

**METHANOLYSIS OF WASTE COOKING OIL (WCO) AND PARAMETRIC
OPTIMIZATION**

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by

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Universiti Teknologi PETRONAS,
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CERTIFICATION OF APPROVAL

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Approved by,

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September 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.

MOHD ESHAR BIN ABDUL HALIM

ABSTRACT

In this study the transesterification reaction is particularly slow due to the oil is sparingly soluble in lower alcohol. However, the slow reaction rate in transesterification reaction can be speed up by using reaction rate increasing technique such as microwave pre-treatment of oil. Waste Cooking Oil (WCO) has been chosen as non-edible oil feedstock for this project. WCO is chosen as it can reduce the cost of production of biodiesel and it is also environmentally beneficial from a waste management viewpoint, since it provides a cleaner way for disposing these products. However, when using waste cooking oil as feedstock, it will affect the transesterification reaction and the biodiesel properties due to foreign substance in the oil formed during frying. In order to design suitable transesterification reaction condition, chemical and physical properties of waste cooking oil has been determined. The interaction and individual effects of transesterification reaction parameter has been study using design of experiment (DOE) software's by using central composite design (CCD) of response surface methodology (RSM). The yield of biodiesel from transesterification of biodiesel pre-treated with microwave shows higher yield at 89.96% at 35 minute compared to 77.53% at 45 minute of transesterification without microwave pre-treatment. The results shows that microwave increase the reaction rate which give more yield in shorter time.

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TABLE OF CONTENTS

CERTIFICATION OF APPROVAL	ii
CERTIFICATION OF ORIGINALITY	iii
ABSTRACT	iv
ACKNOWLEDGEMENT	v
TABLE OF CONTENTS	vi
LIST OF FIGURES	ix
LIST OF TABLES	x
LIST OF ABBREVIATIONS	xi
CHAPTER 1: INTRODUCTION	1
1.1 Background of Study	1
1.2 Problem Statement	3
1.3 Objective	4
1.4 Scope of Study	4
1.5 Relevancy of Project	5
CHAPTER 2: LITERATURE REVIEW	6
2.1 History of Biodiesel	6
2.2 Transesterification	7
2.3 Waste Cooking Oil as Source of Biodiesel Feedstock	9
2.4 Acid and Alkali Catalyzed Two-Step Transesterification	9
2.5 Microwave Energy Role in Biodiesel	10
2.6 Transesterification Reaction Assisted By Microwave Heating	11
2.7 Variables Affecting Transesterification Reaction	12
CHAPTER 3: METHODOLOGY	13
3.1 Project Activities	13

3.2	Gantt Chart & Key Milestones	14
3.4	Materials and Chemical	14
3.5	Characterization of WCO	15
3.5.1	Determination of Acid Value and AcidNumber of WCO.....	16
3.5.2	Determination Specific gravity of WCO.....	17
3.5.3	Determination of Viscosity of WCO	17
3.5.4	Determination Calorific Value using Bomb Calorimeter	18
3.6	Design of Transesterification experiment.....	18
3.6.1	Esterification of WCO.....	19
3.6.2	Transesterification of WCOZ.....	20
3.7	Catalyst preparation for transesterification reaction.....	20
 CHAPTER 4: RESULT AND DISCUSSION.....		21
4.1	Characterization of WCO	21
4.1.1	Determination of Acid Number	21
4.1.2	The percentage of (FFA).....	22
4.1.3	Determination of Specific gravity.....	23
4.1.4	The Determination of Viscosity	23
4.1.5	Determination of WCO Calorific Value.	24
4.1.6	Properties of WCO.....	24
4.2	Preliminary experiment	24
4.2.1	Esterification Experiment.....	24
4.2.2	Preliminary Transesterification Experiment	25
4.3	Transesterification without microwave pre-treatment.....	27
4.3.1	Optimization of transesterification of WCO.....	27
4.3.2	Effect of the reaction variables on FAME yield.	30
4.3.3	Optimum reaction conditions for transesterification	34
4.4	Microwave energy pre-treated transesterification	35
4.4.1	Optimization Microwave energy transesterification.	35
4.4.2	Effect of the reaction variables on FAME yield	39
4.4.3	Optimum reaction conditions Microwave energy.....	42

4.5	Summary for optimization of FAME yield	42
CHAPTER 5:	CONCLUSION AND RECCOMENDATION	44
5.1	Conclusion	44
5.2	Future work	45
REFERENCE	46
APPENDICES	48

LIST OF FIGURES

Figure 1. 1	Energy Usage by Sector Including Detail for Residential	1
Figure 2. 1	Overall Transesterification Process	7
Figure 2. 2	Flow diagram of biodiesel production from WCO	8
Figure 3. 1	Esterification of WCO	19
Figure 4. 1	Plot of experimental FAME yield versus predicted yield	30
Figure 4. 2	FAME% yield plots vs reaction temperature and reaction time	31
Figure 4. 3	FAME% yield plots vs Catalyst / Oil ratio and reaction time.....	32
Figure 4. 4	FAME% yield plots vs Catalyst / Oil ratio and reaction temperature..	32
Figure 4. 5	FAME% yield plots vs Methanol / Oil ratio and reaction temperature	33
Figure 4. 6	FAME% yield plots vs Methanol / Oil ratio and reaction time	33
Figure 4. 7	FAME% yield plots vs Methanol / Oil ratio and Catalyst / Oil ratio...	34
Figure 4. 8	Plot of experimental FAME yield versus predicted yield	38
Figure 4. 9	FAME% yield plots vs reaction temperature and reaction time	39
Figure 4. 10	FAME% yield plots vs methanol/oil ratio and reaction time.....	39
Figure 4. 11	FAME% yield plots vs MWHT and reaction time.....	40
Figure 4. 12	FAME% yield plots vs methanol/oil ratio and catalyst/oil ratio.....	40
Figure 4. 14	FAME% yield plots vs MWHT and methanol/oil ratio	41
Figure 4. 13	FAME% yield plots vs MWHT and catalyst/oil ratio.....	41

LIST OF TABLES

Table 1. 1	Quantity of Waste Cooking Oil Produced in Selected Countries	2
Table 3. 1	Standard Chemicals for Transesterification of Biodiesel	15
Table 4. 1	Result of Acid Value	22
Table 4. 2	Viscosity Result from Bomb Calorimeter.....	23
Table 4. 3	Properties of WCO.....	24
Table 4. 4	FFA value after esterification experiment	25
Table 4. 5	Transesterification without pre-treatment of microwave.....	26
Table 4. 6	Transesterification with pre-treatment of microwave.....	26
Table 4. 7	Range of variables for design experiment RSM.....	26
Table 4. 8	Experimental range and level of the independent variables	27
Table 4. 9	Experimental design matrix by CCD technique for transesterification along with experimental and predicted FAME yields.....	28
Table 4. 10	Regression Coefficient for FAME yield transesterification.....	29
Table 4. 11	Optimum reaction conditions for transesterification.....	34
Table 4. 12	Experimental range and level of the independent variables.....	35
Table 4. 13	Experimental design matrix by CCD technique for microwave energy pre-treated transesterification along with experimental and predicted FAME yields.....	36
Table 4. 14	Regression Coefficient for FAME yield transesterification.....	37
Table 4. 15	Optimum Condition of microwave energy pre-treated transesterification	42
Table 4. 16	Optimization summary.....	42

LIST OF ABBREVIATIONS

List of symbols

WCO	Waste Cooking Oil
RSM	Response Surface Methodology
FFA	Free Fatty Acid
CCD	Central Composite Design
DOE	Design of Experiment
NaOH	Sodium Hydroxide
H ₂ SO ₄	Sulphuric Acid
FAME	Fatty Acid Methyl Ester
MWHT	Microwave Heating Time

CHAPTER 1

INTRODUCTION

1.1 Background of Study

During the century, the modernization in the life style and the significant growth of population has caused the increase in consumption of energy. This demand has been provided by the use of fossil resources, which caused the crisis of the fossil fuel depletion, high price of fuel and endangered environment. Two of the main contributors of this increase of energy demand have been the transportation and the basic industry sectors, being the largest energy consumers refer figure 1 below.

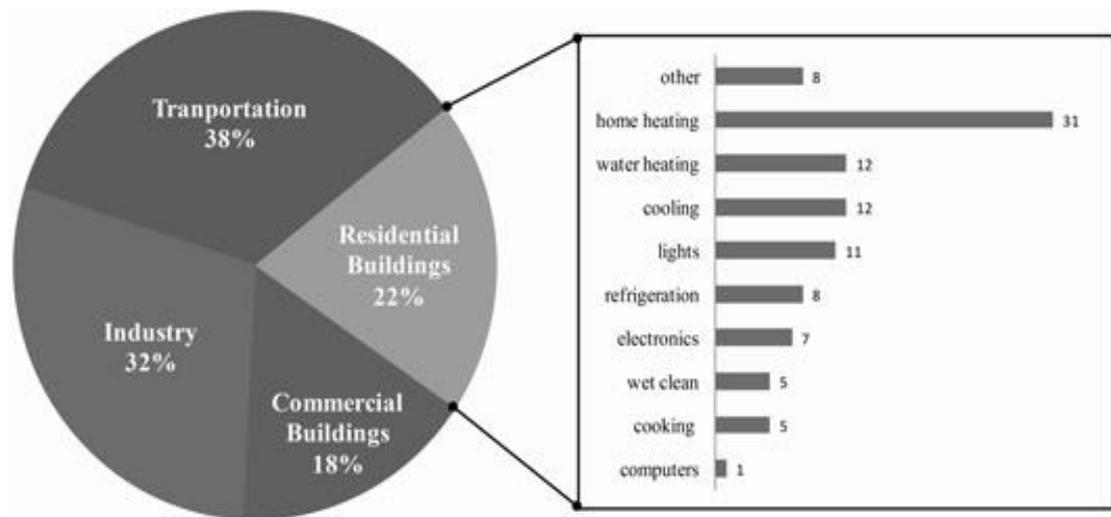


Figure 1. 1 Energy Usage by Sector Including Detail for Residential
(Perez L. et al., 2008)

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 from renewable resources is one of the most attractive alternative fuels currently being developed because of its low emissions and its desirable chemical characteristics, such as being non-toxic and biodegradable (Saidina et al.,2011). Biodiesel basically produced from vegetable oils, animal fat or trap grease is gaining importance as a renewable and substitute to petro diesel. However, the use of a food source or edible oil to produce biodiesel at the expense of the millions of people facing hunger and starvation around the world has received harsh criticism from several non-governmental organisations (NGOs) worldwide due to the increase in the demand for vegetable or edible oil and unnecessary clearing of forests for plantation (Tan et al, 2011).

Table 1. 1 Quantity of Waste Cooking Oil Produced in Selected Countries (Chen Y et al., 2009)

country	quantity (million tons/year)
China	4.5
Malaysia	0.5
United States	10.0
Taiwan	0.07
Europe	0.7–10
UK	0.2
Canada	0.12
Japan	0.45–0.57
Ireland	0.153

A possible solution to overcome this problem is to use non-edible oil. WCO which is less expensive than edible oil, can be used as a possible feedstock. It is reported that the prices of biodiesel will be reduced approximately to the half with the use of low cost feedstock (Kemp W, 2006). Annually, about million tons of WCO is generated from selected countries in the world as shown in Table 1 above. The disposal of WCO cause environmental problem when disposed incorrectly. Therefore, using WCO not only reduce the cost producing biodiesel but it also can reduce the pollution of the environment for the countries.

