MICROWAVE ENERGY PRETREATED TRANSESTERIFICATION OF *JATROPHA CURCAS L*. OIL IN THE PRESENCE OF PHASE TRANSFER CATALYST (PTC)

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CERTIFICATION OF APPROVAL

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

Approved by,

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(DR. SINTAYEHU MEKURIA HAILEGIORGIS)

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SEPT 2014

CERTIFICATION OF ORIGINALITY

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

(SUHAIQAH SYARFINAZ BINTI MAT SAID)

ABSTRACT

The transesterification reaction process in biodiesel production is very slow due to the sparingly solubility of vegetable oils with lower molecular alcohols. In this present work, in order to study the transesterification reaction process, crude *jatropha curcas L*. oil which is one of non-edible oil was used to produce biodiesel. With the aim to increase the rate of reaction during that process, the microwave energy pretreated jatropha oil assisted by phase transfer catalyst (PTC) was studied. This project was carried out by using design expert software of response surface methodology (RSM) with Centre Composite Design (CCD) technique. Optimum conditions were established statically. At optimum condition, 99.22%w/wt within 26 minutes reaction time of FAME yield was observed when the reaction was conducted with microwave heat pretreated oil in the presence of PTC. It was also demonstrated that a FAME yield gain of 3.57% for a reaction conducted using microwave energy pretreated oil transesterification reaction assisted by PTC as compared to microwave untreated transesterification reaction in the absence of PTC. As compared to base catalyzed transesterification, for the same condition obtained an increment 12.6% of FAME yield. Hence, use of microwave energy pretreatment of oil and use of PTC is promising to increase the rate of reaction and yield of FAME.

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Abbreviations and Nomenclature

NaOH	- Sodium Hydroxide
CTMAB	- Cetyltrimethylammonium Bromide
H_2SO_4	- Sulphuric Acid
MWHT	- Microwave Heating Time
Wt. %	- Weight Percent
w/wt. %	- Weight per Weight Percent
°C	- Degree Celsius
N	- Normality
FAME	- Fatty Acid Methyl Esters
PTC	- Phase Transfer Catalyst
g	- gram

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Global energy consumption is increasing rapidly with the growing of population and technology development. It is estimated that the total world energy demand to increase from 505 quadrillion British Thermal unit (BTU) in 2008 to 770 quadrillion BTU in 2035 shown in Figure 1 [1]. The highest energy consumption source is fossil fuels which account for 87% [2]. However the existing fossil fuels are expected to be depleted in less than half century. Therefore, energy dependence on fossil fuels and the rising global energy demand are becoming the concern all over the world. Apart from that, the environment and its ecosystem are also affected by the greenhouse gases (GHG) emitted through the usage of fossil fuels from vehicles such as carbon dioxide CO_2, nitrous oxide N_2O, etc.

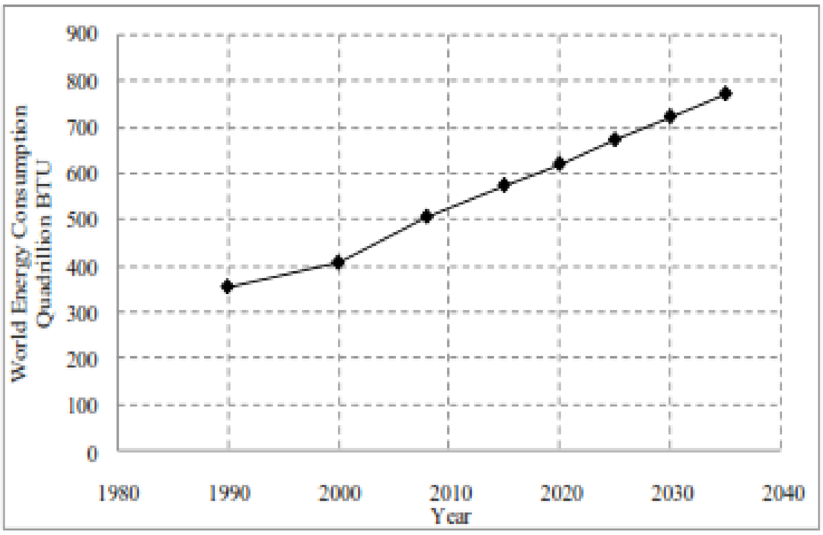

Figure 1: Projected world energy consumption from 1990 to 2035 in quadrillion BTU (source: IEO 2011 [1])

Therefore, exploration for environmental friendly alternative energy and feedstock with zero net carbon emission is essential for sustainable development.

