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MICROWAVE ENERGY PRE-TREATED ETHANOLYSIS OF WASTE COOKING OIL (WCO) & PARAMETRIC OPTIMIZATION

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CERTIFICATION OF APPROVAL

Microwave Energy Pre-treated Ethanolysis of Waste Cooking Oil & Parametric Optimization

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A project dissertation submitted to the Chemical Engineering Programme
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Approved by,

(Dr Sintayehu Mekuria Hailegiorgis)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
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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 specified in the references and acknowledgement, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(MUHAMMAD FIKRI BIN HAMZAH)

ABSTRACT

Exploration for environmental friendly alternative energy is essential to complement depleting and environmentally unfriendly fossil fuels. Renewables energy such as biodiesel is gaining increased attention at global level. One other hand, edible oil as a raw material and processing costs are adversely affecting the economic viability of biodiesel technology. Currently, more than 95 % of biodiesel raw material feedstock sources are from edible oil sources which competes with food processing industries affecting both the economics of biodiesel and food industries. Transesterification reaction is a very slow reaction due to limited solubility of low molecular weight alcohol in vegetable oil. The slow reaction rate of transesterification increases the processing cost of biodiesel which ultimately increase the cost of biodiesel as a fuel. Use of non-edible oil such as used cooking oil (WCO) can reduce the high cost of edible oil sources. The slow transesterification rate can also be increased by using reaction rate increasing techniques such as microwave heat pretreatment of oil and use of rate enhancement agent such as phase transfer catalysis along with the conventional catalyst. In the present research work, the concept of microwave pre-treatment of oil for transesterification of waste cooking oil were utilized. To design appropriate transesterification reaction conditions, physical and chemical properties of WCO were investigated. The Individual and interaction effects of transesterification reaction parameters were studied using design of experiment (DOE) software's such as central composite design (CCD) of response surface methodology (RSM). After Investigation of the parametric effect, optimum reaction condition for maximum yield was established experimentally using CCD of RSM. At optimal conditions of 7.5 ethanol: oil molar ratio, 1.5 wt% NaOH concentration, 3 minutes pre-treatment of oil with microwave energy, 45℃ reaction temperature & 22.5 minutes of reaction time, it was determined that about 98.72 wt% FAEE yield was obtained as compared to 86.24wt% FAEE yield obtained with oil untreated with microwave energy at optimal concentration of 7.5 ethanol: oil molar ratio, 1.5 wt% catalyst concentration, 45℃ and 60 minutes of reaction time. This resulted in about 12.48 wt% gain in FAEE yield while reducing the reaction time.

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ABBREVIATIONS AND NOMENCLATURE

WCO : Waste Cooking Oil

NaOH : Sodium Hydroxide
CTMAB : Cetyltrimethylammonium Bromide
H2SO4 : Sulphuric Acid
MWHT : Microwave Heating Time
Wt. % : Weight Percent
w/wt. % : Weight per Weight Percent
°C : Degree Celsius
N : Normality
FAEE : Fatty Acid Eethyl Esters
g : gram

CHAPTER 1: INTRODUCTION

1.1 Background of Study

Global energy consumption is rising rapidly with increasing population and modernization. The total world energy demand is estimated to rise from 505 quadrillion British thermal unit (BTU) in 2008 to 770 quadrillion BTU in 2035 as presented in Figure 1.1. About 88% of the world energy consumption is based on fossil fuels. World liquid energy consumption is also estimated to increase from 85.7 million barrels per day in 2008 to 112.2 million barrels per day in 2035 [1-4]. At the existing production rate, the global proven reserves of crude oil and natural gas are estimated to be fully consumed in a half century [5].

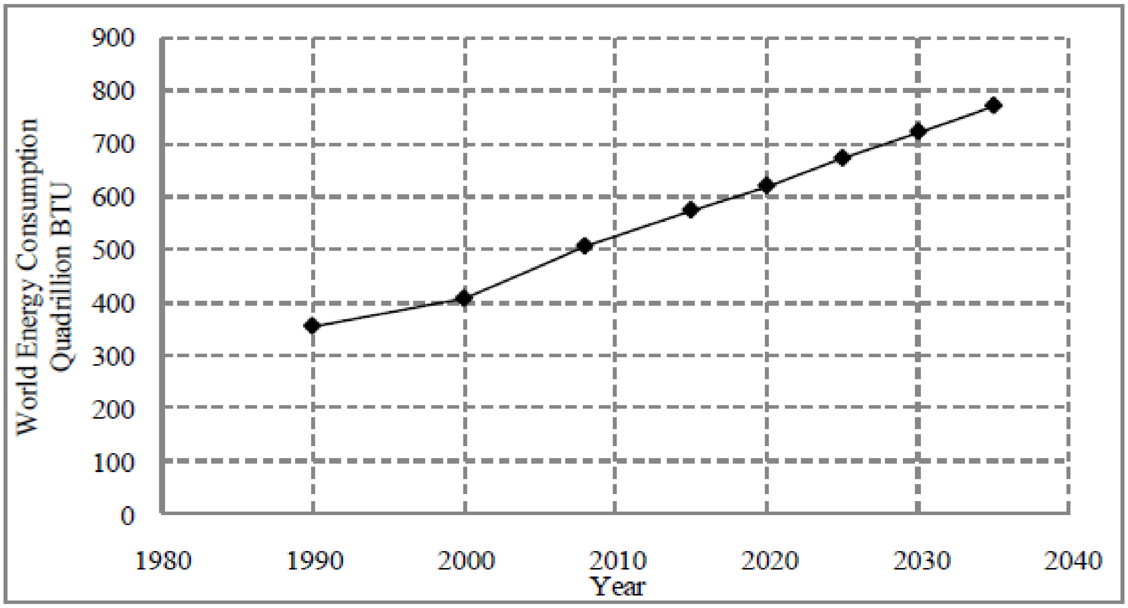


Figure 1.1: Projected world energy consumption from 1990 to 2035 in quadrillion BTU (source: IEO 2011[2])

With the increasing demand for energy from the fossil fuels, the environment and its ecosystems are getting polluted by the emission of greenhouse gases such as carbon dioxide. Carbon dioxide emissions related to use of energy was also estimated to increase from 30.2 billion metric tons in 2008 to 43.2 billion metric tons in 2035[1]. Associated global warming, melting of the polar ice cap, glaciers, rising sea levels and devastating weather patterns can affect life on earth irrecoverably. Exploration for alternative renewable fuels and chemical feedstocks with zero net carbon dioxide emissions is necessary for sustainable development. Currently renewable energy fuels account for about 11% of the total world energy supply [5].

Biomass, obtained by photosynthesis, is a versatile renewable feedstock that can be converted into different types of bio-fuels (solid, liquid and gas) [5, 6]. It contributes up to 77.4% of the current renewable energy supply. Bio-fuels include bio-ethanol, bio-methanol, biodiesel and bio-hydrogen. Biodiesel is gaining increasing attention as it can substitute effectively for petro diesel [7]. Biodiesel can be produced by transesterification of a wide range of feedstocks such as vegetable oils, animal fats, used frying oils, etc with alcohols [8, 9]. The feedstock source can be region specific. Thus, soybean oil is used in the United States; rapeseed oil (canola oil) is used in Europe while palm oil is used in Indonesia and Malaysia. Biodiesel offers promising benefits such as biodegradability, good lubricity, high cetane number, high flash point, higher combustion efficiency and low polluting emission to the environment compared to petro-diesel [9, 10].

Biodiesel is composed of methyl or ethyl esters produced from vegetable oil or animal oil and has fuel properties similar to diesel fuel which renders its use as biofuel. Biodiesel offers many benefits: (a) serves as alternative to petroleum-derived fuel, which implies a lower dependence on crude oil foreign imports; (b) provides favorable energy return on energy invested; (c) reduces greenhouse emissions in line with the Kyoto Protocol agreement; (d) lowers harmful gaseous emissions;(e) biodegradable and nontoxic fuel, being beneficial for reservoirs, lakes, marine life, and other environmentally sensitive areas [7-9]. It has been realized that local biodiesel production can address challenges related to energy independence, economic prosperity, and environmental sustainability in any nation. Towards this, the United States (US) and Europe have encouraged large scale industrial biodiesel production. For example, biodiesel production in the US has increased from 75 million gallons in 2005 to 250 million gallons in 2006 and 450 million gallons in 2007, with an expected total capacity of well over 1 billion gallons in the next few years [10,11].

Transesterification is a chemical reaction between triglycerides present in the oils or fats and such as methanol or ethanol to form esters and glycerol in the presence of a catalyst or at high pressure and temperature [11, 12]. The molecular weight of ester molecule is about one-third of its parent vegetable oil molecule and has a viscosity approximately one tenth of the viscosity of vegetable oils and twice that of petro-diesel fuel. The physical characteristics of esters produced by transesterification are very close to those of petro-diesel fuel. Vegetable oils or animal fats are esters of saturated and unsaturated mono-carboxylic acids with the tri-hydric alcohol glycerides. The most common fatty acids of vegetable oils are palmitic acid (C16:0, no double bond), stearic acid (C18:0, no double bond), oleic acid (C18:1, one double bond) and linoleic acid (C18:2, two double bond). All the three OH groups can be esterified with alcohol [13, 14]. Stoichiometrically, one mole of triglycerides reacts with three moles of alcohol to produce three moles of esters and a mole of glycerol as shown in Figure 1.2.

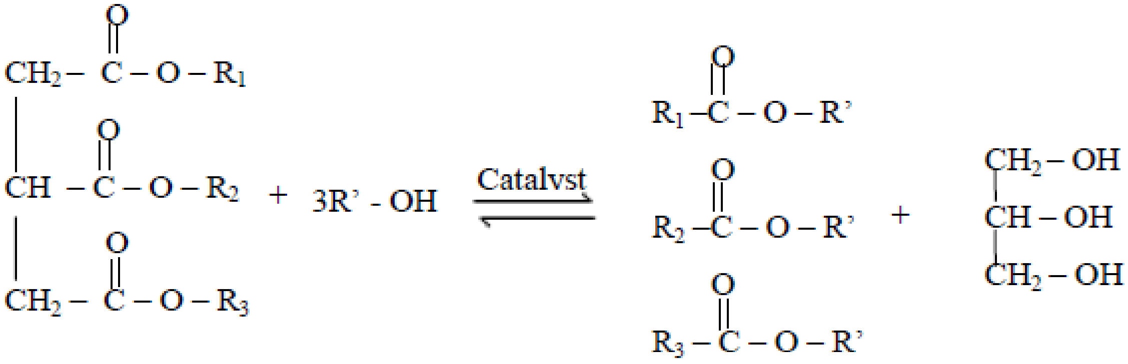


Figure 1.2: Transesterification reaction of vegetables oils

As vegetable oils are sparingly soluble in lower alcohols, the transesterification reaction is slow due to the limited mass transfer rate between the two immiscible phases [15]. Several techniques such as mixing, co-solvent addition, higher temperature, higher pressure, super critical alcohol, ultra sonication and microwave irradiation have been investigated to enhance the reaction rates.

The global markets for biodiesel are entering a period of rapid, transitional growth, creating both uncertainty and opportunity. In years 2008 to 2012, the global edible oil production increased from 137.7 to 150 million tons; about 85% was used as food while about 13% was used for biodiesel production and the remaining 2% for other non-food industrial inputs [16]. Currently, more than 95% of biodiesel is made from edible oil sources such as rapeseeds, soybeans, sunflower and palm [14, 20]. The capacity for biodiesel production increased from 2.2 million tons per year in 2002 to 32.6 million tons per year in 2008; however, biodiesel production was only 1.9 million tons per year in 2002 and 11.1 million tons per year in 2008 as presented in Figure 1.3. Biodiesel industry had to compete with food processing industry for the all-important raw material - edible oils. This resulted in the rise of edible oil prices affecting the economics of biodiesel production as well as food prices. Even now, it has been reported that feedstock cost alone accounts for 75% of the biodiesel production cost [8].

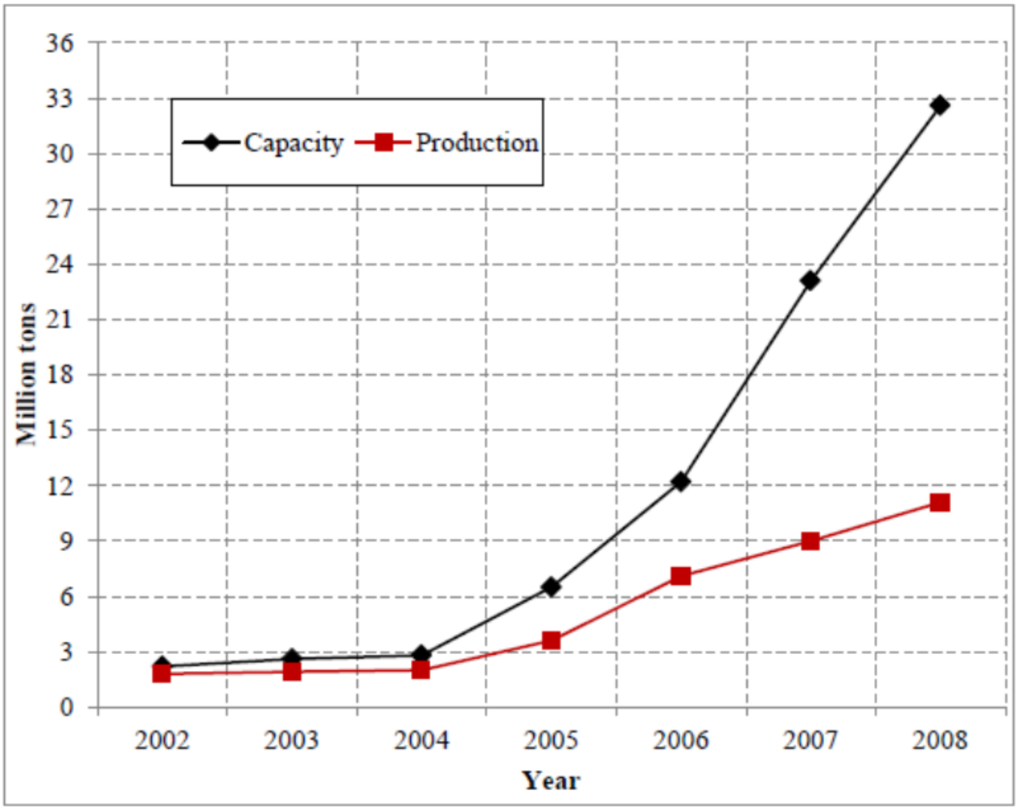


Figure 1.3: World biodiesel production and capacity from 2002 to 2008 [21]

Energy demand in Malaysia is expected to grow at a rate of 5 to 7.9% for the next 20 years due to its fast growing industrialized economy [5]. Natural gas (43.4%), crude oil (38.2%), coal (15.3%) and the renewable resources (3.1%) contribute to the required energy mix in 2008 [5]. Malaysia is a major palm oil producer and exporter. The government of Malaysia adopted the National Biofuel Policy in 2006 to further promote the production and consumption of biodiesels [5]. In the same year, Envo diesel has been introduced to further strengthen the utilization of biodiesel as a renewable diesel. Envo diesel was a mixture of 5% blend of processed palm oil with 95% petro-diesel.