Mainly the biodiesel can be produced by common process known as transesterification. In this study, WCO is used as non-edible oil feedstock of this biodiesel production. However, WCO contain a lot of impurities and high free fatty acid (FFA) which will affect the yield of biodiesel. So, WCO need to go for physical and chemical treatment before undergo transesterification process. Meanwhile, transesterification reaction rate is too slow due to limited solubility of alcohol in oil. Therefore, microwave energy pre-treated transesterification of WCO is studied to enhance the reaction rate.

1.2 Problem Statement

The main challenges of biodiesel to be used as a renewable fuel is its high biodiesel production cost. It is necessary to keep the cost of production under control to make the biodiesel technology feasible by using alternative low-priced feedstock and enhancement technique to increase the reaction process. The usage of edible oils as a source of feedstock for biodiesel production won't 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. Therefore, using alternative cheap non – edible oil feedstock which in this research is WCO is necessary to reduce the cost of production. WCO is available in any local restaurant and it is wise to use to the WCO as feedstock, rather than throw it to the drain and cause pollution. Thus, this research will consider WCO as the feedstock for biodiesel. Transesterification is a slow reaction but it can be enhanced by microwave energy pre-treated of non-edible oils. WCO has high content of free fatty acid that will form soap. Therefore, reacting WCO with acid before, will help to lower down the free fatty acid content in the WCO before further reaction.

1.3 Objective

The objective to be achieved for this study includes:

To investigate transesterification of WCO with methanol that is preheated with Microwave energy; this includes:

- Investigation of the effect of preheating WCO with microwave energy on the rate of transesterification reaction.
- Study the individual and interaction effect of reaction variables on transesterification reaction of WCO.
- Optimization of reaction parameters by statistical experimental design technique of response surface methodology (RSM)

1.4 Scope of Study

In the present research work, to achieve the affirmation research objectives, WCO will be used as a source of non-edible oil sources and characterized to determine its physical and chemical properties. Transesterification reactions with pre-treated microwave energy will be conducted to investigate the effect of reaction variables such as alcohol to oil ratio, catalyst to oil ratio, reaction temperature 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. Two step transesterification technique was selected for production of biodiesel by using WCO. The first step is esterification which use sulphuric acid (H_2SO_4) and methanol to lower the FFA value to below 1%. And the next step is the transesterification by using alkali catalyst, Sodium Hydroxide (NaOH) NaOH was selected as alkaline catalyst because of fastest reaction time and also it can give higher yield percentage of the biodiesel.

1.5 Relevancy of Project

It is important to discover the new source of renewable energy before the current energy used today supplied by fossil fuel is depleted. Methanolysis of WCO and parametric optimization is an important project because it can be use as substitute for 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 WCO.

CHAPTER 2

LITERATURE REVIEW

2.1 History of Biodiesel

Biodiesel basically can be refers as any diesel fuel substitute derived from renewable source. Specifically the definition of biodiesel is mono alkyl esters of long chain fatty acids derived from renewable lipid feedstocks, such as vegetable oils and animal fats, for use in compression ignition e.g. diesel engines (Howell, 1997) and also it must meet the special requirements such as the ASTM and the European standards. Methanol usually the most common alcohol used in the production of mono alkyl esters and it often label as methyl ester to this type of esterified biodiesel. The same label is applied to the higher order alcohols such as ethanol and propanol called ethyl esters and propyl esters respectively.

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. The high viscosities pose a problem in modern diesel engine which run in fuel-injection system as it is sensitive to viscosity change. To avoid the problem occur, the oil need to reduce its viscosity in order to improve performance as it can be done by four techniques which are Dilution, micro emulsification, pyrolysis, and transesterification. The most common technique is transesterification where the methyl ester produced has a high cetane number, low viscosity and improved heating value compared to those of pure vegetable oil which results in shorter ignition delay and longer combustion duration and hence low particulate emissions. 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).

Recent studies shows that, by addition of small portion of biodiesel in petroleum diesel, the lubricity of sulfur free petroleum diesel can be restored. This way the pollution cause by Sulfur Oxide (SO_x) and CO₂ emission can be reduced. Even though, biodiesel have same or better performance as compared to petroleum diesel, but biodiesel is biodegradable, environmentally friendly and also it contain non-toxic substance (Srivastava et al., 2000).

2.2 Transesterification

The transesterification is the reaction where converting large branched of triglycerides into smaller straight-chain molecules of methyl esters, using an alkali or acid as catalyst (M. Charoenchaitrakool & J. Thienmethangkoon, 2011) which the catalyst act to increases the rate of the reaction and also the yield.

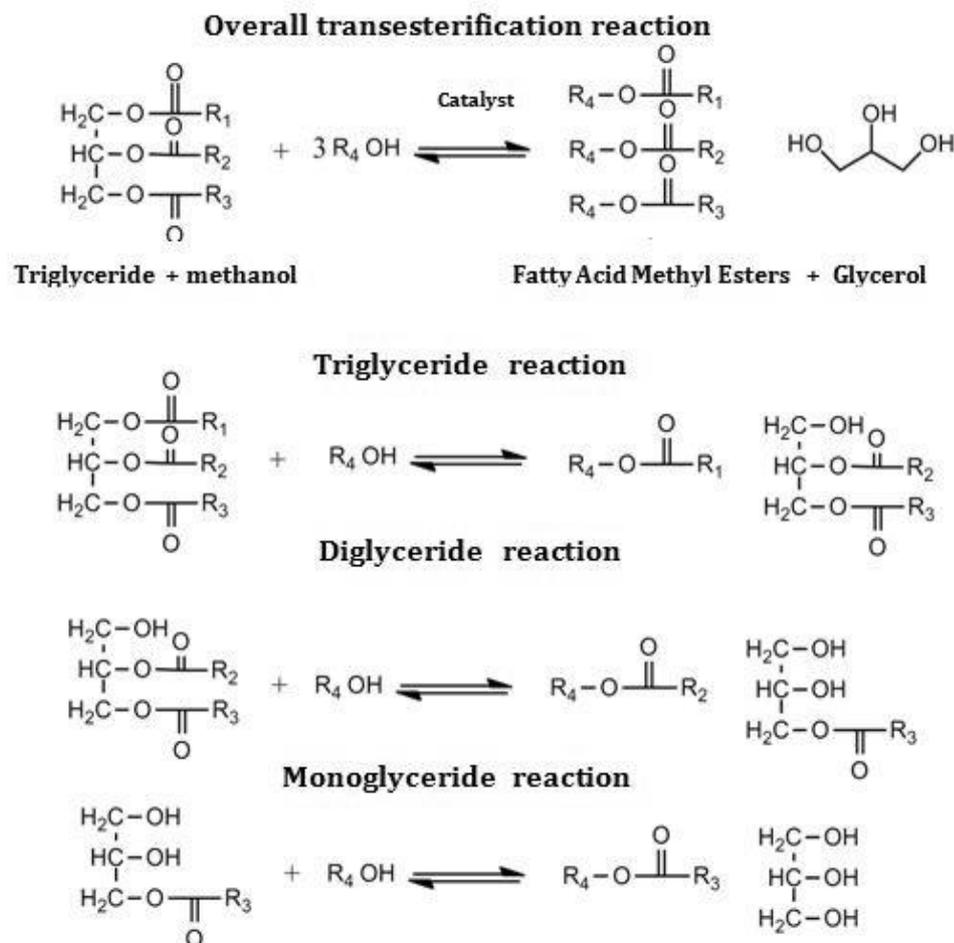


Figure 2. 1 Overall Transesterification Process (Ganesh L., 2012)

This reaction occurs stepwise, with monoglycerides and diglycerides as intermediate products. Each step produces an ester and, as a consequence, generates three ester molecules from one triglyceride molecule (Math M. et al., 2010).

The "R" groups are the fatty acids, which are usually 12 to 22 carbons in length. The large vegetable oil molecule is reduced to about 1/3 its original size, lowering the viscosity making it similar to diesel fuel. The reaction produces three molecules of an ester fuel from one molecule of vegetable oil. The transesterification process of converting vegetable oils (Triglycerides) to biodiesel is shown in Figure 2. The transesterification reaction is a reversible one, hence excess alcohol shifts the equilibrium to the product side (Marmesat S. 2007). For this research WCO is chosen and before going for transesterification, WCO must undergo pre-treatment process which consists of physical treatment mainly includes filtration for removing suspended solids of the WCO. Meanwhile chemical treatment processes involve acidic esterification as shown in figure 2.2 below.

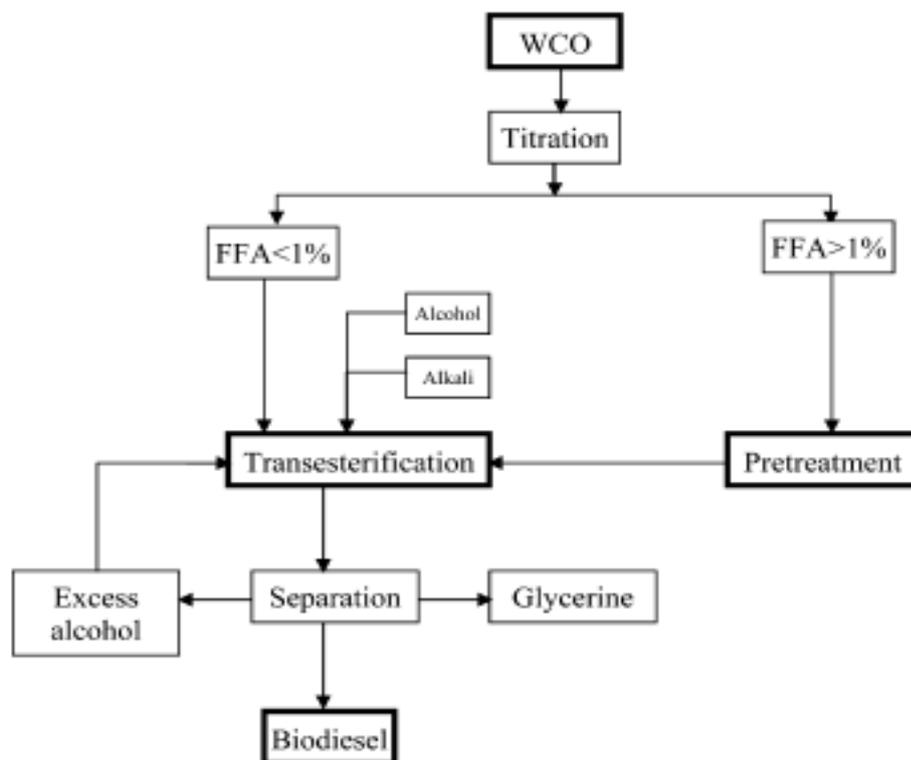


Figure 2. 2. Flow diagram of biodiesel production from WCO (Ganesh L., 2012)

2.3 Waste Cooking Oil as Source of Biodiesel Feedstock

In this context, WCO is a promising alternative for producing biodiesel because it is a cheaper raw material and it reduces the need to use land for edible oil producing crops. WCO are currently collected from large-scale food processing and service facilities. In fact, the quantities of WCO available for biodiesel production are relatively high. The properties of the WCO are somewhat different from fresh vegetable oils because of the physical and chemical changes mainly due to oxidative and hydrolytic reactions that take place during frying (Srivastava A et al., 2000).