Currently, in both developing and industrialized countries biofuels is at the top option as an alternative energy. This is because by 2020 biofuels production is expect to increase quadruple from its current usage [2]. Biofuels is consisting of bioethanol, biodiesel and biohydrogen. Amongst these types of biofuels, biodiesel is getting global attraction. This is due to its versatile source of raw material and the use of the fuel by mixing at any proportion with petrol based diesel or directly to the existing fossil fuel based engine without modification. Besides that, biodiesel is currently being used in Europe and USA to reduce air pollution problem and the dependency energy sources on fossil fuels [2].

Currently, vegetable oils are the promising feedstock for production of biodiesel. Vegetable oils consist of edible and non-edible oils. In biodiesel production edible oils such as rapeseed, soybean, sunflower, palm and coconut oil are widely used. More than 95% of biodiesel is made from edible sources [4]. However, this causes competitiveness in edible oil market as it is extensively used in food processing industries thus resulting in rising of edible oils and biodiesel price. Therefore, choosing the cheapest feedstock is important to minimize the cost of biodiesel production. Various researches have been made on the uses of non-edible oils sources. As non-edible oils do not have to compete with food processing industries, utilization of non-edible oil is believed can reduce the total biodiesel production cost.

Transesterification is the most common process for the production of biodiesel. This process is widely known as the best process for biodiesel production as it can reduce the viscosity of triglycerides. However, there is a weakness in this process where the reaction rate is very slow due to the limited solubility of alcohol in vegetable oil. In order to enhance the reaction rates of transesterification process, microwave energy pretreated transesterification of jatropha curcas oil in the presence of alkaline phase transfer catalyst (PTC) is being studied. In this project, jatropha curcas oil is being used as a non-edible oil feedstock for biodiesel production.

1.2 Problem Statement

Nowadays, worldwide attention has been drawn on biodiesel as a promising source of renewable energy that can reduce dependency on fossil fuels. Biodiesel can be produced from transesterification reaction of vegetables oils or animal fats with methanol in the presence of suitable catalyst. However, sparingly solubility of vegetable oils with lower molecular alcohols such as methanol and ethanol slows transesterification reaction process. Besides that, the cost for the most of feedstock sources (edible oil) in biodiesel production is high due to the market competitiveness with food processing industries. Therefore, it is vital to search for low cost of raw material for biodiesel production and new alternatives or technologies to increase the reaction rates of transesterification reaction. In this project, the non-edible oil jatropha curcas is proposed to be used as the raw material for transesterification reaction. Meanwhile, to enhance the rate of reaction, it is proposed that the Phase Transfer Catalyst (PTC) is being used in transesterification reaction plus the feed to be preheated with microwave energy before the reaction.

1.3 Objectives

This project ultimately seeks to achieve the following:

i) To investigate transesterification reaction rate of microwave energy pretreated jatropha curcas oil assisted by phase transfer catalyst (PTC).

ii) Study the individual and interaction effect of reaction variables on transesterification reaction of jatropha curcas oil.

iii) Conduct optimization for maximum biodiesel yield.

1.4 Scope of Study

In the present research work, to achieve the affirmation research objectives, jatropha curcas oil will be used as a source of non-edible oil sources 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 ration, catalyst concentration, reaction temperature, mixing rate and reaction time on the yield of biodiesel. The interaction effect of reaction variables will be studied using statistical tools of response surface methodology (RSM) and optimum operating conditions will be established. Conversions of triglycerides with time at different reaction conditions will be measured to investigate the rate of reaction and order of reaction equations.

1.5 Relevancy of the project

This project is important because it discuss the current issue which is finding the new source of renewable energy that can reduce the dependency on fossil fuels. This issue has getting an attention from every nation especially developed and industrialized countries. Therefore, investigation on how to solve and improve this problem is needed. This study will provide information in the future for transesterification reaction rate of microwave energy pretreated jatropha curcas oil assisted by phase transfer catalyst (PTC). Besides, the suitability of jatropha curcas oil as a source of biodiesel feedstock also will be discussed.

1.5 Feasibility of the project

This project is feasible to be conducted in a time scope of two semesters which consist of 8 months of studies. This is because, to determine the characteristics of jatropha curcas oil, conducting the transesterification reaction of the oil, and also the analysis of the oil will require a short time. Therefore 8 months of duration provided is enough to complete this study.

CHAPTER 2

LITERATURE REVIEW

2.1 Historical background of vegetable oil as a fuel

In 1893, Rudolf Diesel developed an engine which was fueled by vegetable oil (peanut oil) and ran on its power for the first time [2]. Within five years of its invention, the efficiency of running Diesel's engine has increased from 26% at initial to 75% efficiency [5]. However, as compared with petroleum diesel the performance was poorer due to its high viscosity of oil. In 1912, Rudolf Diesel reflected in his two published articles "*the use of vegetable oils for engine fuels may seem insignificant today, but such oils may become, in the course of time, as important as petroleum and coal-tar products of the present time*". [6] .The biofuels demand in America is increases started from the year of 1890's to 1920's. Unfortunately, during that duration of years the petroleum industries discovered large reservoir and more advanced technologies. Resulting the alteration on Diesel's engine into petroleum-based fuels usage in 1940 [5].