1.2 Problem Statement

Fossil fuels such as coal, natural gas and crude oil supply most of the world energy demand (88%). As the results of this, usage fossil fuels contributes to CO2 emission which are 30.2 BMT in 2008 to 43.2 BMT in 2035.Renewable fuels and chemical feedstock's with zero net carbon dioxide emissions is necessary for sustainable development. One such option is biodiesel. The reason why biodiesel is chosen is due to its close and similar properties to the petroleum-based diesel.

As mentioned earlier, currently more than 95 % of biodiesel raw material feedstock sources are from edible oil such as rapeseeds, soybeans, sunflower and crude palm oil. Use of edible oil as feedstock's for biodiesel will compete with food industry. This is unavoidable because primary use of edible nowadays is for food industry. As a result, there will be an increase in both price of raw material (edible oil) and also food. It is necessary to keep the cost of production under control to make the biodiesel technology viable by using alternative cheap feedstocks and effective environmental friendly reaction pathways. One such option is using non-edible oil sources such as waste cooking oil (WCO).

While many research has been conduct in order to find a better solution to produce biodiesel, transesterification reaction has proven its capability to produce a better yield of biodiesel with a higher rate of reaction compared to the conventional method being used. However, the current biodiesel technology challenge is that the transesterification rate to produce biodiesel is still very slow. This happens due to the limited solubility of alcohol present in the oil.

Nowadays, huge quantities of waste cooking oils and animal fats are available throughout the world, especially in the developed countries. Management of such oils and fats pose a significant challenge because of their disposal problems and possible contamination of the water and land resources. Even though some of this waste cooking oil is used for soap production, a major part of it is discharged into the environment. WCO is cheap and renewable but currently disposed of inadequately. Furthermore, the governments penalize the direct discharge of WCO into drainage, sewer and open land and rivers. Countries such as USA, Canada, Russia and China produce millions of metric tons of waste cooking oil per year. On the other hand, this will also generates huge amount of WCO as non-edible biodiesel feedstocks.

Thus, this research or project work will consider WCO as the feedstock's for biodiesel production through transesterification of WCO as a non-edible oil sources. The slow reaction rate of transesterification can be enhanced by pretreatment of feed by microwave energy irradiation of waste cooking oil.

1.3 Objectives

The objectives of this research are as follow:

I. To investigate transesterification reaction of waste cooking oil with ethanol as the solvent.
II. To investigate the effect of microwave pretreatment of waste cooking oil on transesterification reaction.
III. To investigate the individual and interaction effect of reaction variables using DOE software.
IV. To optimize reaction variables for maximum yield

1.4 Scope of Study

In the present research work, to achieve the affirmation research objectives, waste cooking oil were used as a source of non-edible oil and characterized to determine its physical and chemical properties. Transesterification reactions will be conducted to investigate the effect of reaction variables such as alcohol to oil ratio, catalyst concentration, reaction temperature, mixing rate and reaction time on the yield of biodiesel. The interaction effect of reaction variables were also studied using statistical tools of response surface methodology (RSM) and optimum operating conditions will be established. Conversions of triglycerides with time at different reaction conditions will be measured to investigate the rate of reaction and order of reaction equations.

1.5 Relevancy of Project

This project is important because it discuss the current issue about finding the new source of renewable energy that can reduce the dependency on fossil fuels in this case the petroleum based diesel. This issue attracts many attentions from every nation especially developed and industrialized countries including Malaysia. Therefore, investigation on how to solve and improve this problem is needed. This study will provide information in the future for transesterification reaction of waste cooking oil in the presence microwave pre-treatment of WCO for biodiesel production.

CHAPTER 2: LITERATURE REVIEW/THEORY

2.1 Biodiesel and its Properties

Biodiesel is a renewable energy that has a potential to cater the problems of dependency on fossil fuels as a highest consumption source of energy and the depletion of petroleum based energy. It is reported by Mofijur M. et. al (2012) within the years of 1980 to 2010, the global primary fuel consumption has increase nearly doubled which is from 6630 million tons of oil equivalent (Mtoe) to 12,002.4 Mtoe . Moreover, according to International Energy Agency, they estimate that global energy consumption will rise 53% by 2030. In Malaysia, petrol diesel consumption has rose from 22 Mton in 2001 to 25.3 Mton in 2010 meanwhile the oil production has drop off from 32.9 Mton in 2001 to 32.1 Mton in 2010 [24]. With the highest consumption on fossil fuels as a source of energy, the environment and its ecosystems are getting polluted by the emission of greenhouse gases (GHG) such as carbon dioxide. It was estimated the carbon dioxide emissions interrelated with energy consumption to increase from 30.2 billion metric tons in 2008 to 43.2 billion metric tons in 2035 [25]. Therefore, searching for environmental friendly alternative energy and feedstock with zero net carbon emission is essential for sustainable development. Biodiesel is one of the top options that have gained worldwide attention.

Biodiesel is a type of oil that has almost similar properties to petroleum diesel that is derived from plants and animals. It is also known as fatty acid methyl esters or FAME. It is renewable, biodegradable, and non- toxic [24]. As it has almost similar properties as petroleum diesel, it can be blended with diesel fuel at any proportion and allows it to be used in a diesel engine without any modification [24]. Furthermore, it is environmental friendly type of energy sources.

2.2 Quality & Standards of Biodiesel

Transesterification reaction of vegetable oil does not go to 100% completion; it reaches equilibrium state at a certain point. The resulting product of transesterification reaction contains fatty acid esters, monoglycerides (MG), diglycerides (DG) and triglycerides (TG) and other minor impurities. The biodiesel standards limit components of biodiesel such as glycerol, mono, di and triglycerides, FFA (by limiting the acid number), residual alcohol (by limiting flash point) and moisture contents. However, from all of these quality parameters, the glycerol content, that is, the free glycerol, MG, DG, TG and acid value are the most important. Thus, the ASTM D6751 limits the free glycerol to 0.02%, the total glycerol to 0.24% and the acid value to 0.5 mgKOH/g as shown in Table 2.1.

Table 2.1: ASTM D6751 and DIN EN 14214 biodiesel standards [19]

Property	Unit	Standard Limit		Test Methods	
		ASTM D6751	DIN EN 14214	ASTM D6751	DIN EN 14214
K.Viscosity at 40oC	mm2/s	1.9–6.0	3.5–5.0	D445	EN ISO 3104
Density at 15oC	kg/m3	-	860–900	–	EN SIO 3675 EN SIO 2185
Flash point	oC	130.0 min	101.0 min	D93	ISO CD3679e
Acid value	mg KOH/g	0.80 max	0.5 max	D664	pr EN 14104
Free glycerol	% (m/m)	0.020 max	-	D6584	EN 14106
Monoglycerides	% (m/m	–	0.8 max	–	pr EN 14105m
Diglycerides	% (m/m)	–	0.2 max	–	pr EN 14105m
Triglycerides	% (m/m)	–	0.2 max	–	pr EN 14105m
Total glycerol	% (m/m)	0.240 max	0.25 max	D6584	pr EN 14105m
Methanol	% (m/m)	–	0.2 max	–	pr EN 141101
Cloud point	oC	–	–	D2500	–
Distillation T90AET	oC	360 max	–	D1160	
Iodine value	–	–	120 max	–	pr EN 14111
Water and sediment	%vol	0.050 max	–	D2709	–
Water content	mg/kg	–	500 max	–	EN ISO 12937
Cetane number	–	47 min	51 min	D613	EN ISO 5165
Sulphated ash	% (m/m)	0.020 max		D874	ISO 3987
Carbon residue	% (m/m)	0.050 max	0.3 max	D4530	EN ISO 10370
Sulfur (S 15 Grade)	ppm	0.0015 max	–	D5453	–
Sulfur (S500 Grade)	ppm	0.05 max	–	D5453	-
Oxidation stability at 110oC	h	–	6	–	pr EN 14112

2.3 Biodiesel Production Technology

Vegetable oils are not suitable for direct use as internal combustion engine fuel due to their high viscosity, (27-54mm2/s compared to 2.7mm2/s of petro-diesel fuel), lower volatility and high reactivity due to its unsaturated hydrocarbon. Direct use of vegetable oil has shown several problems such as:

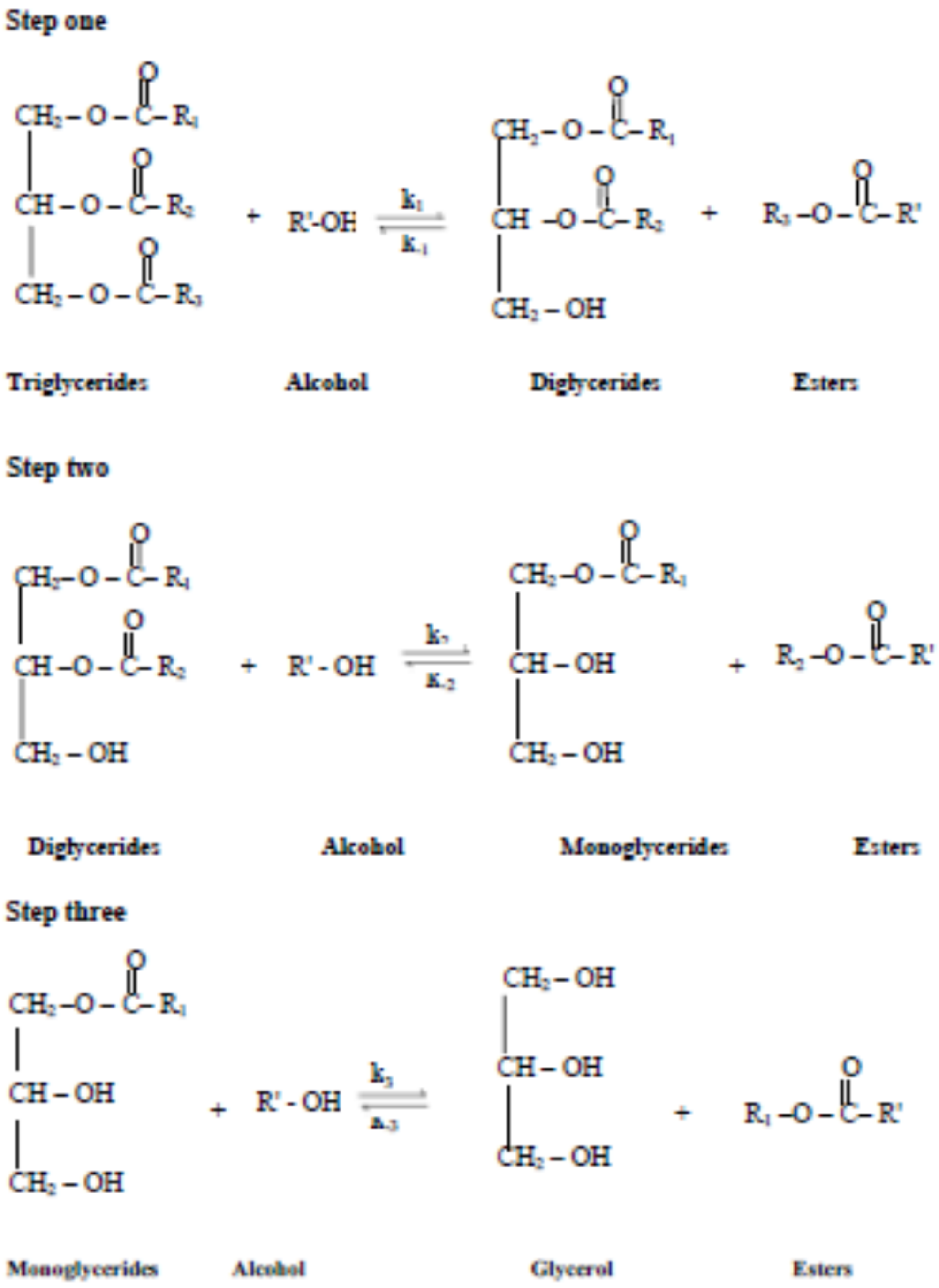
- Coking and trumpet formation on the injectors
- Oil ring sticking
- Thickening and gelling of the lubricating oil
- Reduced power and fuel economy[26]

In order to overcome the problems posed by direct use of vegetable oils, different methods such as dilution, micro emulsion, pyrolysis and transesterification were proposed to modify the chemical and physical properties of vegetable oil [27]. However, transesterification is the most suitable method to lower the viscosity of vegetable oil and commercially established process to convert vegetable oils or animal fats to biodiesel [28].

Transesterification is a chemical reaction between triglycerides present in the oils or fats and alcohols to form esters and glycerol in the presence of catalyst or at high pressure and temperature [29]. Methanol is the most preferred alcohol because it is the most cheapest and available alcohol. Other alcohols such as ethanol, propanol, butanol and amyl alcohol can also be used in place of methanol.

The molecular weight of ester molecule is about one-third of its parent vegetable oil molecule. WCO has viscosity of 10 times or more than regular diesel. The physical characteristics of esters produced by transesterification are quite similar to those of diesel fuel. Stiochiometrically, 1 mole of triglycerides reacts with 3 moles of alcohol to produce 3 moles of esters and 1 mole of glycerol. It consists of three consecutive reversible reaction steps [30].