It has been reported that WCO possess much higher acid value because it contains large amount of free fatty acids (FFA) along with moisture which are required to be removed to prevent soap formation as FFA of WCO are sensitive to alkali catalyst. Therefore, for the feedstock with high free fatty acids, it is essential to have a pre-treatment stage before subjecting it to transesterification process. The amounts of WCO generated by homes and restaurants are increasing rapidly due to the tremendous growth in human population. Moreover, the increment in food consumption has also contributed to the production of huge amounts of WCO. However, many harmful compounds are produced during the frying of vegetable oils. So, the use of WCO as a raw material for biodiesel production instead of its management as a toxic residue will reduce waste treatment costs.

2.4 Acid and Alkali Catalyzed Two-Step Transesterification

The most pressing problems of transesterification are slow reaction process, the separation of methyl ester (biodiesel) with glycerol and saponification. To eliminate the problem two-step acid and alkali catalysed transesterification is conducted. In the first step, the esterification of FFA with acid catalysts to decrease FFA levels to lower than 1% and in the second step, the transesterification of WCO with alkali catalysts. Two-step systems have more advantages including no acidic waste treatment, high efficiency, low equipment cost and easy recovery of catalyst compared to the limitations of single step reaction. Various researches have proven that two-step transesterification is better than the single-step process because it can produce higher yield and conversion into biodiesel production.

The two-stage acid- and- alkali-catalysed transesterification can be used to avoid the problems associated with the separate use of base or acid catalysts such as saponification and slow reaction time. In the first stage, esterification of FFA present in WCO is carried out using acid to decrease the FFA level to less than 1%. In the second stage, transesterification of the treated WCO is performed using an alkaline catalyst. Despite its advantages the two-stage method also faces the problem of catalyst removal in both stages. The problem of catalyst removal in the first stage can be avoided by neutralizing the acid catalyst, but in the second stage, extra alkaline catalyst should be used to eliminate the problems. However, the use of extra catalyst increases the saponification process in the second stage.

2.5 Microwave Energy Role in Biodiesel

Lately, microwaves have been received a main attention due to their ability to complete chemical reactions in very short times. It 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. While transesterification of oils to produce biodiesel is a well-established method, there exist conversion and energy utilization inefficiencies in the process which result in the high cost of biodiesel mainly associated with heating method in the process. Microwave-assisted transesterification, on the other hand, is energy-efficient and quick process to produce biodiesel from different feedstocks (Stuerga D et al., 2002).

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 A et al., 2010) . Due to these advantages, microwaves provide for tremendous opportunities to improve biodiesel conversion processes from different feedstock and oil. Microwaves have the ability to induce reactions even in solvent-free conditions offering “Green Chemistry” solutions to many environmental problems related to hazardous and toxic contaminants (Varma RS., 1999) 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 is high of product yields (Larhed M., et al., 2002).

2.6 Transesterification Reaction Assisted By Microwave Heating

Microwaves transfer energy to samples directly and this energy completes the reaction. The interaction of microwaves occurs when the molecule has a dipole moment; in this case, the dipole tries to align itself up with the applied electric field, which with its continuous oscillation, causing a continuous alignment of the dipoles. This constant movement of molecules causes an increase in kinetic energy and thus the heating of the material. The substances used in the current search are polar substances: for this reason, after irradiation with microwaves there is a rapid increase in temperature. The microwave energy interacts with the sample at the molecular level, thus heating becomes more efficient. For a very short time there is a localized overheating since the continuous interaction of the molecules generates energy (A.A. Refaat et al., 2008).

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). The microwave interaction with the reaction compounds (triglycerides and methanol) results in a large reduction of activation energy due to increased dipolar polarization, ionic conduction, and interfacial polarization mechanisms. This causes localized rapid and superheating of the reaction materials. The microwave effect on the transesterification reaction is twofold: (1) enhancement of reaction by a thermal effect, and (2) evaporation of methanol due to the strong microwave interaction of the material (Loupy, A. 2009).

Polar solvents with low molecular weight and high dielectric constant, irradiated by microwave, undergo a rapid increase in temperature, thus reaching faster their boiling point. Generally, for chemical reactions that use microwaves as a means of heating, the solvents used are water, methanol, ethanol and acetone. 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.

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.

2.7 Variables Affecting Transesterification Reaction

The rate of transesterification reaction of oils and fats is affected by various process parameters such as the free fatty acid (FFA) and water in the oil, the type of catalyst and their concentration, the ratio of alcohol to oil, reaction temperature, agitation speed and reaction time. Each parameter is equally significant to determine the quality and quantity of biodiesel produced and to achieve high conversion rates (Demirbas A., 2009).

Although transesterification reaction can be performed at room temperature, the process is strongly influenced by the reaction temperature. The ideal reaction temperature is often near the boiling point of alcohol. However, the reaction can be carried out at different temperatures, depending on the physical and chemical properties of the oil used. The catalyst content is also dependent on the type of oil used in the transesterification process and the type of catalyst. Transesterification reactions are reversible. Thus, excess alcohol is needed to shift the reaction toward the forward direction. Therefore, the alcohol-to-oil ratio is one of the most sensitive factors that affect the final biodiesel yield.

CHAPTER 3

METHODOLOGY

3.1 Project Activities

Literature Review
<ul style="list-style-type: none">• Further understanding on the concept of esterification and transesterification reaction of WCO is carried out.• More review on the literature is done to understand more about mechanism and effect of microwave pre-treatment on transesterification reaction.
Experiment
<ul style="list-style-type: none">• Experiment was design for transesterification experiment with the microwave pre-treatment and without using microwave.• Design of Experiment (DOE) by RSM 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
<ul style="list-style-type: none">• The yield of Biodiesel for both experiment is recorded.• 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
<ul style="list-style-type: none">• The optimization of biodiesel yield and variable affecting the yield was investigated based on the result collected.• The dissertation report of the whole experiment is prepared.

3.2 Gantt Chart & Key Milestones

No.	Details	Week																								
		1	2	3	4	5	6	7	MID-SEM BREAK							8	9	10	11	12	13	14				
1	WCO Properties Experiment	■																								
2	Preliminary Experiment		■	■	■	■	■	■	■																	
3	Transesterification Experiment				■	■	■	■	■					■	■	■	■	■								
4	Submission of Progress Report													●												
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)																									

• Process	●
• Suggested milestone	■

3.3 Materials and Chemical

Waste Cooking Oil WCO sample was collected from local restaurants located around Taman Maju, Seri Iskandar, and Perak, Malaysia. A sample of 5 litre of WCO were collected and stored under room temperature. Chemicals used for transesterification reaction, pro-analysis chemicals, alkaline catalyst, and phase transfer catalysts and standard chemicals for biodiesel analysis are as below:

Table 3. 1. Standard Chemicals for Transesterification of Biodiesel

Description	Purity	Supplier
Alcohol		
Ethanol	≥ 99.7%	N/A
Catalyst		
Sodium hydroxide (alkaline catalyst)	≥ 99%	Merck chemical
Cetyltrimethylammonium bromide (PTC)	≥ 99%	Sigma Aldrich
Pro-analysis chemicals		
Iso-propanol	>99.8%	Merck chemical
N-hexane	≥ 99%	
N-heptanes	≥ 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-trimethylsilyltrifluoroacetamide (MSTFA)	GC grade	
Pyridine	≥ 99%	

3.4 Characterization of WCO

WCO contain high free fatty acids (FFA) and also unsaturated fatty acid. The acid value is to determine the FFA% that contain in WCO before undergo transesterification reaction. Further characterization that need to determine is the saponification value which is to provide a measure of fatty acid glyceride. Meanwhile iodine value is one of important characterization that need to determine which its purpose to gives a measure level of unsaturation fatty acid glyceride in WCO.

Calorific value of the oil is an indicator of its fuel value; viscosity and density of the oil provides an indication of its usability as a fuel. Procedures used to measure these properties are as follow in the below section.

3.4.1 The Determination of Acid Value and Acid Number in the WCO

The free fatty acid (FFA) value in WCO can be obtain by determine the acid value of the WCO. According to ASTM D 974-06, the definition of acid number is the quantity of base expressed in milligrams of potassium hydroxide per gram of sample to a specified end point. One of the important factor to design the transesterification reaction experiments is a FFA percentage of the oil because it can lead to formation of soap in the biodiesel fuel, it also will affect the quality of biodiesel as a fuel. Therefore, the determination of the acid value of the oil is important to transesterification reaction as well as the acid value of biodiesel is also very important to produce biodiesel fuel that meet the international requirements of biodiesel as a fuel and also more effective compare to petroleum diesel fuel. By using the titration method, the acid number of the WCO can be determined which is calculated as below:

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

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)

The acid percentage due to FFA in a sample was assumed to be due to the contribution of presence of oleic and stearic acid components. The FFA percentage due to each of these components may be estimated by dividing the acid value by 1.99 and 2.81 respectively.

Therefore, in order to express in terms of free fatty acids as percent, divide the acid value in mg KOH/g with average value of stearic and oleic acid refer to equation below.

$$\text{FFA \%} = \frac{\text{Acid Value}}{K} \quad (2)$$

3.4.2 Determination Specific gravity of WCO

Procedure to determine density of WCO are as follow:

1. A 50 ml beaker was weigh on the weighing balance and the weight was recorded.
2. 10ml of WCO is poured into the weighed beaker and weigh the beaker that contain WCO.
3. The weight of the beaker with the WCO is recorded. The density is calculated by using equation below

$$\text{Density} = \frac{\text{Mass with oil (g)} - \text{Mass of beaker(g)}}{\text{Volume of the oil(ml)}} \quad (3)$$

To get the value of specific gravity of WCO, the density of oil is divided by the density of water which is 1 g/ml.

3.4.3 Determination of Viscosity of WCO

Determination viscosity of WCO was conducted by using viscometer. The procedure are as follows:

1. The spindle is selected and attached to the handle. The temperature and speed is selected.

2. The handle is lowered so that the spindle closer to the plated. The handle is locked. This to allow the spindle and plate come to an equilibrium.
3. Handle is raised and sample of WCO placed onto the plate. The handle is lowered and locked.
4. The spindle is allowed to equilibrate to the temperature control setting. The run time for rotating is set and the run key is pressed. Then, result is collected.

3.4.4 Determination of the Calorific Value of WCO using Bomb Calorimeter

The calorific value of WCO was determined by using bomb calorimeter equipment. The equipment is booked and a sample of WCO was sent to UTP personnel to conduct the experiment. The result is recorded.

