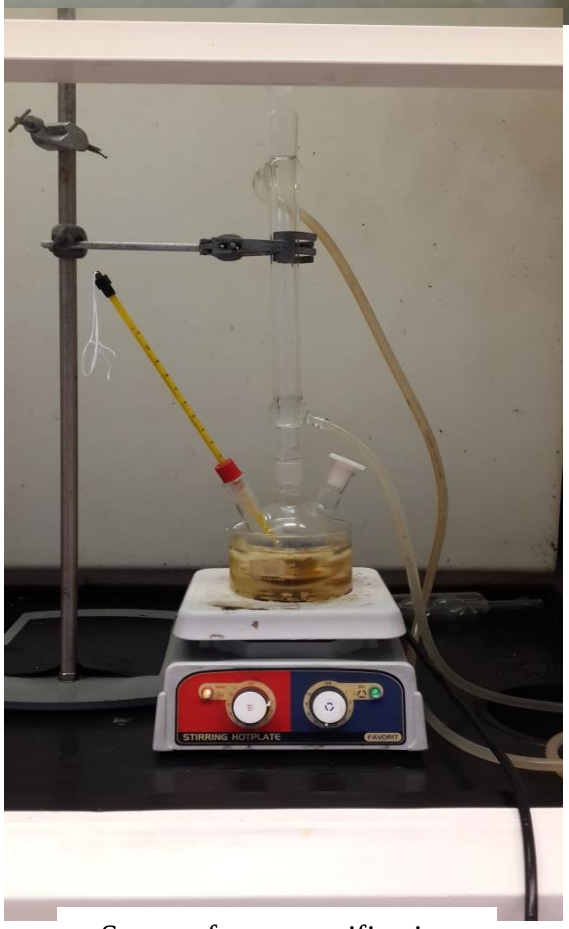
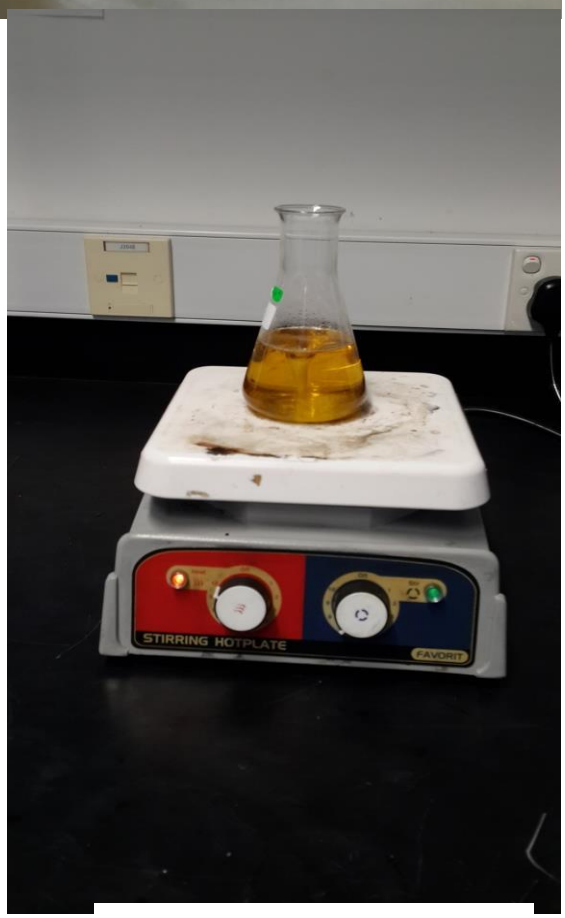
APPENDIX

Experiments Picture





Set up of transesterification reaction



Acid value determination

Separation of oil and water