The first step involves formation of diglycerides molecule, the second step involves formation of monoglycerides and the last step is the formation of glycerol. In each step one mole of ester is formed as illustrated in Figure 2.1. Since it is an equilibrium reaction, large excess of alcohol need to be used to shift the equilibrium towards formation of esters and glycerol.



Where: R_1, R_2, R_3 = carbon chain of the fatty acids
R' = alkyl group of the alcohol

Figure 2.1: Stepwise transesterification or alcoholysis of vegetable oil

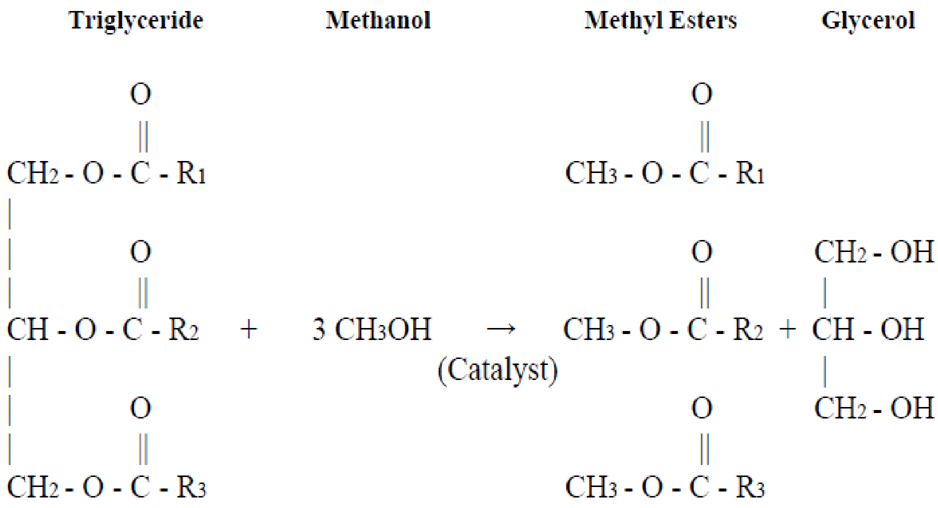


Figure 2.2: Overall transesterification or alcoholysis of vegetables oils

2.4 Variables transesterification reaction affecting

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 [23].

2.5 Microwave Role in Biodiesel Production

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 feedstock's [21,22]. Microwave energy, a non-conventional heating method is utilized in biodiesel production in two main stages: 1) oil extraction and 2) chemical transesterification reaction. Biodiesel production involves mixing of appropriate ratios of oil, methanol or ethanol(solvent) and catalysts .The mixture is then processed through a microwave reactor followed by separation of products to yield biodiesel and glycerin.

2.6 Microwave Pre-treatment of Non-Edible oil

Recently, microwaves have received increased attention due to their ability to complete chemical reactions in very short times. Few advantages with microwave processing can be listed as rapid heating and cooling, cost savings due to energy, time and work space savings, precise and controlled processing, selective heating, volumetric and uniform heating and reduced processing time. 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 [20]. Due to these advantages, microwaves provide for tremendous opportunities to improve biodiesel conversion processes from different feedstock and oils.

2.7 Waste cooking oils as Source of Biodiesel Feedstock

Figure 2.2 below shows the global analysis on consumption of vegetables oils from year 1995-2014. From the graph, there is an increase in the vegetables oils consumption throughout the year 1995-2014. This trend will continue to increase as time progress as there will be an increase in population in the world.

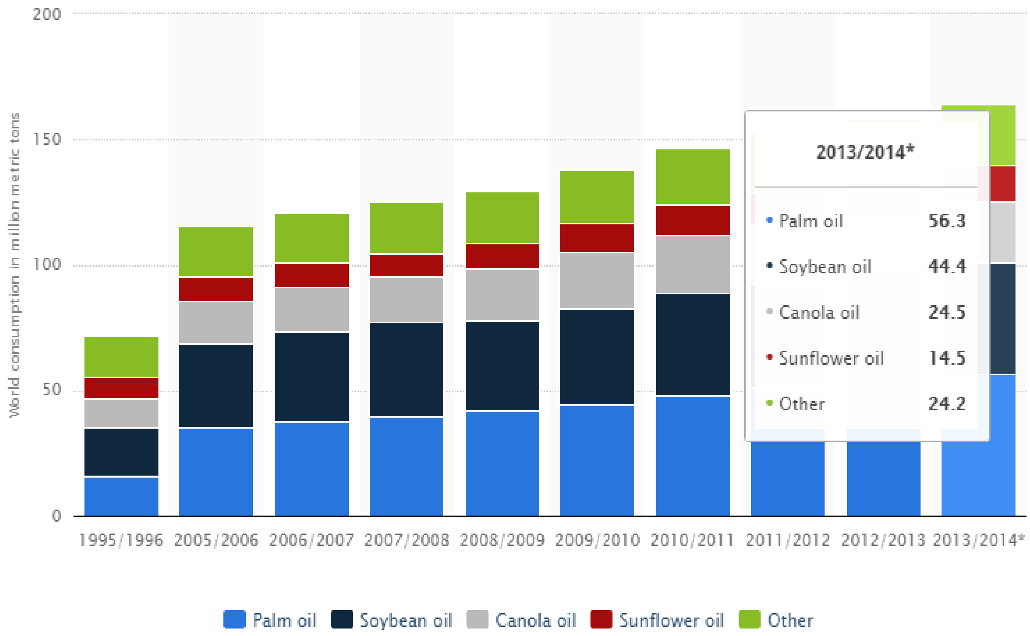


Figure 2.3: Global consumption of vegetable oils from 1995/1996 to 2013/2014, by oil type (in million metric tons)

Among the vegetables oils used, palm vegetables oils are being consumed at the highest rate which is approximately at 56.3 million MT/year. This is because palm oil contributes the most in food industry. Other oils such as soybean, canola and sunflower oil also used primarily in food industry. The total vegetables oil consumed at year 2014 is approximately 163 million MT/year which will also generates huge amount of waste cooking oil as a source of non- edible oil feedstock's.

CHAPTER 3: METHODOLOGY

3.1 Introduction

Overall process flow diagram of the research methodology to investigate transesterification of WCO with and without and microwave pre-treatment of WCO followed in the present study is presented in Figure 3.1. Materials used are presented in section 3.2. Experimental methods used for characterizations of WCO are described in section 3.3. Purification methods of WCO are discussed in section 3.4. Experimental design plan for the transesterification of WCO and parametric optimization are discussed in section 3.5. Section 3.6 describes the Gantt chart of this project work.

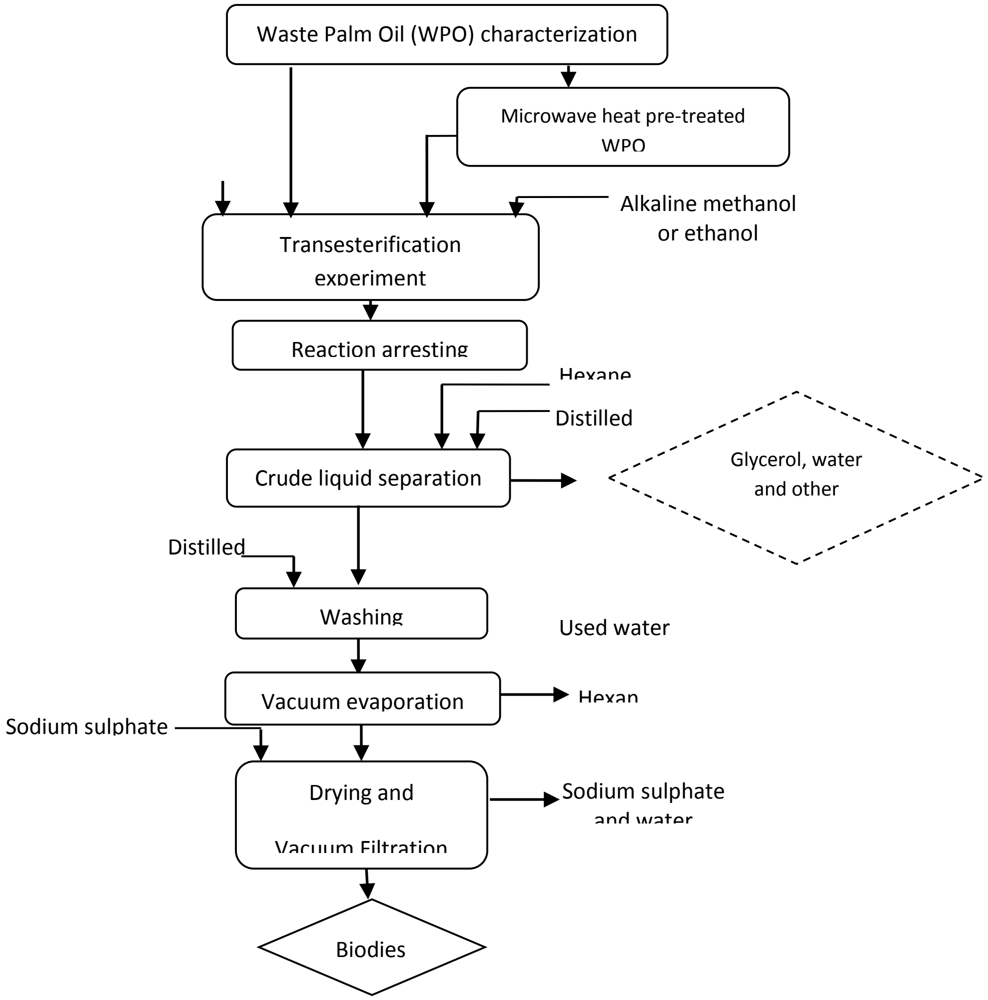


Figure 3.1: Process flow of transesterification of waste cooking oil of the present study

3.2 Materials and Chemicals

Waste cooking oil sample was collected from local restaurants located around Taman Maju, Seri Iskandar, 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 standard chemicals for biodiesel analysis in gas chromatograph are presented below:

Table 3.1: List of chemical used in research

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-proponol	>99.8%	Merck chemical
N-hexane	≥ 99%	
N-heptanes	≥ 99.5%	
Potasium hydroxide	0.1 N	
Iodine	≥ 99.99%	
Sodium sulphate	≥ 99%	
α-Naphtholphthalein	≥ 99%	
Acetic acid	Reagent grade	
Diethyl ether	Reagent grade	
Reference standards kit for GC		
1,2,4 butanetriol	GC grade	
Tricaprin	GC grade	
Glycerin	GC grade	
Monoolein	GC grade	
Diolein	GC grade	
Triolein	GC grade	
N-Methyl-N-trimethylsilytrifluoroacetamide (MSTFA)	GC grade	
Pyridine	≥ 99%	

3.3 Experimental Approach Characterization of Waste Cooking 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 provides an indication of its usability as a fuel. Methods used to measure these properties are presented in the following sections.

3.3.1 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. FFA percentage of oil is one of the important factors to design transesterification reaction experiments. The acid value of biodiesel fuel also affects the quality of the biodiesel as fuel. Thus, determination of the acid value of the oil prior to transesterification reaction as well as the acid value of biodiesel is very essential to produce a biodiesel fuel that satisfies international requirements of biodiesel as a fuel. The acid number of waste cooking oil and the corresponding biodiesel produced will be determined using titration method of American Oil Chemists Society, AOCS Official Methods cd 3d-63, revised 2003. According to AOCS Official Methods cd 3d-63, revised 2003, the acid number is calculated as;

$$Acid\ value, mg\,KOH/g \quad = \quad (A-B) * \frac{N * 56.1}{w} \tag{3.1}$$

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 procedures of the experiment are as follows:

1) A solvent mixture consisting of equal parts by volume of isopropyl alcohol and toluene is prepared.
2) 0.1 N KOH is prepared
3) Phenolphthalein solution is added to the required amount of solvent in ratio of 2ml to 125ml and neutralize with KOH to a faint pink colour.
4) The sample size is determined from the following Table 3.2:

Table 3.2: 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 volume of KOH used is recorded and calculated
6) Perform a blank titration using a solvent mixture consisting of equal parts by volume of isopropanol and toluene.
7) The volume of KOH used is recorded and calculated.
8) The acid number is calculated.

The acid percentage due to FFA in a sample was assumed due to the contribution of presence of lauric,oleic and palmitic FFA acid components. The FFA percentage due to each of these components may be estimated by dividing the acid value by 1.99, 2.81 and 2.56, respectively. In this studies, according to Gas Chromatography Mass Spectroscopy (GCMS) results the highest percentages of FFA in a sample of waste cooking oil is oleic acid. Therefore, in order to express in terms of free fatty acids as percent, divide the acid value in mg KOH/g with 2.81

$$FFA\,\% = \frac{Acid\ value}{K} \tag{3.2}$$

$$Where: K = (0.0199 * Oleicacid) + (0.0281 * Lauricacid) + (0.0251 * Palmiticacid)$$

3.3.2 Determination of Saponification Value

Saponification value is the amount of alkali, in milligrams of potassium hydroxide, necessary to convert 1 gram of oil into soap. After transesterification is complete, the left over catalyst and some soap formed tend to concentrate in the glycerol phase. However, some soap may be left in the biodiesel phase. During design of transesterification reaction experiment, it is important to know the amount of soap formed when alkaline catalyst is used and how effective the washing process is in removing soap formed and left over catalyst. In the present work, AOCS Cd 3b-76 titration procedure was used to estimate the saponification value of both waste cooking oil and biodiesel. Mathematically, it is expressed as;

$$Saponification\ value = (A - B) * \frac{N * 56}{w} \tag{3.3}$$

Where: w = weight of sample taken, g

A = volume of KOH required for blank titration, ml

B = volume of KOH required for sample titration, ml

N = normality of KOH solution, mol/l

3.3.3 Determination of Iodine Value

Iodine value or iodine number is the measure of the total amount of unsaturated fatty acids in the oil. It is the measure of the number of grams of iodine which will combine with 100 grams of the oil. The method specified by AOCS official method 993.20 was used in order to determine the iodine value. Then the iodine value (I.V) is determined by the expression:

$$Iodine\ value = (A - B) * \frac{N * 12.69}{W} \tag{3.4}$$

Where: N = Normality of sodium thiosulphate ($Na_2S_2O_3$) used; mol/l

A = Volume of sodium thiosulphate used for blank; ml

B = Volume of sodium thiosulphate used for determination, ml

W = weight of the sample, g

3.3.4 Determination of viscosity

The viscosity of waste cooking oil was tested by using viscometer units. 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 waste cooking oil 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 is for rotating is set and the run key is pressed. Then, result is collected.