3.5 Design of Transesterification experiment

Design expert software is used in this transesterification experiment, which is a Response Surface Methodology (RSM) software. Basically, this software is a statistical tool for experimental design and identification of optimal condition. For this project, the Central Composite Design (CCD) technique of RSM will be used for experimental design in order to investigate the individual and interaction effect of reaction variables. CCD also was used to determine the optimum reaction condition for transesterification of WCO with presence of microwave pre-treatment. In the CCD, there are four parameters that used for the base design which are weight percent of NaOH to oil, molar ratio of methanol to oil, reaction time and lastly, the temperature of the reaction. From the software, two models of experiment were designed. One of the model was transesterification reaction without microwave pre-treatment and the other one was transesterification reaction with microwave pre-treatment.

3.5.1 Esterification of WCO

Before going for Transesterification WCO need to undergo esterification to reduce the FFA value. The procedure is s follow:

1. A two neck round bottom flask reactor equipped with a reflux condenser magnetic stirrer and a thermometer are used and setup as figure below.
2. 50g of WCO is prepared and placed in the round bottom flask reactor.
3. 12:1 molar ratio of methanol to oil is mixed with 3.5 wt% of sulphuric acid to oil is prepared.
4. A magnetic stirrer is placed into the reactor flask and set to 400 rpm.
5. The mixture of methanol and sulphuric acid is added to the reactor flask and the reaction is started and left for 60 minutes.
6. After 60minutes, the liquid mixtures is transferred to a separation funnel. The separation processes requires several hours to form a clear phase separation between the top layers containing the purified WCO and the bottom layer mainly water.
7. The bottom layer is removed and top layer is recovered .The recovered WCO can be further use for transesterification reaction.

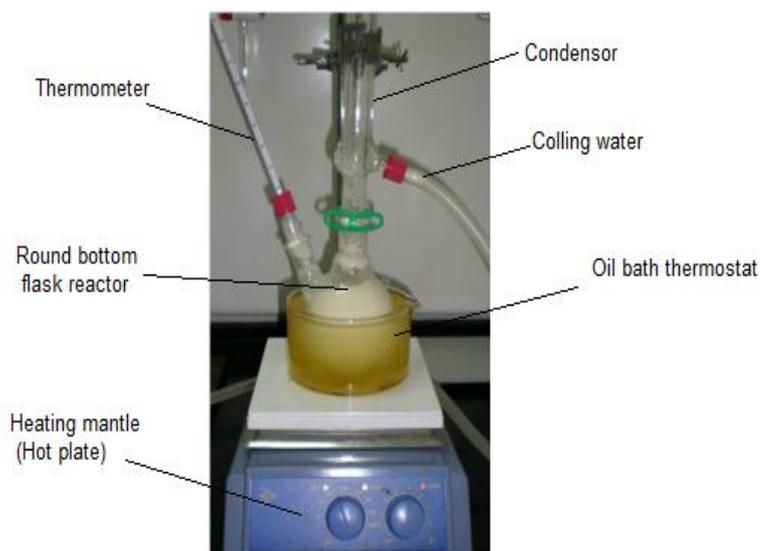


Figure 3. 1 Esterification of WCO

3.5.2 Transesterification of WCO

The WCO from esterification will be used in this experiment to produce Fatty Acid Methyl Ester (FAME) or biodiesel. The procedure for transesterification are as follow:

1. A two neck round bottom flask reactor equipped with a reflux, a magnetic stirrer and a thermometer is used.
2. 10g of WCO is prepared and placed in the flask
3. The WCO is preheated in microwave at the desired duration of time
(*For Transesterification without microwave, step 3 is omitted.)
4. A magnetic stirrer is placed into the reactor flask and set to 400 rpm.
5. NaOH catalyst is prepared (based on DOE by RSM) is placed into the reactor flask and the reaction is started.
7. After a specified reaction time, the reactor is withdrawn from the thermostat. The liquid mixtures is transferred to a separation funnel. The separation processes requires several hours to form a clear phase separation between the top layer that contains biodiesel while the bottom layer containing glycerol, unreacted methanol, sodium hydroxide, WCO and water.
8. The top layer is recovered and the yield is recorded by weight difference.

3.6 Catalyst preparation for transesterification reaction

For preparation of catalyst NaOH – 1.5 Wt% to 10g of oil. The procedure are as follow:

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

CHAPTER 4

RESULT AND DISCUSSION

4.1 Characterization of WCO

4.1.1 Determination of Acid Number

w - Mass of WCO = 10.077 g

A - Volume of standard alkali used in titration = 12.15 ml

B - Volume of standard alkali used in blank titration = 0.5 ml

*To prepare 0.1 N of KOH can be calculated by using equation (4) and (5) below.

$$\text{Normality} = \frac{\text{gram of solute}}{\text{amount solvent} \times \text{e.w}} \quad (4)$$

$$\text{e. w} = \frac{\text{Molecular weight of KOH}}{\text{valence } \bar{e}} \quad (5)$$

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

Gram of solute = 0.1N × 1000ml × 56.1
= 5.61g of KOH needed in 1L of water

$$\begin{aligned} \text{Acid Value, mg KOH/g} &= \frac{(A-B) \times N \times 56.1}{w} \\ &= \frac{(12.15-0.5) \times 0.1N \times 56.1}{10.077} \\ &= 6.486 \end{aligned}$$

Table 4.1 Result of Acid Value

	#1 Experiment	#2 Experiment	#3 Experiment
Mass of WCO, w	10.077	10.076	10.065
A	12.15	14.25	13.30
B	0.5	0.6	0.5
Acid value	6.486	7.598	7.134

$$\begin{aligned} \text{Average of Acid Value} &= \frac{6.486 + 7.598 + 7.134}{3} \\ &= 7.0727 \end{aligned}$$

4.1.2 The percentage of (FFA)

Where:

- Oleic Acid = 1.99
- Stearic Acid = 2.81

$$\text{Total} = 1.99 + 2.81 = 4.8$$

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

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

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

$$\text{FFA \%} = \frac{7.0727}{2.47} = 2.86\%$$

* Since the value of the FFA is more than 2% so Esterification need to be done before going for transesterification reaction.

4.1.3 Determination of Specific gravity

Mass of Beaker with oil = 43.139g

Mass of Beaker without oil = 34.43g

Volume of WCO = 10ml

$$\text{Density} = \frac{(43.139 - 34.43)g}{10 \text{ ml}} = 0.8709 \text{ g/ml}$$

Density of water = 1 g/ml

$$\text{Specific Gravity} = \frac{0.8709 \text{ g/ml}}{1 \text{ g/ml}} = 0.8709$$

From the data above, the specific gravity for WCO is 0.8709

4.1.4 The Determination of Viscosity

The result obtained for viscosity determination is as follows:

Temperature = 40 °C

Speed = 250 rpm

Table 4. 2. Viscosity Result from Bomb Calorimeter

	Spindle 1	Spindle 2	Spindle 3	Spindle 4	Spindle 5	Spindle 6
cP	43.2	23.0	120	180	56	90
%	9.7	2.4	3.9	1.2	0.4	0.1

The value of viscosity was taken at the highest percentage. Based on the result tabulated above, at 9.7 % the viscosity of WCO is 43.2 cP and this value is higher than petroleum based diesel. This value is higher as compared to petroleum based diesel fuel which is 1 cP at 40 °C .Therefore, WCO need to undergo transesterification reaction to reduce its viscosity.

4.1.5 Determination of WCO Calorific Value.

The calorific value of castor oil was obtained from bomb calorimeter experiment which is 38774 J/g. The value of calorific value of WCO is lower than petroleum diesel which is 43100 J/g but the calorific value of WCO is high enough to be considered feasible as a fuel.

4.1.6 Properties of WCO

The properties of WCO is tabulated in Table 4.3 below.

Table 4.3 Properties of WCO

Properties of Waste Cooking Oil	Value
Specific gravity	0.8709
Viscosity (cP)	43.2
Calorific Value (kJ//g)	38.774
FFA content (%)	2.86
Molecular weight (g/mol)	850

4.2 Preliminary experiment

4.2.1 Esterification Experiment

The FFA content of WCO is high. Thus, it is required to undergo esterification to reduce the FFA content in the oil. In this experiment, H₂SO₄ and methanol is used to treat the oil.

Table 4. 4 FFA value after esterification experiment

Run	1	2
Mass of WCO	10.092	10.002
A	4.55	4.80
B	0.52	0.6
Acid value(mg KOH/g)	2.24	2.35
Average	2.30	
FFA%	0.93	

From the table 4.4 above, it shows that the FFA value reduce to 0.93%. Since FFA content is below than 2% the WCO can undergo transesterification reaction.

4.2.2 Preliminary Transesterification Experiment

Transesterification without microwave pre-treatment and microwave pre-treatment transesterification were carried out in order to determine the range of variables value in RSM experiment design. The result are tabulated below:

Mass of WCO : 10g stirring speed: 400 rpm.

Weight percent of NaOH : 1.5 w/w %.

Reaction time : 60 minutes.

Reaction Temperature : 60 °C

Microwave heating time (MWHT) : 2 minutes

(* for microwave pre-treatment transesterification)

Table 4. 5 Transesterification without pre-treatment of microwave

Methanol / oil molar ratio (mol/mol)	FAME yield (Wt %)
6 : 1	61.62
9 : 1	68.94

Table 4. 6 Transesterification with pre-treatment of microwave

Methanol / oil molar ratio (mol/mol)	FAME yield (Wt %)
6:1	72.9
9:1	81.4

$$FAME\ yield = \frac{\text{weight of oil after transesterification}}{\text{weight of oil}} \quad (6)$$

The FAME yield is calculated by using the equation (6) above. The result shows that at 9:1 methanol to oil molar ratio with microwave pre-treatment gives the highest biodiesel yield which is 81.94 wt% compared to 68.94 wt% without microwave pre-treatment. The FAME yield can be further improved by proposed several range of variables for the design experiment. The range of variables are shown at table

Table 4. 7 Range of variables for design experiment RSM

Variables	Range
Methanol to oil ratio(mol/mol)	4.5 - 9
NaOH concentration (wt %)	1 – 2.0
Reaction temperature (°C)	40 - 60
Reaction time (min)	30 - 60

4.3 Transesterification without microwave pre-treatment

The transesterification of WCO using NaOH as catalyst with methanol was investigated. To achieve the objective, the optimization of transesterification reaction is conducted and the individual and interaction effect of the reaction variables on FAME yield is investigated.

4.3.1 Optimization of transesterification of WCO

Four independent variables: Methanol to oil molar ratio (A), NaOH concentration (B), reaction temperature (C), and reaction time (D) has been chosen as it is effect the FAME yield. Mass of WCO and stirrer speed were kept constant at 10 gram and 400 rpm respectively for all the experiment.

The range of variable from table 4.8 below will be used to study the individual and interaction effect of process variables and the optimal conditions to get the maximum FAME yield. The study were investigated by using central composite design (CCD) technique of RSM. The RSM experimental design gives each reaction variable with 5 different levels from low (-2), (-1), (0) and to high (1), (2). The experiment range and level of the independent variables is shown in table below;

Table 4. 8 Experimental range and level of the independent variables

Variables	Coded Symbol	Range and Levels				
		-2	-1	0	1	2
Methanol	A	4.5	6	6.75	9	11.25
NaOH	B	0.5	1	1.5	2	2.5
Temperature	C	30	40	50	60	70
Time	D	15	30	45	60	75

The experiment carried out according to the design of experiment by CCD technique of RSM as a function of un-coded variable with total of 31 experiment. The experimental and predicted FAME yield for transesterification are presented in table below:

Table 4. 9 Experimental design matrix by CCD technique for transesterification along with experimental and predicted FAME yields

Run	Methanol / Oil (mol/mol)	Catalyst / Oil (wt %)	Reaction Temp (°C)	Reaction Time (min)	Yield FAME %	Predicted Yield %
1	6.75	1.5	50	15	64.8	65.5246
2	9.00	1.0	60	30	70.24	69.0396
3	11.25	1.5	50	45	63.4	60.4646
4	4.50	2.0	40	60	68.97	70.77
5	4.50	1.0	60	30	60	58.9408
6	9.00	2.0	60	30	57.24	59.1692
7	6.75	1.5	50	45	76.56	75.6071
8	4.50	2.0	40	30	70.51	70.85
9	6.75	1.5	50	45	76.56	75.6071
10	6.75	2.5	50	45	65.07	63.5629
11	6.75	1.5	50	45	76.56	75.6071
12	6.75	0.5	50	45	53.73	55.5613
13	6.75	1.5	30	45	77.53	78.27
14	6.75	1.5	50	45	76.56	75.6071
15	9.00	2.0	40	60	58.34	59.8908
16	9.00	2.0	40	30	53.77	55.9846
17	4.50	1.0	40	60	60.96	58.9025
18	4.50	1.0	60	60	56.88	55.5996
19	4.50	2.0	60	30	65.76	65.1879
20	6.75	1.5	50	45	76.56	75.6071
21	4.50	2.0	60	60	73.08	72.6542
22	9.00	2.0	60	60	71.22	70.0379
23	9.00	1.0	40	60	59.27	58.1363
24	9.00	1.0	40	30	63.12	65.0375
25	2.25	1.5	50	45	64.53	67.2496
26	6.75	1.5	50	45	76.56	75.6071
27	6.75	1.5	70	45	69.57	70.6979
28	9.00	1.0	60	60	69.34	69.1008
29	6.75	1.5	50	45	76.56	75.6071
30	6.75	1.5	50	75	66.73	66.0896
31	4.50	1.0	40	30	68.14	69.2063

Based on the Table, it is observed run 13 has the highest FAME yield which is 77.53% and 78.27% predicted yield at 6.75 methanol to oil molar ratio, 1.5 wt% of

NaOH to oil ratio, 30 °C reaction temperature and 45 minutes reaction time. The FAME yield is calculated by using the following formula:

Table 4. 10 Regression Coefficient for FAME yield transesterification

Coefficient	Estimate	T value	P value
Constant	12.4883	1.1	0.288
A - Methanol / Oil (mol/mol)	5.0189	2.096	0.052
B - Catalyst / Oil (wt %)	55.03	5.087	0
C - Reaction Temp (oC)	0.218	-0.833	0.417
D - Reaction Time (min)	-0.1368	-0.088	0.931
AA	-0.6516	-6.599	0
BB	-17.7596	-8.815	0
CC	-0.0166	-1.945	0.07
DD	-0.0115	-5.725	0
AB	-3.0594	-4.88	0
AC	0.1252	4.213	0.01
AD	0.0364	1.663	0.116
BC	0.1509	0.975	0.344
BD	0.3171	3.576	0.003
CD	0.01	2.295	0.036

The response surface design is analysed based on the FAME yield in order to determine the constants of the quadratic equation which is shown in the Table. Based on the constants of quadratic equation, statistical model equation is established to estimate the FAME yield. The statistical model equation are shown as below

$$\text{FAME yield} = 12.4883 + 5.0189A + 55.03B + 0.218C - 0.1368D - 0.6516AA - 17.7596BB - 0.0166CC - 0.0115DD - 3.0594AB + 0.1252AC + 0.0364AD + 0.1509BC + 0.3171BD + 0.01CD$$

Where A is methanol to oil molar ratio, B is NaOH concentration, C is reaction temperature and D is reaction time.

Table 4.10 shows the P and T values for the variables which obtained from the regression analysis based on un- coded variables. The P-value must be less than 5% in

order for the variables to have a significance effect on the response values. Meanwhile, the T-value indicate the higher significance of the corresponding coefficient the model. From this it can be concluded, the linear terms A (Methanol / Oil), B (NaOH / Oil), had more influenced on the yields of FAME significantly while the C (reaction temperature) and D (Reaction time) has least significance due to the high p-value (>0.05). All the quadratic coefficients of A^2 , B^2 and D^2 have a significant effect on the yield of FAME. The interaction terms involving reaction temperature C^2 have least significance.

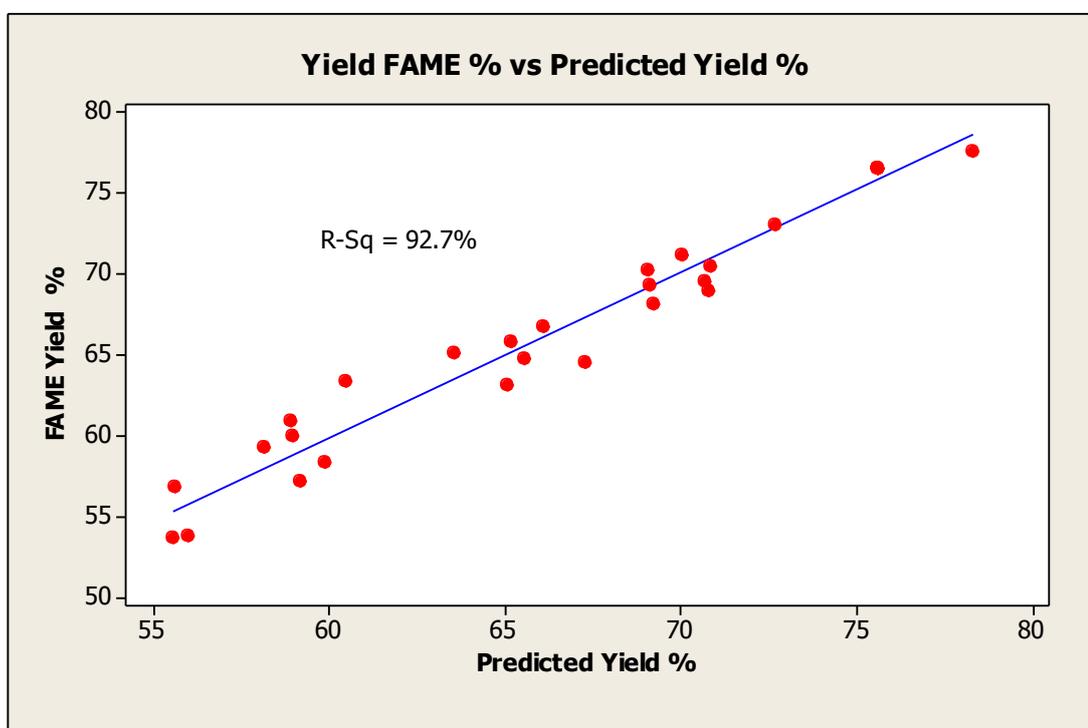


Figure 4. 1 Plot of experimental FAME yield versus predicted yield

The graph plotted as shown in the figure 4.1 shows the experimental FAME yield with the predicted values. Linear trend are shown between the experimental values versus predicted values with the R^2 statistic value of 0.927. The value shows that the 92.7% of the experiment values for transesterification is reliable.

4.3.2 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 three factors at their centre point level were plotted in a three dimensional surface with the contour plot at the bottom as shown in Figure 4.2. Good interaction between two variables on the response are indicated by the elliptical shape of the contour plot. Meanwhile if the contour plot is in circle shape, this indicates that less interaction effect between the variables to affect the response.

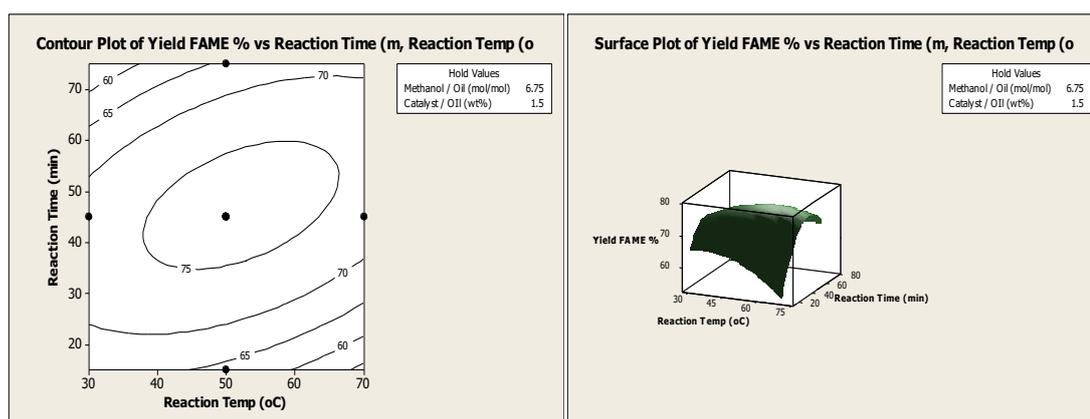


Figure 4. 2 FAME% yield plots vs reaction temperature and reaction time

Figure 4.2 (a) shows FAME yield as a function of reaction temperature and reaction time. The yield of FAME improved with increasing both of the parameters. Increasing temperature up until 50°C will provide more yield. Similarly, for reaction time the yield increase when time increase until 45 minute and reduce when exceed. This is due to high temperature and longer reaction time promotes the saponification reaction.

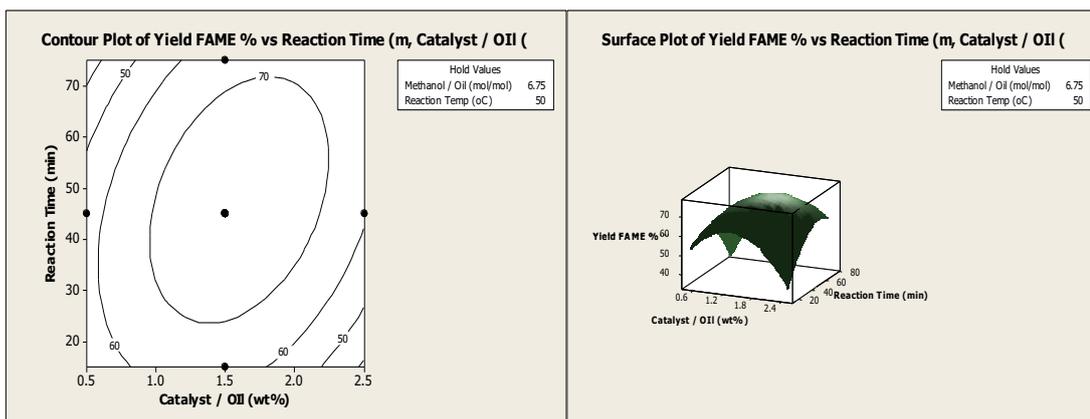


Figure 4. 3 FAME% yield plots vs Catalyst / Oil ratio and reaction time

Figure 4.3 illustrates the effects of NaOH concentration and reaction time towards the FAME yield. Increasing the NaOH concentration can give positive effects on FAME yield up until 1.5 wt %. Continuing increase the NaOH concentration causes the saponification reaction to occur thus reduced the FAME yield. The reaction time increases the FAME yield at range of 45 to 50 minutes.