3.3.5 Specific Gravity

The procedure are as follows:

1) A measuring cylinder is weigh on the weighing machine and the weight is recorded.
2) 11.5 ml waste cooking oil is pour into a measuring cylinder and the weight is recorded.
3) The density waste cooking oil is calculated by using the equation below:

$$Density = (Mass\ of\ beaker\ with\ oil - Mass\ of\ beaker\ without\ oil)/Volume\ of\ oil$$

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

3.3.6 Determination of calorific value

The calorific value of waste cooking oil was determined by using bomb calorimeter equipment. A sample of waste cooking oil was sent to the required personnel in UTP to undergo the bomb calorimeter experiment.

3.4 WCO oil purification (esterification reaction).

Since waste cooking oil contains certain amount of chunks, impurities or solid deposition as a result from cooking, it is necessary to purify the oil to ensure the transesterification reaction proceed accordingly and avoid any side reaction that may occur.

3.4.1 Removal of chunks

Filtering WCO oil will eliminate the chunks of food and other particles before it is used for further processes. Chunks can contain water and other impurities that will affect the biodiesel production processes and the quality of biodiesel produced. The chunks need to be removed using a filtration processes

i. Appropriate filter such as cotton cloth filter were used to separate chunks from WCO. Before that, the oil was heated to about 50℃ to reduce the viscosity for easiness of filtration.
ii. Once the oil was separated, smaller suspended particles were allowed to settle so they doesn't attach to the heating element and muck up the processor. This process was conducted several times until no more solid depositions are present.
iii. Once separation was completed, the WCO were transferred to a screw cape bottle to make ready for esterification process.

3.4.2 Esterification reaction (FFA conversion)

The saturated or unsaturated mono-carboxylic acids that occur naturally in fats, oils or greases but are not attached to glycerol backbones are known as free fatty acids (FFAs). The presence of higher amount of FFAs in oil can result in higher amount of acid value of oil. WCO usually contain a high amount of FFAs. When alkaline catalyst is used to promote the transesterification reaction in WCO feed stocks with high FFAs, the FFAs reacts with the alkaline catalyst and soap will be formed as shown in the Figure 3.2. The formation of soap is the undesirable product in transesterification reaction as more catalyst is required to replace the catalyst lost due to soap formation. The presence of soap increases the viscosity (formation of gel) and emulsification resulting in difficulties in separation of biodiesel from glycerol resulting in excessive washing and low yield of biodiesel. For alkaline catalysed transesterification reaction, the maximum amount of FFAs in the oil needs to be less than 2 or 3%. However, additional catalyst is required to compensate the catalyst lost due to saponification.

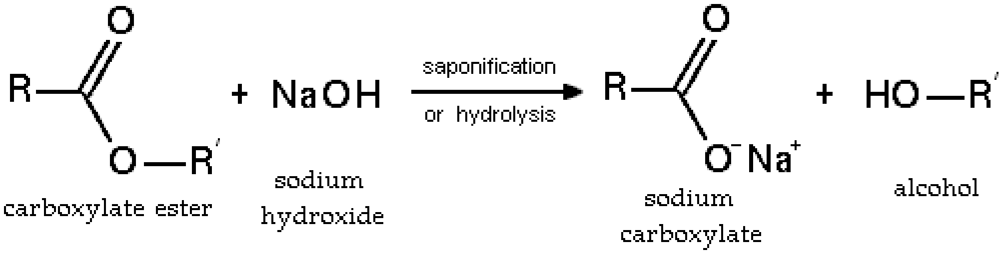


Figure 3.2: Saponification of FFA during transesterification reaction

3.4.2.1.1 *Purification of waste cooking oil (esterification) experimental procedure*

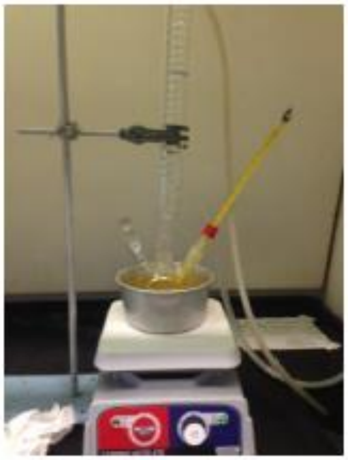


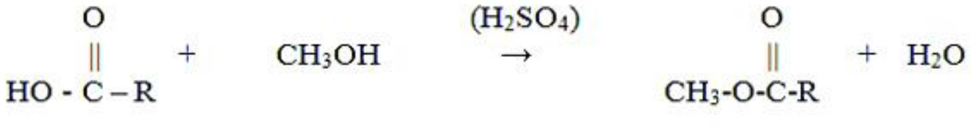
Figure 3.2: Esterification experimental set-up

The procedure are as follow:

1. A two neck round bottom flask reactor equipped with a reflux condenser (to prevent loss of alcohol), a magnetic stirrer and a thermometer are used.

2. 50g of waste cooking oil is prepared and placed in the round bottom flask reactor.
3. 12:1 molar ratio of ethanol to oil is mixed with 3.5 wt% of sulphuric acid to oil is prepared in a separate flask.
4. A magnetic stirrer is placed into the reactor flask and set to 400 rpm.
5. The heat is turned on and allowed for the oil bath to reach 60^{0}C. The flask will be immersed in an oil bath immediately to maintain the reaction temperature.
6. The mixture of ethanol and sulphuric acid is added to the reactor flask and the reaction is started.
7. The reaction is left for 60 minutes.
8. After 60minutes, 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 layers that contains ethanol sulphuric acid and impurities while the bottom layer containing the purified WCO.
9. The bottom layer is recovered and then be washed with warm (50 – 60 ^{0}C) water several times to remove contaminants.
10. The recovered purified waste cooking oil can be further use for transesterification reaction.

Feed stocks with high content of FFAs such as WCO require special process or pre-treatment to be used in biodiesel production. The common pre-treatment method is esterification of FFAs with ethanol in the presence of acid catalyst (usually sulphuric acid) as shown in Figure 3.3. Once the FFAs are reduced to the minimum value, the reaction further proceeds with base catalysed transesterification reaction.



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

Figure 3.3: Esterification of free fatty acid

In the present work, WCO FFA purification using Acid esterification were conducted using the following methods:

Required amount of WCO is poured into the flask and heated up to 60˚C. The 45 to 50 % v/v ethanol is added with the preheated WCO and stirred for a few minutes. 1.5 to 2.5 % of sulfuric acid is added with the mixture. Heating and stirring should continue about 45 to 60 min at atmospheric pressure. After completion of this reaction, the mixture is poured into a separating funnel for separating the excess alcohol, impurities and sulfuric acid. The excess alcohol, sulfuric acid and impurities moves to the top layer and is separated from the oil. The lower layer is separated for further processing of transesterified into ethyl ester. This process is expected to reduce the acid value of WCO to less than 1% of FFA.

3.4.3 Transesterification Reaction Experimental Approach

A two neck round bottom flask reactor equipped with a reflux condenser (to prevent loss of alcohol), a magnetic stirrer and a thermometer will be used. Ten grams of purified WCO were prepared and placed in the round bottom flask reactor. Required amount of alkaline ethanol mixed will be prepared in a separate flask, preheated to the reaction temperature and then added to the round bottom flask reactor to start the reaction. The flask will be immersed in a silicon oil bath thermostat immediately to maintain the reaction temperature. The reactor assembly is shown in Figure 3.4.

After a specified reaction time, the reactor will be withdrawn from the thermostat. The liquid mixtures will be transferred to a separation funnel and will be diluted with distilled water to arrest further reactions. N-hexane will be added to extract alkyl esters and enhance the clarification of the mixture into two phases. The separation processes requires several hours to form a clear phase separation between the top layer that contains mixture of alkyl ester and n-hexane mixture while the bottom layer containing glycerol, ethanol, sodium hydroxide, water and unspent oil.

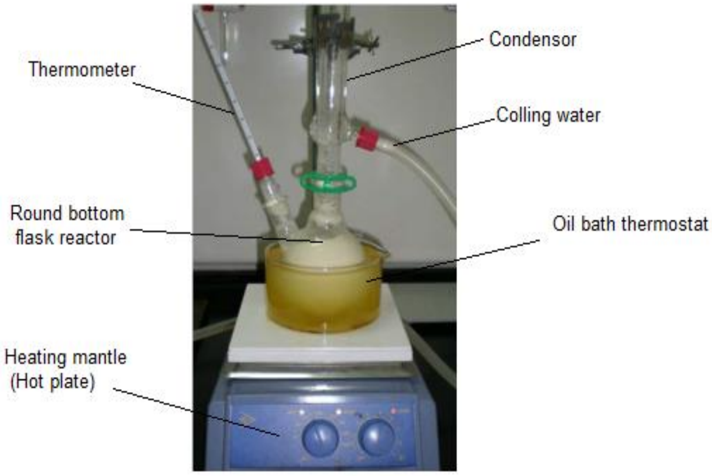


Figure 3.4: Batch reactor for transesterification of waste cooking oil

The top layer will be recovered and then washed with warm (50 - 60^{o}C) water several times to remove contaminants; traces of moisture in the washed top layer (containing hexane and alkyl esters) were removed by passing the mixture through an adsorption column of sodium sulphate particles. Alkyl ester produced will be recovered by evaporating n-hexane from the mixture using a rotary vacuum evaporator operating at a temperature of 70^{o}C, 200 mmHg and a rotational speed of 20 rpm. The recovered alkyl ester will be weighed and stored in a screw capped bottle for further analysis.

This procedure were used in all the experiments to investigate yields of ethyl esters for microwave pretreated and untreated WCO. Optimal operating conditions will be investigated with or without microwave pretreatment of WCO by statistical tool of response surface methodology (RSM).

3.4.4 Statistical Experimental Design for investigating the individual and cross effects of reaction variables to determine optimum operating conditions

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

The experimental results were fitted using a polynomial quadratic equation in order to correlate the response variables. The general form of the polynomial quadratic equation shown in equation (3.5) was used to develop a model that predicts (estimates) the yield of alkyl esters (FAEE) at designed reaction variable combination.

$$\mathrm{Y_i} = \beta_{\mathrm{o}} + \sum_{\mathrm{i=1}}^{\mathrm{k}} \beta_{\mathrm{i}} X_i + \sum_{i=1}^{k} \beta_{ii} X^2 + \sum_{i=1}^{k}\sum_{j=1}^{k} \beta_{ij} X_i X_j \qquad (3.5)$$

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

The variable X_i was coded according to equation (3.6).

$$x_i = \frac{X_i - X_i^*}{\Delta X_i} \qquad (3.6)$$

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

3.5 Gantt Chart

No	**Details**	**Week**													
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
1	Selection of Project Topic: Microwave energy pretreated ethanolysis of non-edible oil	🟩	🟩												
2	Preliminary Research Work: Research on literatures related to topic		🟩	🟩	🟩	🟩	🟩								
3	Submission of Draft Project Proposal.						▲								
4	Submission of Project Proposal.							▲							
5	Proposal defence.								🟩	🟩	🟩				
6	Project Work: Study on research scope and method.								🟩	🟩	🟩				
7	Project Work: Further investigation on the project and do modification if necessary.								🟩	🟩	🟩	🟩	🟩	🟩	
8	Submission of Interim Report.													▲	
9	Oral Presentation.														🟩

CHAPTER 4: RESULTS & DISCUSSION

4.1 Waste Cooking Oil Characterization

4.1.1 Acid number determination

The free fatty acid composition of waste cooking oil for this research work mostly composed of linoleic (46%) and oleic (45.4%). Thus according to AOCS Official Method Cd 3d-63, acid value need to be divided by 2.81 to obtain the free fatty acid (FFA) value. From the Table 4:1, it was determined that the free fatty acid (FFA) content was very high which 9.44%. This is not a good condition in producing biodiesel because the presence of high FFA in a vegetable oil can cause the formation of soap. This is happened during the alkaline catalysed transesterification where the alkaline catalyst will partially neutralize the FFA in the oil producing soap thus reducing the biodiesel yield [16]. Several studies reported that FFA content in vegetable oil must be less than 3% to undergo transesterification reaction [17,18]. As the FFA content in waste cooking oil is high, thus two-step transesterification reaction is required. Waste cooking oil need to be undergo acid catalysed transesterification (esterification) to reduce the FFA content before can proceed to alkali catalysed transesterification.

Table 4.1: The result for the acid determination value

Run	1	2
Mass of Waste Cooking Oil (g)	2.6743	2.5783
Titration Starting Point (ml)	3.1	2.0
Titration End Point (ml)	15.4	11.6
Volume of KOH used (ml)	12.3	13.6
Blank titration starting point (ml)	0	0.6
Blank titration end point (ml)	0.5	1.2
Volume KOH used (ml)	0.5	0.6
Acid value(mg KOH/g)	24.75	28.27
Average (Mg KOH/g)	26.51	
Percentage of FFA	9.44%	

4.1.2 Specific Gravity Determination

Table 4.2 summarize the results in determination of density and specific gravity of waste cooking oil. From the results it was estimated that the density of waste cooking oil is 0.9146 g/ml (914.6 kg / m3). Based on the density, the specific gravity of WCO was calculated to be 0.91.

Table 4.2 Density & specific gravity determination of WCO

Experiment	Value
Mass of measuring cylinder (g)	72.4161
Mass of measuring cylinder with WCO (g)	90.7096
Mass of waste cooking oil (g)	18.2935
Volume of waste cooking oil (mL)	20
Density of waste cooking oil (g/mL)	**0.9146**
Density of water (g/mL)	1.000
Specific gravity of waste cooking oil	**0.9146**

4.1.3 Viscosity Determination

The value of viscosity was taken at the highest percentage of torques at 40oC and 250 rpm. Based on the result tabulated above, at 2.7% the viscosity waste cooking oil is 43.38cP. This value is higher as compared to petroleum based diesel fuel which is 2.7cP at 40 ℃ [19]. Therefore waste cooking oil need to undergo transesterification reaction in order to reduce its viscosity to a range similar with petroleum based diesel thus make it work effectively as fuel in standard diesel engine.