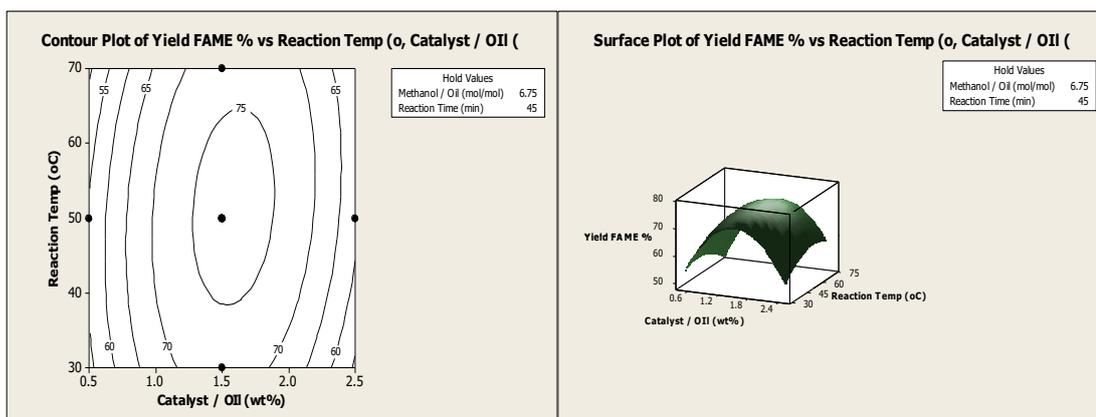


Figure 4. 4 FAME% yield plots vs Catalyst / Oil ratio and reaction temperature

Figure 4.4 shows the interaction effects between NaOH concentration and reaction temperature. The yield of FAME improved with increasing both of the parameters. The maximum yield is observed at 70 to 75 % FAME yield with 1.3 to 1.8 wt% and 45 to 55 °C reaction temperature.

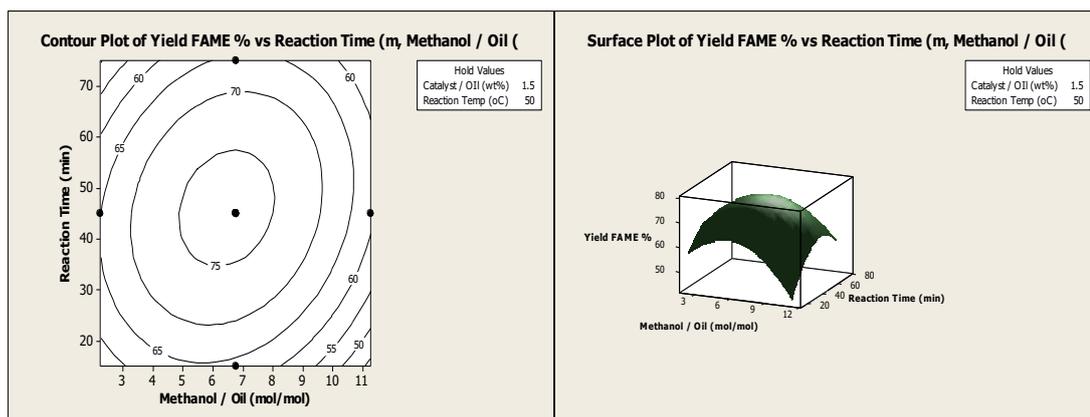


Figure 4. 6 FAME% yield plots vs Methanol / Oil ratio and reaction time

Figure 4.5 presents the effects of methanol to oil molar ratio and reaction time towards the FAME yield. The methanol to oil and reaction time has least significance on FAME yield. Further longer the reaction time and increase the methanol to oil ratio beyond its optimum value reducing the FAME recovery process because it favors saponification reaction. Maximum yield can be obtain at 6 to 7.5 of methanol to oil ratio and reaction time at 40 to 50°C.

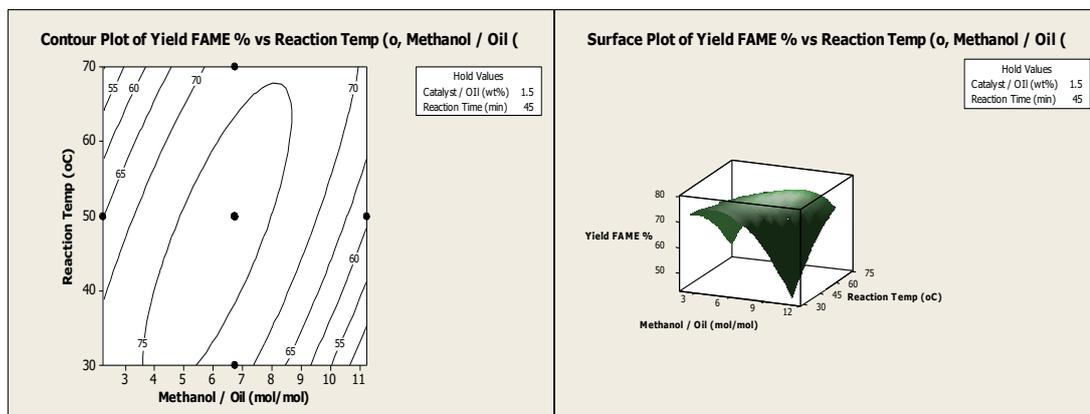


Figure 4. 5 FAME% yield plots vs Methanol / Oil ratio and reaction temperature

Figure 4.6 presents the yield of FAME as a function of methanol to oil molar ratio and reaction temperature. Both of these parameters has a good interaction effect. The FAME yield increase in the range from 4 up to 7 of methanol to oil ratio meanwhile the temperature give great significance on the FAME yield. However, further increase the temperature caused the reduction of FAME yield. This is because, transesterification under high temperature promotes saponification reactions.

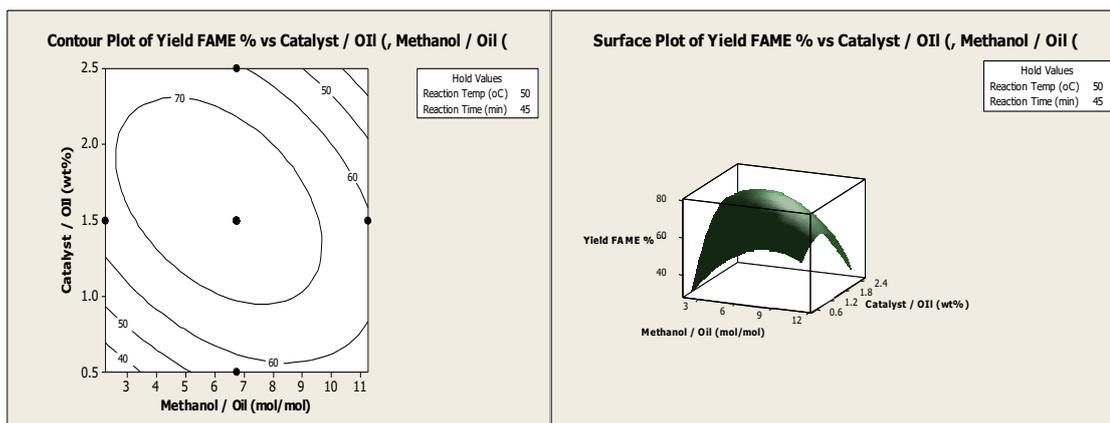


Figure 4. 7 FAME% yield plots vs Methanol / Oil ratio and Catalyst / Oil ratio

Figure 4.7 depicts the interaction effects of methanol to oil molar ratio and catalyst concentration. From the contour plot, The FAME yield started to decrease when the methanol volume reaches to a certain marginal level which is about 9.5 methanol to oil molar ratio. Over loading of methanol reduced the concentration of the catalyst thus affect the catalytic reaction. Apart from that, it is also lead to the solubility problem where the product FAME/biodiesel easily dissolved in glycerol phase thus reduced the biodiesel recovery process. For the NaOH concentration, it was observed that increasing the NaOH concentration successfully increased the FAME yield. However, further increased the NaOH concentration favors the saponification reaction thus reduced the FAME yield.

4.3.3 Optimum reaction conditions for transesterification

Table 4. 11 Optimum reaction conditions for transesterification

Variable	Low	Optimum	High
Methanol / Oil Ratio (mol/mol)	2.25	6.75	11.25
Catalyst / Oil Ratio (wt %)	0.5	1.5	2.5
Reaction Temperature (°C)	30	30	70
Reaction Time (min)	15	45	75

From the RSM analyzation, it was observed that the maximum optimum FAME yield is 77.53% for microwave energy pre-treated transesterification WCO.

4.4 Microwave energy pre-treated transesterification

For this part, the WCO will be enhanced by microwave energy pre-treated at the beginning of the experiment before conducting transesterification.

4.4.1 Optimization Microwave energy pre-treated transesterification

FAME yield is dependent on four independent variables which are Microwave heating time [MWHT] (*A*), methanol to oil molar ratio (*B*), NaOH concentration (*C*), and reaction time (*D*). For all the experiment, 10 g of WCO, stirrer speed of 400 rpm and reaction temperature at 50 (°C) 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-treated transesterification. According to RSM experimental design technique, it was considered that each reaction variable can take five different levels from low (-2), (-1), (0), (1) and to high (2). The experiment range and level of the independent variable is shown in the table 4.12 below:

Table 4. 12 Experimental range and level of the independent variables

Variables	Coded Symbol	Range and Levels				
		-2	-1	0	1	2
MWHT (min)	A	1	1.5	2	2.5	3
Methanol / Oil ratio (mol/mol)	B	2.25	4.5	6.75	9	11.25
Catalyst / Oil ratio (Wt %)	C	0.5	1	1.5	2	2.5
Time (min)	D	25	30	35	40	45

The experiment carried out according to the design of experiment by CCD technique of RSM as a function of un-coded variable with total of 31 experiment. The experimental and predicted FAME yield for transesterification for microwave energy pre-treated transesterification are presented in table below:

Table 4. 13 Experimental design matrix by CCD technique for microwave energy pre-treated transesterification along with experimental and predicted FAME yields

Run	MWHT (min)	Methanol / Oil ratio (mol/mol)	Catalyst / Oil ratio (Wt %)	Reaction Time (min)	FAME Yield %	Predicted Yield %
1	1.5	9.00	1.0	30	78.34	80.3742
2	2.0	6.75	1.5	35	87.23	86.2200
3	2.0	2.25	1.5	35	68.95	65.2542
4	1.5	4.50	1.0	40	75.67	75.5075
5	2.0	6.75	1.5	35	87.23	86.2200
6	1.0	6.75	1.5	35	89.96	88.6592
7	1.5	9.00	1.0	40	76.33	80.2500
8	1.5	4.50	2.0	30	73.20	75.3858
9	2.0	6.75	1.5	25	84.33	80.8908
10	1.5	4.50	1.0	30	74.55	75.8117
11	2.5	4.50	2.0	30	78.96	78.2833
12	2.0	6.75	1.5	35	87.23	86.2200
13	2.0	6.75	1.5	45	81.23	77.6775
14	1.5	9.00	2.0	30	77.51	76.3383
15	2.0	6.75	0.5	35	78.37	72.1875
16	2.5	9.00	2.0	30	68.39	72.3008
17	2.0	6.75	2.5	35	69.86	69.0508
18	2.0	6.75	1.5	35	87.23	86.2200
19	1.5	4.50	2.0	40	72.14	73.4217
20	2.0	6.75	1.5	35	87.23	86.2200
21	2.0	6.75	1.5	35	87.23	86.2200
22	2.5	9.00	1.0	40	70.54	72.1025
23	2.0	11.25	1.5	35	67.31	64.0142
24	2.5	4.50	1.0	40	70.88	74.2950
25	2.0	6.75	1.5	35	87.23	86.2200
26	2.5	4.50	2.0	40	73.48	75.1942
27	2.5	9.00	2.0	40	67.41	69.3917
28	2.5	9.00	1.0	30	71.39	73.3517
29	3.0	6.75	1.5	35	82.55	83.4092
30	1.5	9.00	2.0	40	75.17	74.5542
31	2.5	4.50	1.0	30	71.36	75.7242

Based on the Table 18, it was observed run 6 has the highest FAME yield which is 89.96 % with predicted yield of 88.6592 % at 1 minutes MWHT, 6.75 methanol to oil molar ratio, 1.5 Wt% NaOH concentration and 35 minutes reaction time.

Table 4. 14 Regression Coefficient for FAME yield transesterification

Coefficient	Estimate	T value	P value
Constant	-125.027	-2.615	0.019
A - MWHT (min)	21.494	1.365	0.191
B - Methanol / Oil (mol/mol)	18.884	5.638	0
C - Catalyst / Oil (wt %)	52.673	3.495	0.003
D - Reaction Time (min)	5.471	2.942	0.01
AA	-3.883	-1.677	0.113
BB	-1.087	-9.503	0
CC	-16.023	-6.919	0
DD	-0.074	-3.177	0.006
AB	-1.597	-2.321	0.034
AC	2.735	0.883	0.39
AD	-0.087	-0.283	0.781
BC	-0.747	-1.085	0.294
BD	-0.002	-0.023	0.982
CD	-0.191	-0.617	0.546

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

$$\text{FAME yield: } -125.027 + 21.494A + 18.884B + 52.673C + 5.471D - 3.883AA - 1.087BB - 16.023CC - 0.074DD - 1.597AB + 2.735AC - 0.087AD - 0.747BC - 0.002BD - 0.191CD$$

Where A is MWHT, B is methanol to oil molar ratio, C is NaOH concentration and D is reaction time.

Table 4.14 shows the P and T values for the variables which obtained from the regression analysis based on un-coded variables. The P-value must be less than 5% in order for the variables to have a significance effect on the response values. Meanwhile, the T-value indicate the higher significance of the corresponding coefficient the model. From this it can be concluded, the linear terms B (Methanol / Oil), C (NaOH / Oil) and D (Reaction time) had more influenced on the yields of FAME significantly while A (MWHT) has least significance due to the high p-value (>0.05). All the quadratic coefficients of B^2 , C^2 and D^2 have a significant effect on the yield of FAME. The interaction terms involving reaction temperature A^2 have least significance.

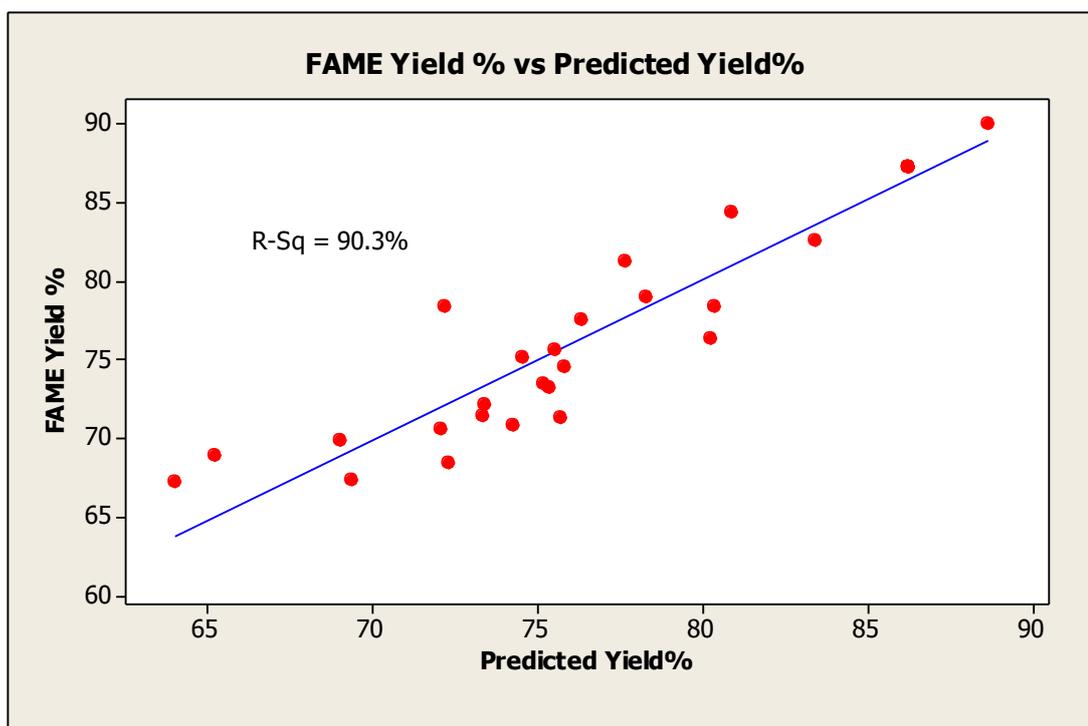


Figure 4. 8 Plot of experimental FAME yield versus predicted yield

The graph plotted as shown in the figure 4.8 compares the experimental FAME yield with the predicted values. Linear trend are shown between the experimental values versus predicted values with the R^2 statistic value of 90.3%. The value shows that the 90.3% of the experiment values for transesterification is reliable.

4.4.2 The Individual and Interaction Effect of the reaction variables on FAME yield

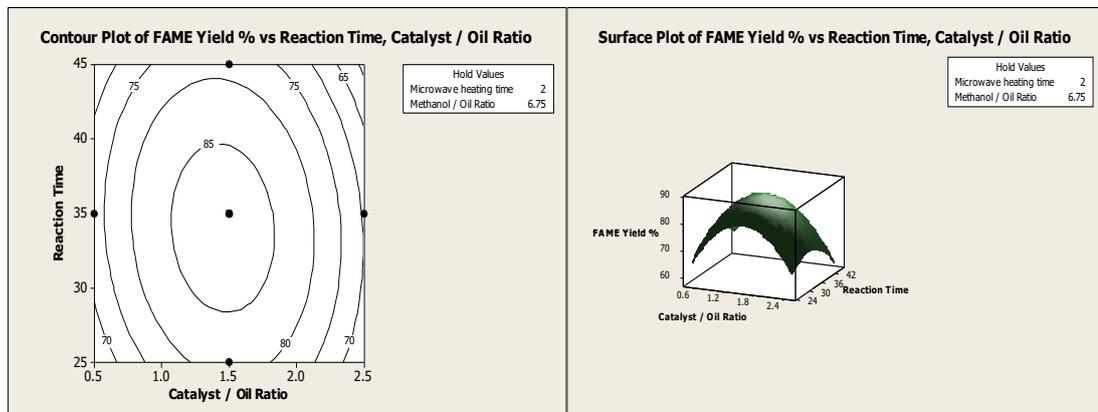


Figure 4. 9 FAME% yield plots vs reaction temperature and reaction time

Figure 4.9 depicts the interaction effects between NaOH concentration and reaction time towards FAME yield. Increasing the reaction time favor the transesterification reaction as the FAME yield is increased. However longer reaction time reduced the FAME yield as it promotes the saponification reaction. Same goes to NaOH concentration, where overloading of NaOH catalyst decreased the biodiesel yield due to the saponification reaction. From maximum yield observed is about 85% at NaOH concentration range between 1.3 to 1.8 wt% and 30 to 40 minutes reaction time.

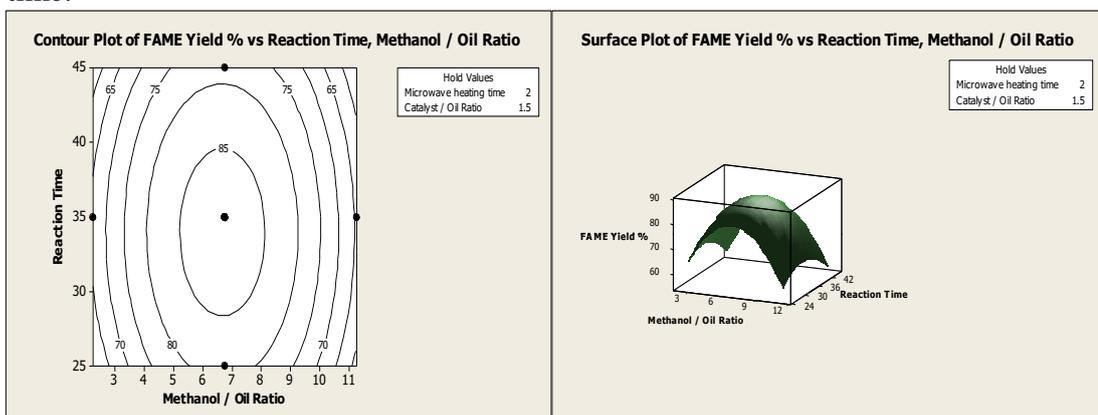


Figure 4. 10 FAME% yield plots vs methanol/oil ratio and reaction time

Figure 4.10 show the maximum FAME yield was observed at range of 5.5 to 7.5 methanol to oil molar ratio and at 30 to 38 minutes reaction time. Increasing the volume of methanol give positive impact towards FAME yield however, overloading the amount of methanol can decrease the biodiesel yield. This is due to the solubility problem.