Table 4.3: The result obtained for viscosity determination

Spindle	% of torques	Viscosity (cP)
2	2.7	43.38
3	-31.1	0
4	0.8	48.00
5	0.2	24.00
6	0.2	60
Waste Cooking Oil Viscosity (cP)		**43.38**

4.1.4 Calorific Value Determination

The calorific value of waste cooking oil obtained from bomb calorimeter experiment is 39.70 kJ/g. This is nearly to the petroleum based diesel energy content which is 43.1 kJ/g. Therefore, with that heating energy value, waste cooking oil is considered as a feasible fuel.

4.1.5 Summary of Waste Cooking Oil Properties

The properties waste cooking oil such as FFA content, viscosity, calorific value and specific gravity are tabulated in the Table 4.4 below:

Table 4.4: Properties of WCO

Properties of Waste Cooking Oil	Value
Specific gravity	0.9146
Viscosity (cP)	43.38
Calorific Value (kJ//g)	39.70
FFA content (%)	9.44 %
Molecular weight (g/mol)	876.35

4.2 Preliminary Experiment Result

4.2.1 Esterification Reaction

The FFA content of waste cooking oil is high. Thus, it is required to undergo two-step transesterification reaction which is acid-catalyzed esterification using sulphuric acid H2SO4. The oil was treated approximately for 1 hour as temperature 70℃. The stirring speed was 400 rpm. The ethanol to oil molar ratio used was 12:1 in order to reduce the FFA content in the oil followed by alkaline catalyzed transesterification to produce biodiesel. After experiment was done, the oil is titrated again to determine the % FFA content. The result in esterification reaction is tabulated in the table 4.5.

Table 4.5: Titration result after acid catalysed transesterification reaction of WCO

Run	**1**	**2**
Mass of Waste Cooking Oil (g)	10.543	10.893
Titration Starting Point (ml)	0	0
Titration End Point (ml)	3.6	3.4
Volume of KOH used (ml)	**3.6**	**3.4**
Blank titration starting point (ml)	4.0	4.0
Blank titration end point (ml)	4.5	4.6
Volume KOH used (ml)	**0.5**	**0.6**
Acid value(mg KOH/g)	1.6495	1.4420
Average (Mg KOH/g)	1.5457	
% FFA	**0.55 %**	

According to AOCS Official Method Cd 3d-63, acid value need to be divided by 2.81 to obtain the free fatty acid (FFA) value. From the table above, it is shown that the FFA content in oil has reduced to 0.55%. It is consider as a good condition to undergo transesterification reaction as the FFA content is below than 3%.

4.2.2 Transesterification Reaction

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

Waste cooking oil : 10g
Stirring speed : 350 rpm
Weight percent of NaOH : 1.5 w/w %
Reaction time : 1 Hour (without microwave heating)
30 Min (with microwave heating)

4.2.3 Reaction without microwave heating

In this experiment, the waste cooking oil was not treated with microwave to study the FAEE yield of biodiesel (ethyl-esters). The transesterification reaction was done for 1 hour for each experiment.

Table 4.6: Experiment done with constant temperature

Ethanol to oil molar ratio	*Reaction Temperature (℃)*	*FAEE yield w/w %*
3	50	61.56
6	50	83.19
9	50	76.42

Table 4.7: Experiment done with different temperature (constant molar ratio)

Ethanol to oil molar ratio	*Reaction Temperature (℃)*	*FAEE yield w/w %*
6	30	56.76
6	45	80.43
6	60	72.82

4.2.4 Reaction with microwave pre-treatment of waste cooking oil (WCO)

In this experiment, the waste cooking oil undergoes microwave pre-treatment before it goes for transesterification reaction in order to study the effect of microwave heating of WCO towards the yield of biodiesel/ethyl-esters produced. The reaction time for this experiment is 30 min.

Table 4.8: Preliminary experiment with constant temperature

Ethanol to oil molar ratio	*Reaction Temperature (℃)*	*FAEE yield w/w %*
3	30	64.58
6	30	85.32
9	30	75.14

Table 4.9: Preliminary experiment conducted with constant ethanol: oil molar ratio

Ethanol to oil molar ratio	*Reaction Temperature (℃)*	*FAEE yield w/w %*
6	30	68.43
6	45	88.57
6	60	76.21

The FAEE yield is calculated by using the following formula:

$$FAEE\ yield = \frac{\text{weight of FAEE after transesterification}}{\text{weight of oil used}} \times 100\%$$

Based on the results obtained, in order to produce higher FAEE/biodiesel several range variables are proposed for the design experiment. The range of variables are as follows:

Table 4.10: Range of variables proposed for experiment

Variables	**Range**
Ethanol to oil ratio	3 - 9
NaOH concentration (w/w%)	0.5 – 1.5 %
Reaction temperature (℃)	30 – 70
Reaction time (min)	30 - 60

4.3 Alkaline Catalyzed Transesterification

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

4.3.1 Optimization of base catalyzed transesterification of waste cooking oil

In this section, yield of Fatty Acid Ethyl-Esther (FAEE) produced is mainly depends on four independent variables: Ethanol to oil molar ratio (A), NaOH concentration (B), reaction temperature (C), and reaction time (D). In all the experiment, 10 g waste cooking oil and stirrer speed of 400 rpm were kept constant. The individual and interaction effect of process variables and the optimal conditions to get the maximum biodiesel yield were investigated by using central composite design (CCD) technique of response surface methodology (RSM) for base catalyzed transesterification reaction. According to RSM experimental design technique, it was considered that each reaction variable can take 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 4.11.

Table 4.11: Experimental range and level of the independent variables

Variables	Coded Symbol	Range & Levels				
		-2	-1	0	1	2
Ethanol	A	4.97731	6	7.5	9	10.0227
NaOH Conc	B	0.659104	1.0	1.5	2	2.3409
Temperature	C	19.7731	30	45	60	70.2269
Time	D	9.54622	30	60	90	110.454

Experiments carried out as a function of the un-coded variables (with coded variables in the parenthesis) prompted by central composite design technique along with the observed biodiesel yield for base transesterification are presented in Table 4.12.

Table 4.12: Experimental design matrix by CCD technique for base catalysed transesterification along with experimental and model predicted yields

No	Ethanol : Oil Molar Ratio	NaOH concentration (%w/w)	Reaction Temperature (℃)	Reaction time (min)	Experimental yield (%)	Predicted yield (%)
1	9	1	60	90	50.23	52.65
2	7.5	1.5	45	9.54622	47.43	48.94
3	9	2	30	30	55.32	57.13
4	6	1	30	30	66.57	65.16
5	9	2	60	30	60.2	63.21
6	9	1	30	90	64.74	66.11
7	7.5	1.5	45	60	84.12	85.73
8	7.5	1.5	45	110.454	75.12	77.43
9	7.5	2.3409	45	60	70.41	72.33
10	7.5	1.5	19.7731	60	68.23	70.12
11	6	1	60	30	71.44	72.36
12	7.5	0.659104	45	60	53.27	54.28
13	10.0227	1.5	45	60	78.28	79.10
14	6	2	60	90	71.34	72.35
15	7.5	1.5	45	60	85.27	86.24
16	6	2	30	90	73.12	75.33
17	7.5	1.5	70.2269	60	77.47	79.18
18	4.97731	1.5	45	60	52.69	54.72

Based on the Table 4.12 above, it is observed run 15 has the highest FAEE yield which is 85.27% and 86.24% experimentally observed predicted yield by RSM model equation 4.1 at 7.5 ethanol to oil molar ratio, 1.5 % wt/wt of NaOH concentration, 45 °C reaction temperature and 60 minutes reaction time.

Table 4.13: Regression Coefficient for FAEE yield (base catalyzed transesterification)

Coefficient	Estimate
Constant	0.427424
A:Ethanol:Oil Ratio	19.6285
B:NaOH Concentration	-57.6801
C:Temperature	1.5675
D:Reaction Ti**me**	-0.675763
AA	-2.13292
AB	9.99308
AC	-0.0706667
AD	0.0937953
BB	-24.3511
BC	0.212333
BD	0.940364
CC	-0.00975628
CD	-0.00723333
DD	-0.00698615

FAEE yield obtained during base transesterification were statistically analyzed by ANOVA in order to determine the constants of the quadratic equation which is shown in the Table 4.13. Based on the constants of quadratic equation, statistical model equation is established to estimate the FAEE yield. The statistical model equation are shown as equation 4.1 below.

$$FAEE\ yield = 0.427424 + 19.6285A - 57.6801B - 0.675763D - 2.13292A^2 + 9.99308AB - 0.0706667AC + 0.0937953AD - 24.3511B^2 + 0.212333BC + 0.940364BD - 0.00975628C^2 - 0.007233CD - 0.00698615D^2$$

(**RSM Model Equation 4.1**)

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

The diagnostic plot as shown in the Figure 4.1 compares the observed experimental FAEE yield with the predicted values obtained using quadratic model equation. Linear trend are shown between the experimental values versus predicted values of the FAEE yield. Since the P-value in the ANOVA table is less than 0.05, there is a statistically significant relationship between FAEE Yield and Predicted Yield at the 95.0% confidence level. The R-Squared statistic indicates that the model as fitted explains 99.3405% of the variability in FAEE Yield. The correlation coefficient equals 0.996697, indicating a relatively strong relationship between the variables. This indicate that the experimental values are nearly same to the predicted values. Apart from that, the R-Squared statistic ($R2 = 0.99$) indicates that the model as fitted explains 99.3405% of the variability in FAEE yield. This implies that, 99.3405% of the experiment values for base catalyzed transesterification is reliable.

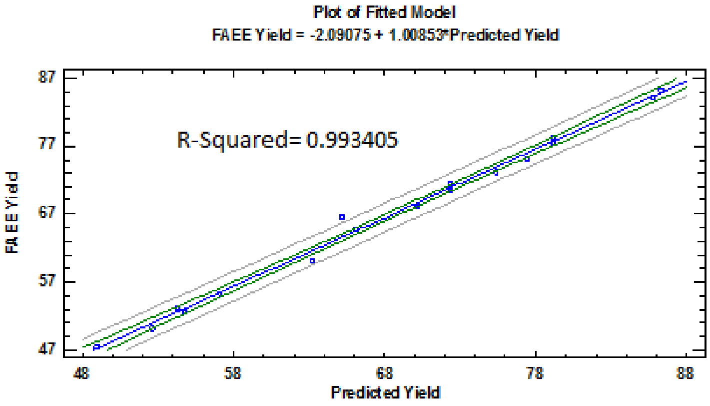


Figure 4.1: The diagnostic plot of experimental FAEE yield (observed) versus predicted FAEE yield for base catalyzed transesterification

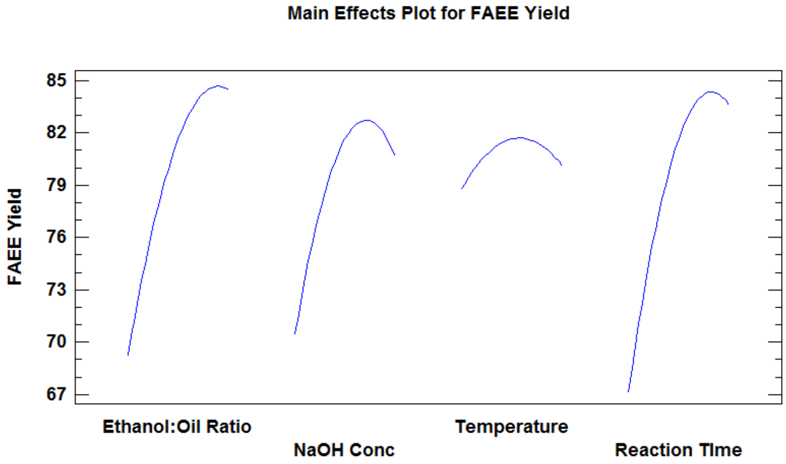


Figure 4.2: Main Effect Plot for FAEE Yield

Figure 4.2 shows the DOE mean plot or main effect plot of factors that exerts effects on FAEE yield. Among the factors analyzed, we can clearly see that the reaction time of transesterification has the most significant impacts on the FAEE yield. However the reaction temperature only have a mild effect towards FAEE yield. For more analyzation, individual interaction effects of reaction variables on FAEE yield were further discuss in the section 4.2.3.

4.3.2 The individual and interaction effect of the reaction variables on FAEE yield

The response surface plots for the yield of FAEE as a function of 3 factors at a time while keeping the other factors at their centre point level were plotted in the three dimensional surface with the response surface contour at the bottom as shown in figure below:

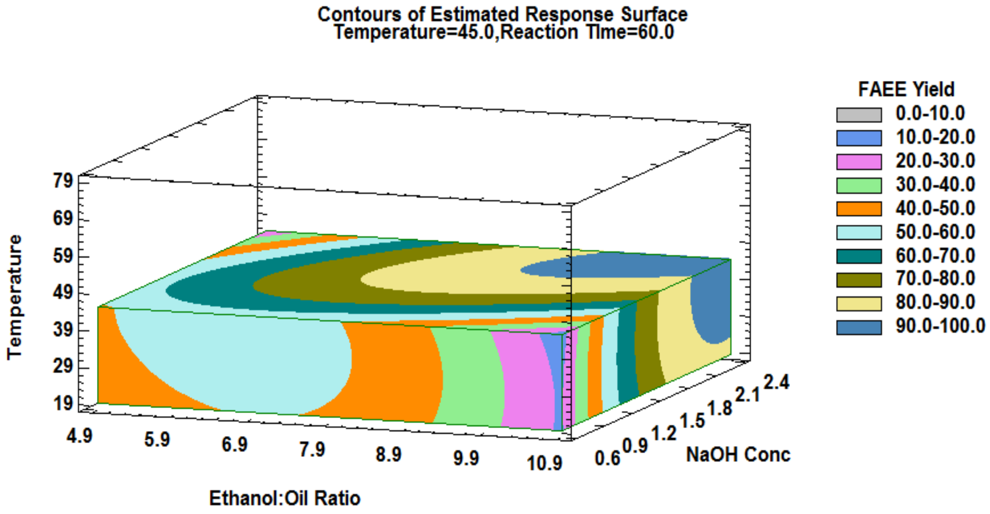


Figure 4.3: 3D Surface Plot with constant Reaction Time

Figure 3.3 depicts the interaction effects of ethanol to oil molar ratio, catalyst concentration (NaOH w/wt%) and reaction temperature on FAEE yield. From the contour plot, it was observed that the increasing volume of ethanol can increase the FAEE yield. However, the FAEE yield started to decrease when the ethanol volume reaches to a certain marginal level which is about 7.9 ethanol to oil molar ratio. Over loading of ethanol 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 FAEE/biodiesel easily dissolved in glycerol phase thus reduced the biodiesel recovery process. It was also observed that increasing the NaOH concentration successfully increased the FAEE yield up to a certain level. However, further increased the NaOH concentration also favors the saponification reaction thus reduced the FAEE yield. From the response surface, the maximum yield was gained with 7.5 ethanol to oil molar ratio and 1.2 % w/wt of NaOH concentration. Meanwhile for the reaction temperature, it was observed that increasing the temperature up to a certain point will also increase the yield of biodiesel. However further increase in temperature does caused the reduction of FAEE yield. This is because, transesterification under high temperature promotes saponification reactions.

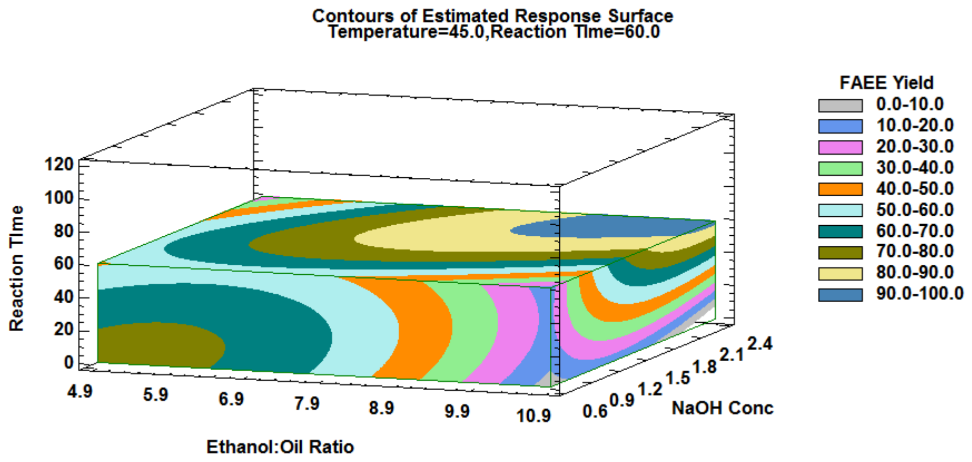


Figure 4.4: 3D Surface Plot with constant Temperature

Figure 4.4 shows interaction of reaction variables with constant temperature at 45℃. It is expected that increasing the reaction time can increased the FAEE yield. However further increase in reaction time beyond its optimum value could reduce the FAEE recovery process. This is because saponification will likely to happen at longer period/reaction time. The optimum reaction time to produce high yield of FAEE is determined to be around 60 min for reaction without microwave pre-treatment of WCO.

Meanwhile, it can be observed that the ethanol: oil molar ratio still give the optimum value within the range of 6.9 to 7.9 and the yield also starts to increase starting at about 1.3 wt% catalyst concentration. As mentioned earlier, increasing the molar ratio of ethanol: oil and catalyst concentration could promote saponification to occur. The formation of soap is the undesirable product in transesterification reaction as more catalyst is required to replace the catalyst lost due to soap formation. The presence of soap increases the viscosity (formation of gel) and emulsification resulting in difficulties in separation of biodiesel from glycerol resulting in excessive washing and low yield of biodiesel.

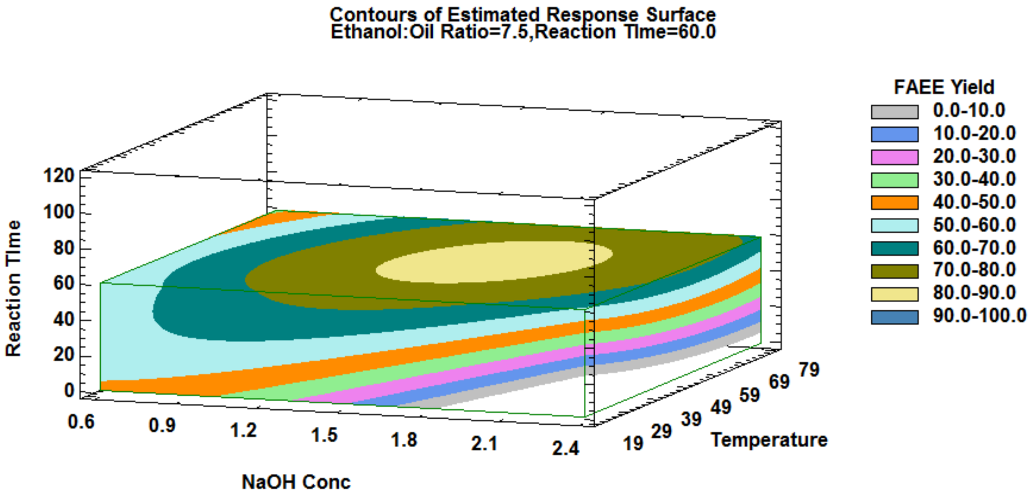


Figure 4.5: 3D Surface Plot with constant Ethanol:Oil molar ratio

Figure 4.5 shows the interaction of variables with volume of ethanol. From the observation, we could see that the maximum yield of FAEE is around 85%. The optimum concentration of NaOH was observed to be 1.2 wt% and the optimum reaction temperature was found to be 42.5 ℃. This is also true in figure 4.6 (plot with 1.5wt% NaOH conc). Increasing the volume of ethanol up to a certain level also gives optimum FAEE yield. However, too high reaction temperature promotes the saponification reaction.

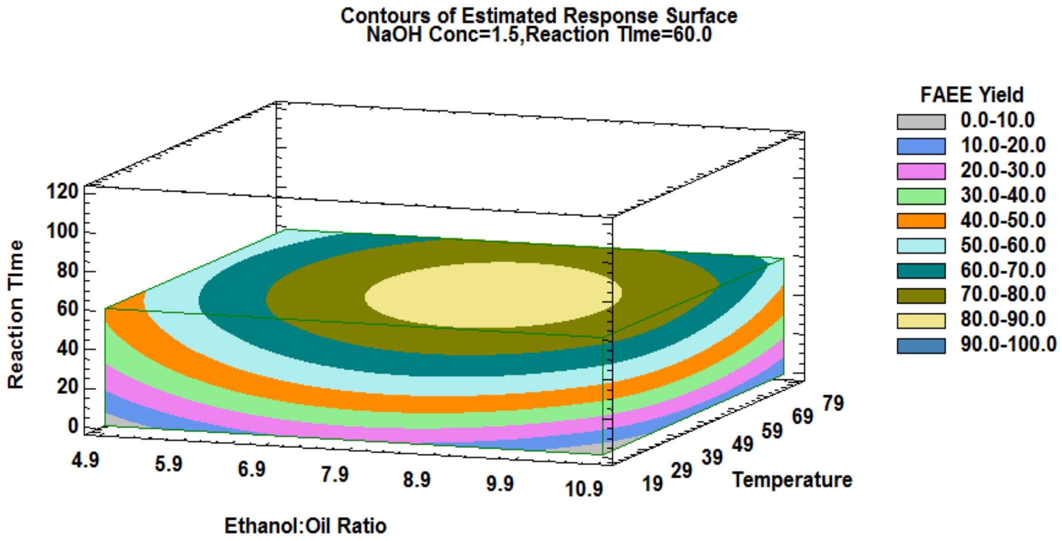


Figure 4.6: 3D Surface Plot with constant NaOH Concentration

4.3.3 Optimum reaction conditions for base catalysed transesterification

From the design expert, RSM analyzation, it was observed that the maximum optimum FAME yield is 86.24% for base catalysed transesterification of waste cooking oil without undergoing microwave pre-treatment.

Table 4.14: Optimum Condition of Base Catalyzed Transesterification of WCO

Factor	Low	High	Optimum
Ethanol:Oil Ratio	4.97731	10.0227	7.5
NaOH Concentration (wt%)	0.659104	2.3409	1.5
Temperature (℃)	19.7731	70.2269	45
Reaction Time (min)	9.54622	110.454	60

4.4 Microwave energy pre-treated transesterification of WCO with alkali catalyst

In this section, the reaction of base catalyzed transesterification of waste cooking oil was enhanced by pre-treating the oil with microwave energy at the beginning of the experiment.

4.4.1 Optimization of Microwave Energy Pre-treated Transesterification with alkali catalyst

FAEE yield produced is mainly depends on four independent variables: - Microwave heating time (A), ethanol to oil molar ratio (B), NaOH concentration (C), and reaction time (D). In all the experiment, 10 g of waste cooking oil, stirrer speed of 400 rpm and reaction temperature at 50 (℃) were kept constant. The individual and interaction effect of process variables and the optimal conditions to get the maximum FAEE yield were investigated by using central composite design (CCD) technique of response surface methodology (RSM) for microwave pretreated transesterification with alkali catalyst (NaOH). 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 4.15 below:

Table 4.15: Experimental range and level of the independent variables

Variables	Coded Symbol	Range & Levels				
		-2	-1	0	1	2
MWHT	*A*	1.318	2	3	4	4.682
Ethanol:oil molar ratio	*B*	4.977	6	7.5	9	10.023
Reaction Temp	*C*	0.323	0.75	1.375	2	2.426
Reaction Time	*D*	19.77	30	45	60	70.23

Experiments carried out as a function of the un-coded variables (with coded variables in the parenthesis) prompted by central composite design technique along with the observed FAEE yield for microwave energy pre-treated transesterification of waste cooking oil) are presented in Table 4.16.

Table 4.16: Experimental design matrix by CCD technique for microwave energy pre-treated transesterification (without PTC) along with the experimental and model predicted yields

No	MWHT (min)	Ethanol:Oil Molar Ratio	Reaction Temperature (℃)	Reaction time (min)	Experimental yield (%)	Predicted yield (%)
1	2	6	30	15	57.98	58.73
2	2	6	60	15	61.43	63.54
3	3	7.5	45	35.1134	81.41	83.78
4	4	9	30	15	72.46	75.09
5	2	9	60	30	65.22	64.32
6	3	7.5	45	9.88655	78.43	79.68
7	2	9	30	30	64.83	66.13
8	3	7.5	45	22.5	95.35	98.72
9	3	10.0227	45	22.5	64.21	65.94
10	3	7.5	70.2269	22.5	61.65.2212	62.47
11	3	7.5	19.7731	22.5	73.99	74.13
12	4.68179	7.5	45	22.5	65.23	67.25
13	4	6	60	30	62.84	63.07

14	3	7.5	45	22.5	94.11	96.71
15	4	6	30	30	67.35	68.14
16	1.31821	7.5	45	22.5	78.13	77.83
17	3	4.97731	45	22.5	61.88	60.11
18	4	9	60	15	75.68	76.38

Based on the Table 4.16, it was observed experimentally that run 8 has the highest FAEE yield which is 95.35% with model equation predicted yield of 98.72% at 3 minutes MWHT, 7.5 ethanol to oil molar ratio, 7.5%w/wt NaOH concentration and 22.5 minutes reaction time.

Table 4.17: T and P values for the regression coefficients in the second order model equation

Coefficient	Estimate	F-Ratio	P-Value
constant	90.2506	2.31	0.2258
A:MHWT	-7.6704	0.08	0.8014
B:Methanol to oil molar ratio	1.38554	0.74	0.4525
C:NaOH Concentration	-2.79635	0.12	0.7487
D:Reaction Time	1.77188	11.64	0.0421
AA	-11.9368	0.3	0.6231
AB	3.59938	0.09	0.7822
AC	-1.2825	0.76	0.4464
AD	-5.76196	26.59	0.0141
BB	-18.0425	0.08	0.8011
BC	1.1675	5.1	0.1091
BD	-14.8879	18.02	0.0239
CC	-14.8535	0.4	0.5701
CD	-2.6975	3.05	0.1791
DD	-6.1102	2.31	0.2258

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.

$$
\begin{aligned}
FAEE\ yield = {} & -421.568 + 37.0166A + 74.5838B + 3.31246C + 9.67982D \\
& - 6.54726A^2 + 1.19979AB - \ 0.04275AC - 0.38413AD - 4.26673B^2 \\
& + 0.0259444BC - 0.661684BD \ - 0.0355806C^2 - 0.0119889CD \\
& - 0.0646039D^2
\end{aligned}
$$

(RSM Model Equation 4.2)

$=$

FAEE yields predicted by this second order model equations were tabulated in the Table 4.16 together with the experimental observation. The second order model equations were evaluated statistically in order to study the significance of the model terms. Table 4.17 shows the P and T values that can indicate the significance of model terms. The P-value must be less than 5% in order for the variables to have a significance effect on the response values. Meanwhile, the F-value indicate the higher significance of the corresponding coefficient the model. The higher the F-value for the corresponding coefficient of the model, the higher will be the effects on that coefficient. In microwave pre-treated transesterification with alkali catalyst 3 effects have P-values less than 5% indicating that they are significantly different from zero at the 95.0% confidence level. Thus, in this experiment, we can conclude that reaction time has the most influence on the FAEE yields as it has the low P-value and high T-value as compared to the other variables.