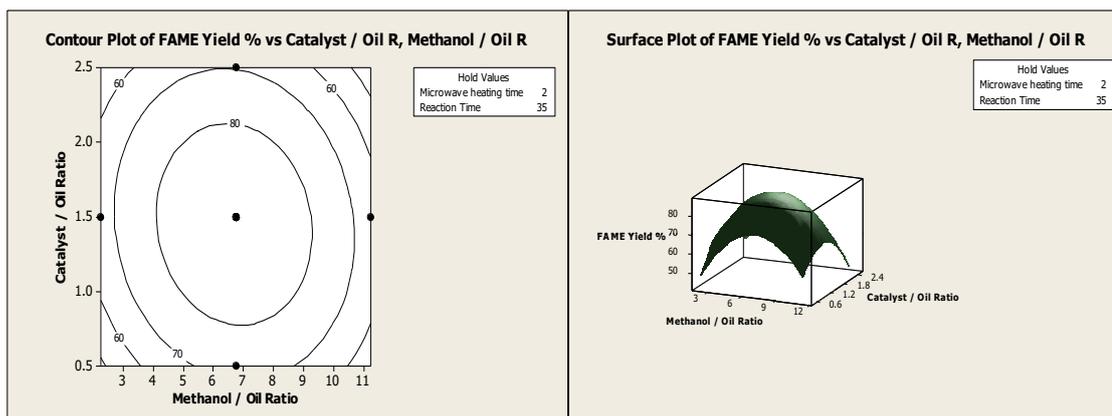


Figure 4. 12 FAME% yield plots vs methanol/oil ratio and catalyst/oil ratio

Figure 4.11 depicts the interaction effects between methanol to oil molar ratio and NaOH concentration towards the FAME yield. Both interaction have least significance effect on FAME yield. The maximum FAME yield was observed at a range 4.5 to 8.5 methanol to oil molar ration and 1 to 2 wt% of NaOH concentration. Increasing both value of methanol to oil molar ratio and NaOH concentration can give positive impacts towards FAME yield however, further increase both variable decreased the FAME yield. This is due to the solubility problem and favouring saponification reaction.

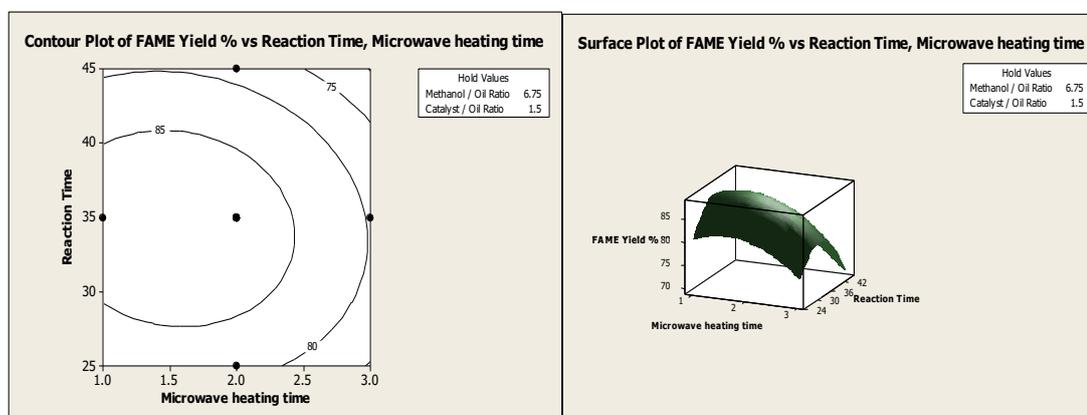


Figure 4. 11 FAME% yield plots vs MWHT and reaction time

Figure 4.12 depicts the interaction between reaction time and microwave heating time. Increasing the time for both variable can 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 at range of 30 to 40 minutes and microwave heating time at 1 to 2.5 min.

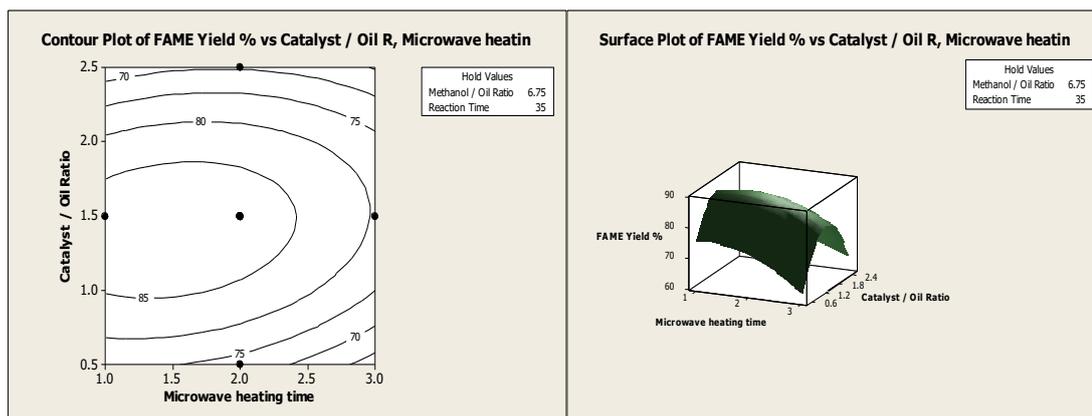


Figure 4. 14 FAME% yield plots vs MWHT and catalyst/oil ratio

Figure 4.13 presents the effects of alkali catalyst (NaOH) on the microwave heating time. The maximum FAME yield can be seen at range of 1 to 2 wt % of NaOH concentration to oil. However, overloading the NaOH concentration can decreased the FAME yield. This is because, high concentration of NaOH favors the saponification reaction thus reduced the biodiesel yield.

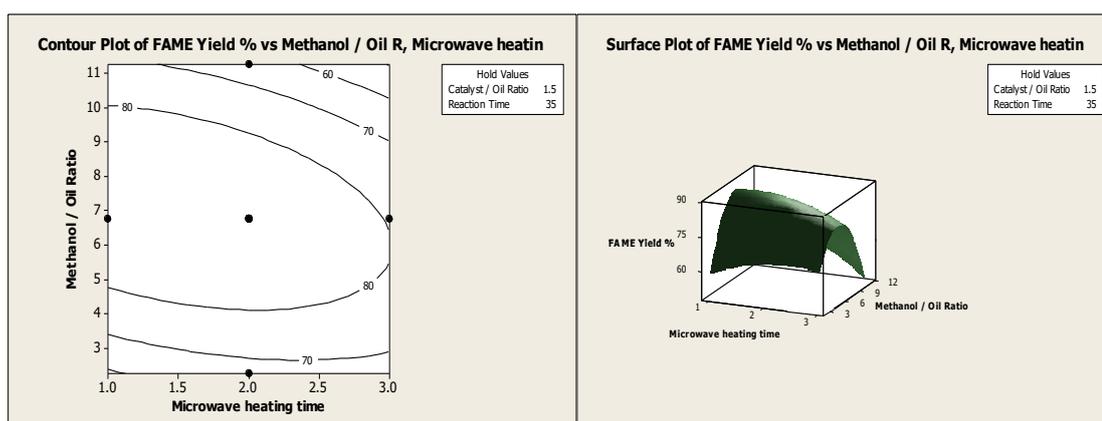


Figure 4. 13 FAME% yield plots vs MWHT and methanol/oil ratio

Figure 4.14 presents the effects of methanol to oil molar ratio to FAME yield with the microwave heating time. Maximum yield was observed at volume of methanol between 7 to 8 molar ratios of methanol to 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 reduce the FAME yield.

4.4.3 Optimum reaction conditions Microwave energy pre-treated transesterification

Table 4. 15 Optimum Condition of microwave energy pre-treated transesterification

Variable	Low	Optimum	High
MWHT (min)	1	1	3
Methanol / Oil Ratio (mol/mol)	2.25	6.75	11.25
Catalyst / Oil Ratio (wt %)	0.5	1.5	3
Reaction Time (min)	25	35	45

From the RSM analyzation, it was observed that the maximum optimum FAME yield is 89.96% for microwave energy pre-treated transesterification WCO

4.5 Summary for optimization of FAME yield

Optimization 1: Transesterification without Microwave energy pre-treated

Optimization 2: Microwave energy pre-treated transesterification

Table below shows the summary of the optimum condition to achieve the maximum of FAME yield as presented by design expert software Minitab RSM technique and optimum condition from experiment results.

Table 4. 16 Optimization summary

Condition Parameter	Optimization 1	Optimization 2
Methanol/Oil (mol/mol)	6.75	1
Catalyst/Oil (Wt %)	1.5	6.75
Reaction Temperature (°C)	30	-
Reaction Time (min)	45	35
MWHT (min)	-	1
FAME yield Wt%	77.53	89.96

From Table 4.16, it can be seen that optimization of microwave energy pre-treated transesterification of WCO has the highest FAME yield. Results shows that 89.96% Wt% of FAME yield can be obtained within 35 minutes reaction time for transesterification reaction that pre-treated with microwave. On the other hand, as compared with transesterification without microwave energy pre-treated oil transesterification obtained 77.53 Wt% at 45 minutes. Thus, it can be conclude that microwave energy can improve the transesterification reaction.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In this project, WCO will be used as non-edible oil feedstock and undergo transesterification process with methanol and NaOH catalyst to produce biodiesel. The WCO will be pre-heated with microwave energy in order to improve the limited solubility between the WCO and methanol and also to increase the rate of reaction before being used for transesterification. Transesterification without microwave energy pre-treated and microwave energy pre-treated transesterification were investigated. Results shows that at optimum condition, 89.96 wt% within 35 minutes reaction time of FAME yield was observed when the reaction was conducted with microwave heat pre-treated oil. It was also demonstrated that a gain 12.43 % of FAME yield for a reaction conducted using microwave energy pre-treated oil transesterification reaction as compared to without microwave pre-treated transesterification reaction (FAME yield=77.53% w/wt). Thus, it can be conclude that microwave energy can improve the transesterification reaction and prove that this method was efficiently and economically feasible for operation.

5.2 Future work

As for the future work and recommendation for this project, the microwave energy pre-treatment transesterification should be done in the presence of phase transfer catalyst (PTC). By using PTC the process can achieve a faster reactions, and obtain a higher 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.

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 WCO 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.

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APPENDICES

a. Calculation of Acid value in Table 4.1

$$\begin{aligned}
 1. \text{ Acid Value, mg KOH/g} &= \frac{(A-B) \times N \times 56.1}{w} \\
 &= \frac{(14.25 - 0.6) \times 0.1N \times 56.1}{10.076} \\
 &= 7.598
 \end{aligned}$$

$$\begin{aligned}
 2. \text{ Acid Value, mg KOH/g} &= \frac{(A-B) \times N \times 56.1}{w} \\
 &= \frac{(13.30 - 0.5) \times 0.1N \times 56.1}{10.065} \\
 &= 7.134
 \end{aligned}$$

b. ANOVA of the fitted quadratic polynomial model on FAME yield Analysis of Variance for Yield FAME % for Experiment (1).

Source	Degree of Freedom	Sum of Squares	Mean Squares	F – Values	P - Value
Regression	14	1676.85	118.776	101.62	0.000
Linear Terms	4	191.61	83.688	71.00	0.000
Square Terms	4	847.23	211.808	179.71	0.000
Interaction Terms	6	638.01	106335	90.22	0.000
Residual Error	16	18.86	1.179	*	*
Lack of Fit	10	18.86	1.886	*	*
Pure Error	6	0.000	0.000	0.000	*

c. ANOVA of the fitted quadratic polynomial model on FAME yield
Analysis of Variance for Yield FAME % for Experiment (2).

Source	Degree of Freedom	Sum of Squares	Mean Squares	F – Values	P - Value
Regression	14	1709.12	122.080	13.96	0.000
Linear Terms	4	97.29	483.93	13.84	0.000
Square Terms	4	1537.02	384.255	43.95	0.000
Interaction Terms	6	74.81	12.649	1.43	0.265
Residual Error	16	139.90	8.744	*	*
Lack of Fit	10	139.90	13.990	*	*
Pure Error	6	0.000	0.000	0.000	*