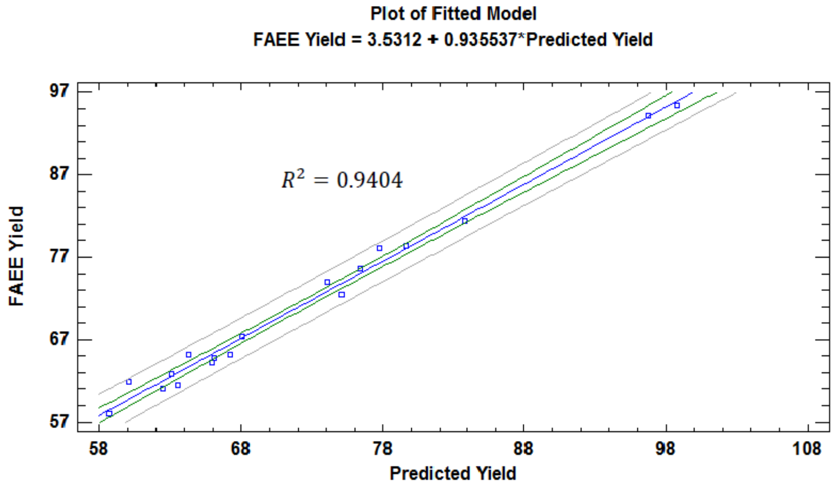


Figure 4.7: The diagnostic plot of experimental FAEE yield (observed) versus predicted FAEE yield for base catalyzed transesterification

Figure 4.7 shows the diagnostic plot of experimental FAEE yield (observed) versus the predicted FAEE yield which have undergo microwave pre-treatment of WCO. Linear trend are shown between the experimental values versus predicted values of the FAEE yield. This indicate that the experimental values are nearly same to the predicted values. Apart from that, the R-Squared statistic ($R2$ = 0.9404) indicates that the model as fitted explains 94.04% of the variability in FAEE yield. This implies that, 94.04% of the experiment values for microwave energy pre-treated transesterification is reliable.

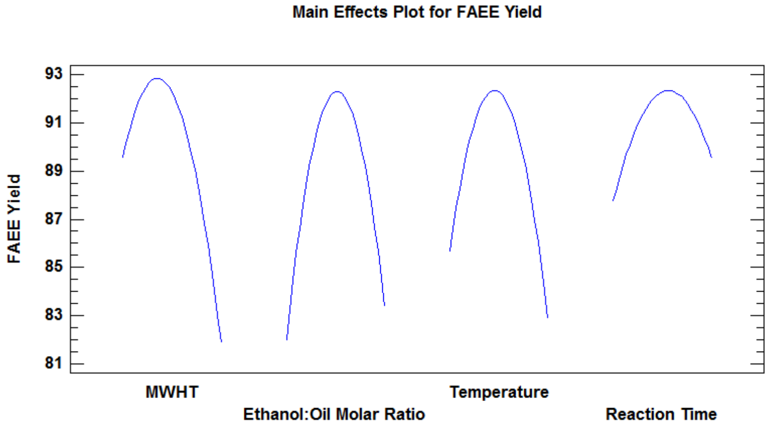


Figure 4.8: The main effect plot on FAEE yield for base catalyzed transesterification with microwave pre-treatment

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

The response surface plots for the yield of FAEE 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 8. 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. From the surface contour plot, it was also determi8ned that the FAEE yield was at the highest for all experiments with microwave pre-treatment of WCO. . In this experiment also, the concentration of NaOH was kept constant at 1.5wt% in order to study the effect of MWHT and transesterification reaction time towards yield of FAEE.

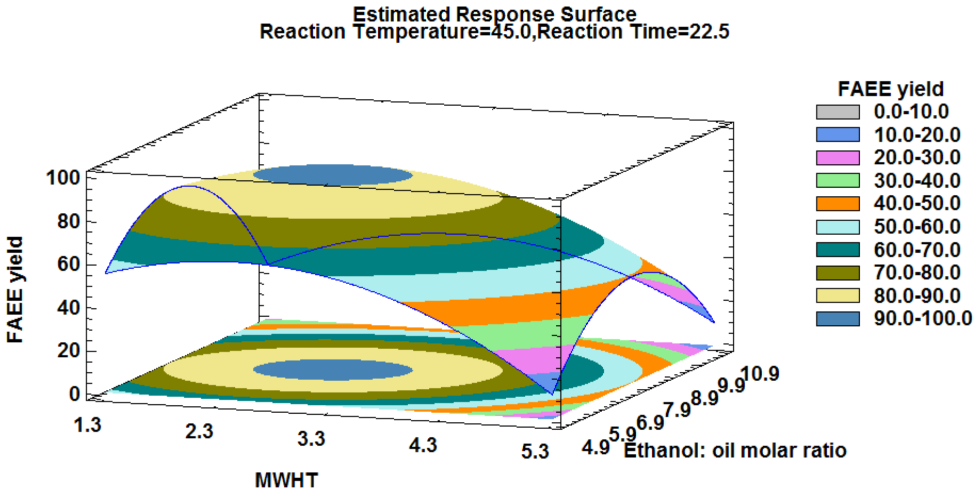


Figure 4.9: Response Surface Plot at constant concentration of NaOH (1.5 wt %)

Figure 4.9 presents the effects of ethanol to oil molar ratio to FAEE yield with the microwave energy pre-treated (min) transesterification. Maximum yield was observed at volume of ethanol at 7.5 molar ratios of ethanol to waste cooking oil. Increasing amount of ethanol can increase the FAEE yield. However, further increase of the volume of ethanol beyond the optimum value can decreased the FAEE yield. This is due to the solubility problem where the product biodiesel can easily dissolve into the glycerol phase that affect the biodiesel recovery process thus reducing the FAEE yield.

From previous analysis, increasing the NaOH concentration can increase the FAEE yield up to a certain marginal value (1.5 w/wt %). However, overloading the NaOH concentration can decreased the FAEE yield. Therefore in this experiment the interaction effect of microwave heating time with the FAEE yield could be studied more clearly. From observations, it is found that the optimum time for the WCO to undergo microwave heating is around 3.3 min.

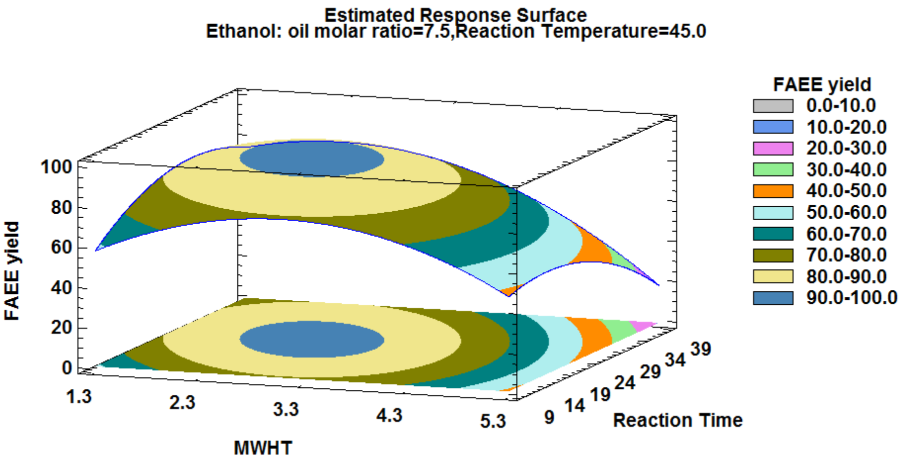


Figure 4.10: Response Surface Plot at constant concentration of NaOH % molar ratio

Figure 4.10 depicts the interaction between reaction time and FAEE yield on microwave energy pre-treated transesterification on waste cooking oil. In this plot, we could observe the relationship between reaction time and FAEE yield. In this case, it is predicted that the reaction time for base transesterification reaction with presence of microwave pre-treatment of WCO should be lower than without microwave pre-heating due to rapid heating & cooling and also selective heating of microwave.

From the observation, increasing the reaction time will increase the FAEE yield. Further increase the reaction time can lead into saponification reaction thus reduced the FAEE yield. At this figure, the maximum biodiesel yield is about 24 minutes of reaction time which is shorter than reaction without microwave heating.

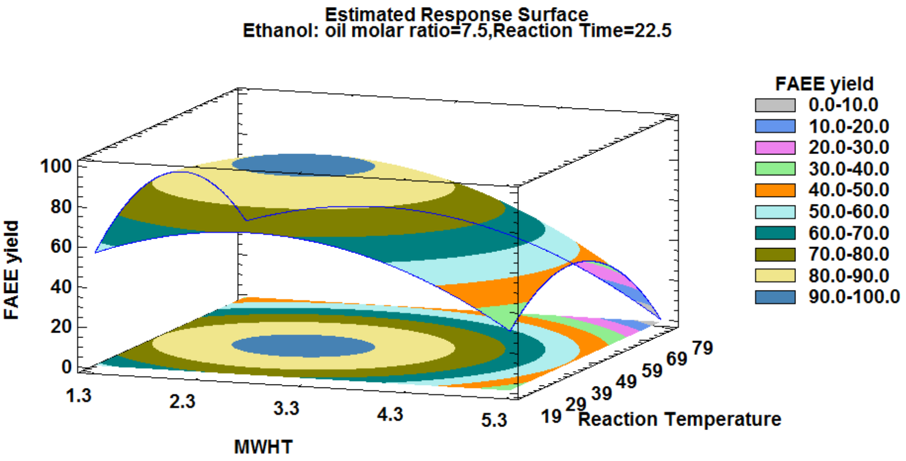


Figure 4.11: Contour Plot at constant concentration of NaOH % & constant reaction time

Figure 4.11 illustrates the interaction effects between reaction temperature and microwave heating time with the maximum FAEE yield. The maximum FAEE yield produced was observed about of 3.5 min MWHT at temperature around 30 °C which is much lower than reaction without microwave pre-treatment (60°C). It was also observed that the yield is higher at for all the plot compared to reaction without microwave heating.

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

Table 4.18: Optimum Condition of Microwave Energy Pre-treated Transesterification

Factor	Low	High	Optimum
MWHT	1.31821	4.68179	3.0
Ethanol:Oil Molar Ratio wt%	4.97731	10.0227	7:5
Temperature	19.7731	70.2269	4.5
Reaction Time	9.88655	35.1134	22.5

From the RSM analyzation, it was observed that the maximum optimum FAEE yield is 98.72% for microwave energy pre-treated transesterification of waste cooking oil.

4.5 Summary for optimization of FAEE yield

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

Optimization 1: Base catalyzed transesterification (without Microwave Heating)

Optimization 2: Microwave energy pre-treated transesterification with alkali catalyst

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

Table 4.19: Optimization summary

Parameters/Condition	**Optimization 1**	**Optimization 2**
MWHT (min)	-	3.0
Ethanol to oil molar ratio	7.5	7.5
NaOH Concentration (w/wt %)	1.5	1.5(constant)
Reaction Temperature (℃)	45	45
Reaction Time (min)	60	22.5
FAEE yield (w/wt%)	86.24	98.72

From Table 4.19, it can be seen that optimization transesterification of waste cooking oil with microwave pre-treatment gives the highest FAEE yield. Base transesterification has the least FAEE yield. Results shows that 98.72% w/wt of FAEE yield can be obtained within 22.5 minutes reaction time for transesterification reaction pre-treated with microwave irradiation. As compared to the base transesterification with the absence of microwave heating the highest FAEE yield obtained was only 86.24 wt%. This shows that in the presence of microwave heating, there was a significant increment of FAEE yield which is around 12.48wt%.

Besides that, it was also observed that the reaction time of transesterification with microwave pre-heating of waste cooking oil was lower than the reaction time for the reaction conducted in the absence of microwave pre-treatment by 37.0 minutes. Thus, it can be conclude that microwave energy pre-treatment of waste cooking oil can improve the yield of FAEE in a transesterification reaction and speed up the reaction at lower mild condition.

CHAPTER 5: CONCLUSION & RECOMMENDATIONS

5.1 Conclusion

Microwave-enhanced organic/inorganic synthesis is considered as green chemistry and a preferred method due to several advantages such as lower energy consumption, substantial reduction in reaction times and solvent requirements, enhanced selectivity, and improved conversions with less by-product formation. Many reactions that do not occur under classical methods of heating can be carried out with high yields under microwave irradiation. Microwaves have the potential for large scale applications specifically in biodiesel production due to their ability to interact with a variety of reagents.

In this present studies, the non- edible oil source, waste cooking oil was used as the raw material for transesterification reaction to produce biodiesel. Base catalysed transesterification and microwave energy pre-treated transesterification were investigated. Results shows that at optimum condition, 98.72%w/wt within 22.5 minutes reaction time of Fatty Acid Ethyl-Esther (FAEE) yield was observed when the reaction was conducted with microwave energy pre-treated of waste cooking oil. It was also demonstrated that a gain of 12.48% of FAEE yield for a reaction conducted using microwave energy pre-treated oil transesterification reaction as compared to transesterification reaction in the absence of microwave pre-heating (FAEE yield=86.24% w/wt).

As compared to alkaline catalysed transesterification, the reaction conducted by using microwave energy pre-treated oil transesterification assisted also has a reduction of 37 min of reaction time. Thus, it can be conclude that microwave energy can improve the transesterification reaction and prove to be efficient and economically feasible for operation. Hence, use of microwave pre-treatment of oil has a promising future in terms of enhancing the transesterification reaction time and also increasing the yield of biodiesel.

5.2 Recommendations for future work

As for future works and recommendation, microwave energy pre-treated transesterification should also be done in the presence of phase transfer catalyst. By using a PTC process, one can achieve faster reactions, obtain higher conversions or yields, make fewer byproducts, and eliminate the need for expensive or dangerous solvents that will dissolve all the reactants in one phase, eliminate the need for expensive raw materials and/or minimize waste problems. Phase-transfer catalysts are especially useful in green chemistry by allowing the use of water so that the need for organic solvents is reduced. Besides that, research should be done with other non-edible oil for example, Kapok oil, Margosa oil, Neem oil and etc. in order to find new alternatives.

Furthermore different type of PTC can also be used as a rate enhancement agent in transesterification reaction for example, benzyltrimethylammonium hydroxide and crown ether. On the other hand, higher quality of biodiesel can be produce through good and reliable equipment. For example, a cleaner biodiesel can obtained if the rotary evaporator equipment is working in the lab. The physical separation/filtration of oil such as removal of chunks and solid depositions should be carried out with a proper filtration technique in order to attain 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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APPENDIX

Figure (a): Untreated/raw waste cooking oil

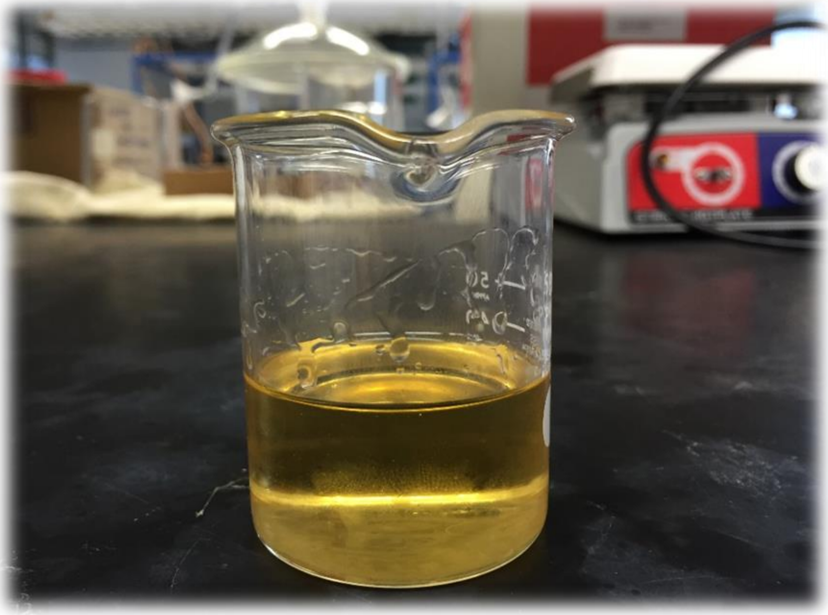


Figure (b): Filtered & Purified WCO

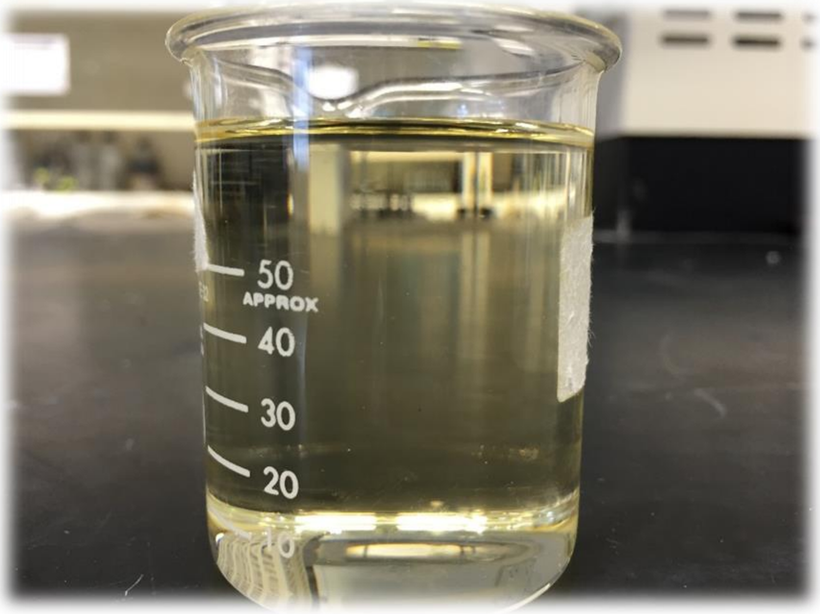


Figure (c): Final oil product after microwave assisted transesterification

(Final Biodiesel Product)

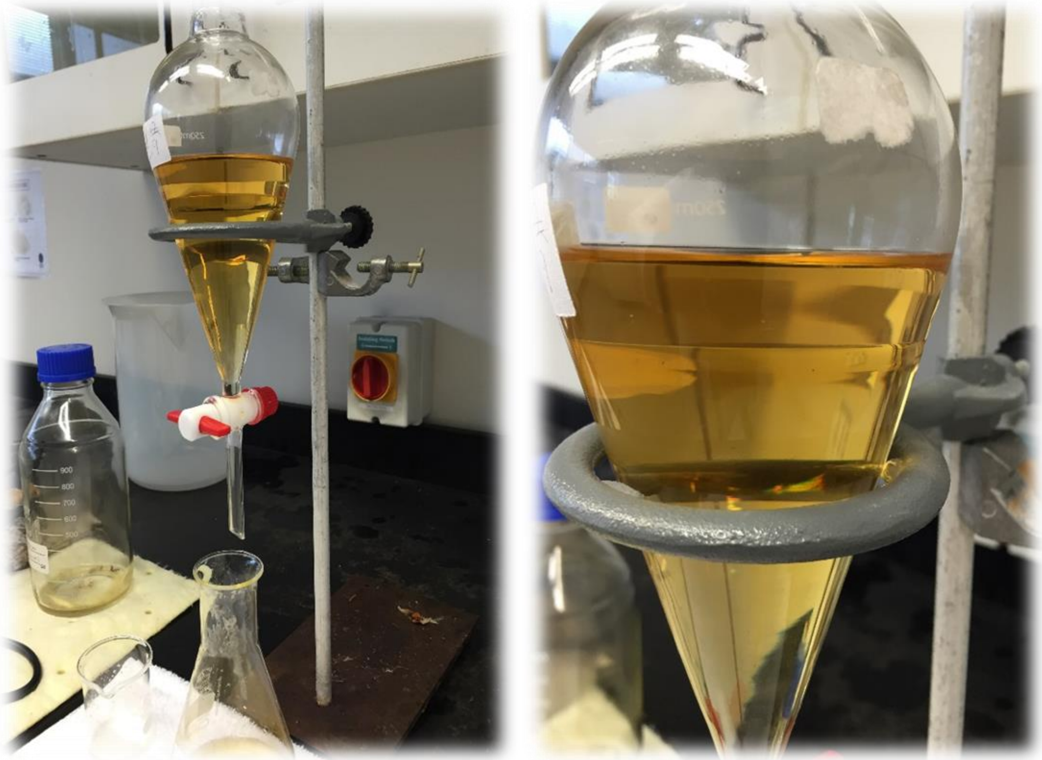
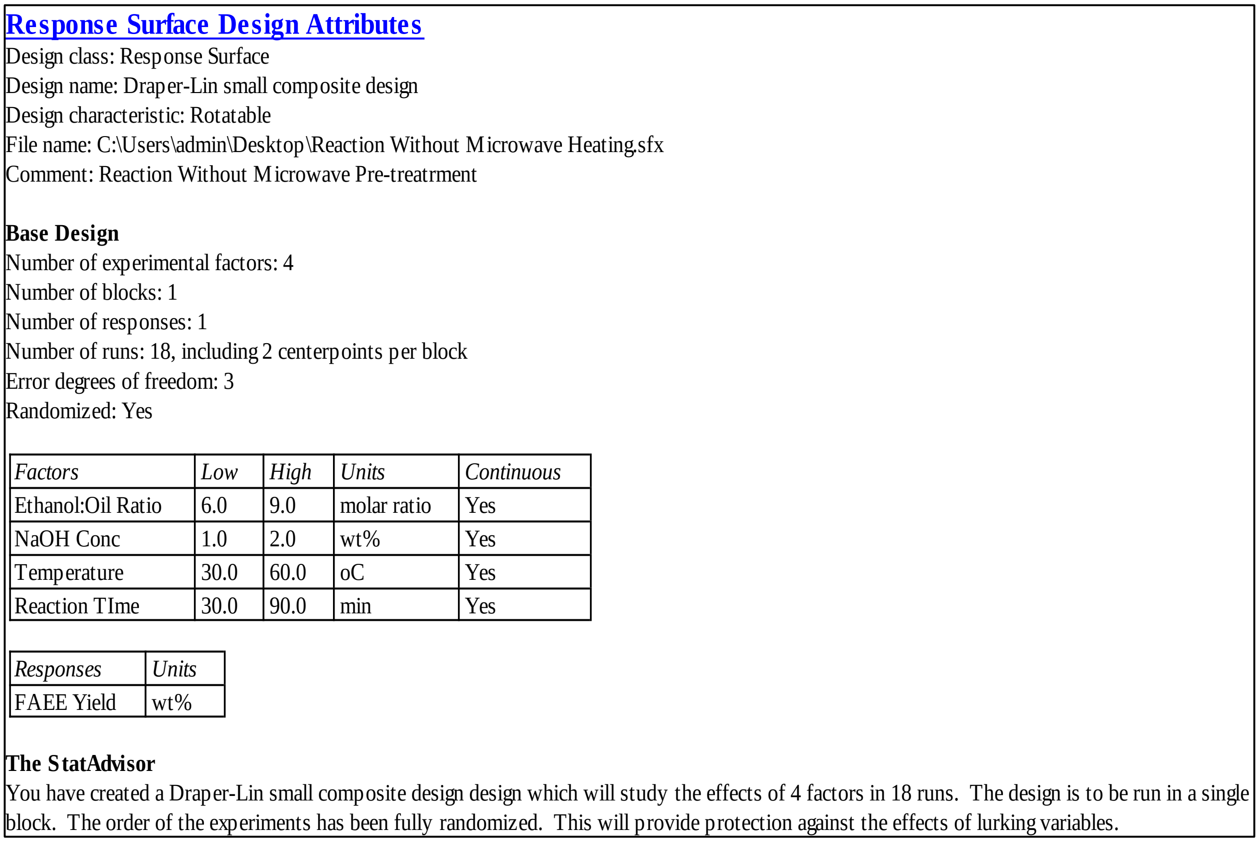


Figure (d): Separation process after transesterification reaction



Response Surface Design Attributes

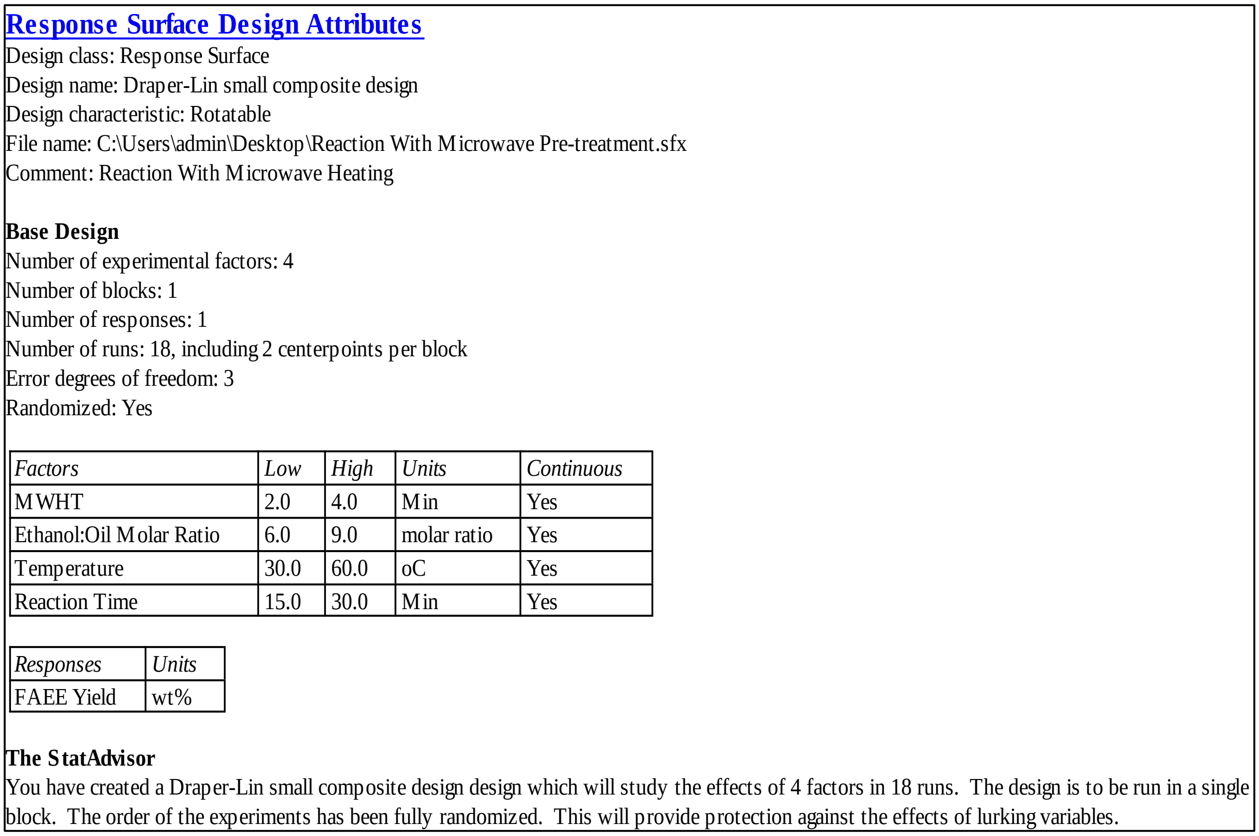
Design class: Response Surface
Design name: Draper-Lin small composite design
Design characteristic: Rotatable
File name: C:\Users\admin\Desktop\Reaction Without Microwave Heating.sfx
Comment: Reaction Without Microwave Pre-treatrment

Base Design
Number of experimental factors: 4
Number of blocks: 1
Number of responses: 1
Number of runs: 18, including 2 centerpoints per block
Error degrees of freedom: 3
Randomized: Yes

Factors	*Low*	*High*	*Units*	*Continuous*
Ethanol:Oil Ratio	6.0	9.0	molar ratio	Yes
NaOH Conc	1.0	2.0	wt%	Yes
Temperature	30.0	60.0	oC	Yes
Reaction TIme	30.0	90.0	min	Yes

Responses	*Units*
FAEE Yield	wt%

The StatAdvisor
You have created a Draper-Lin small composite design design which will study the effects of 4 factors in 18 runs. The design is to be run in a single block. The order of the experiments has been fully randomized. This will provide protection against the effects of lurking variables.



Response Surface Design Attributes

Design class: Response Surface
Design name: Draper-Lin small composite design
Design characteristic: Rotatable
File name: C:\Users\admin\Desktop\Reaction With Microwave Pre-treatment.sfx
Comment: Reaction With Microwave Heating

Base Design
Number of experimental factors: 4
Number of blocks: 1
Number of responses: 1
Number of runs: 18, including 2 centerpoints per block
Error degrees of freedom: 3
Randomized: Yes

Factors	*Low*	*High*	*Units*	*Continuous*
MWHT	2.0	4.0	Min	Yes
Ethanol:Oil Molar Ratio	6.0	9.0	molar ratio	Yes
Temperature	30.0	60.0	oC	Yes
Reaction Time	15.0	30.0	Min	Yes

Responses	*Units*
FAEE Yield	wt%

The StatAdvisor
You have created a Draper-Lin small composite design design which will study the effects of 4 factors in 18 runs. The design is to be run in a single block. The order of the experiments has been fully randomized. This will provide protection against the effects of lurking variables.