2.2 Biodiesel and its Properties

Biodiesel is a renewable energy that has a potential to cater the problems of dependency on fossil fuels. It is defined as the mono alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, for use in compression-ignition (diesel) engines. This specification is for pure (100%) biodiesel prior to use or blending with diesel fuel, US National Biodiesel Board (2008). Energy content, physical and chemical properties of biodiesel fuels are similar compared to the conventional diesel fuel. Therefore, there is no need of modifications done to any diesel engine for it to run with biodiesel fuel. Biodiesel possesses better lubricant properties which enhance engine yield and extend engine life [20]. In fact, biodiesel have high flash point (close to 150^0C), and does not produce explosive vapors which makes transportation, handling and storage are safer compared to conventional diesel fuel [21]. Biodiesel fuel can be made from new or used vegetable oil and animal fats. In contrast to conventional fuel, pure biodiesel is biodegradable, nontoxic and essentially free of sulphur and aromatics.

2.3 Technologies Used in Biodiesel Production

Biodiesel are known with the problem of high viscosity of vegetable oil that caused it has poor performance compared to petrol diesel. However, numbers of researches has been done to overcome or minimize this problems associated with the viscosity such as pyrolysis, microemulsification, blending (diluting) and transesterification. However, transesterification is the most widely employed process to reduce the viscosity of vegetable oil in biodiesel production [5].

2.4 Transesterification Reaction

Basically, transesterification is a process where vegetable oil or animal fats (triglycerides) is being converted into chemicals called long-chain mono alkyl esters, or biodiesel [3]. Stiochiometrically, 1mole of fat/oil are reacted with 3 mole of short chain alcohol (usually methanol- 3mole) in the presence of catalyst to form 3 mole of biodiesel/esters and a mole of glycerol [2]. These separate into three layers, with glycerol sink at the bottom, soap at the middle and biodiesel floats on top [3]. Transesterification is a reversible chemical reaction. It consists of three consecutive reactions. The first step is one chain of fatty acid is removed from triglyceride molecules to form diglyceride molecules followed by the broken of another chain of fatty acid from diglyceride to form monoglyceride as a second stage. Lastly, the monoglyceride molecule is converted into glycerol by the breaking of the final chain. It is an equilibrium reaction, thus large excess of alcohol is used to shift the reaction to form glycerol and esters [2]. The chemical equation of this process is shown in Figure 2.

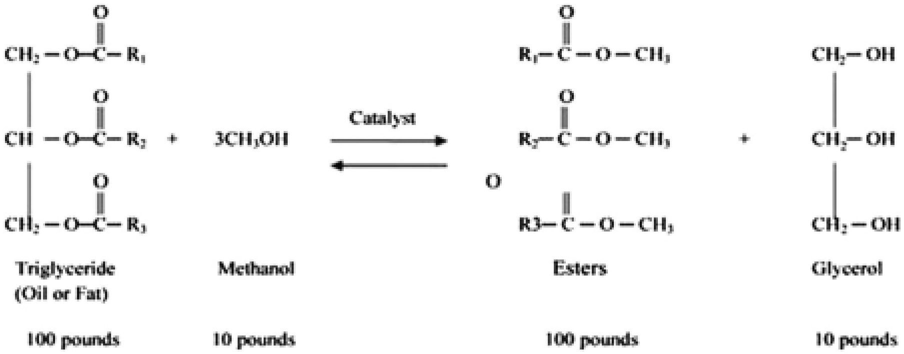

Figure 2: Chemical reaction of transesterification [2]

2.5 Microwave Energy Assisted Transesterification Reaction

Microwave irradiation is one of the methods that can enhance transesterification reaction. This is a well-established method of accelerating chemical reactions because it delivers the energy directly to the reactant. This technology act as an energy stimulant and speeds up the reaction rates process efficiently (from hours to minutes). It also employs a lower alcohol-oil ratio resulting the formation of by-product reduces. This microwave irradiation activates the smallest degree variance of reacting molecules by applying a continuously changing electrical and magnetic fields. Therefore, the charged ions can interact easily with slightly lesser diffusion limitation. Besides that, this technology can improves catalyst activity and selectivity and also minimizes energy consumption [5,10,11]. It has reported by Lertsathapornsuk et. al (2003) that the best conversion yield was obtained within 30s for three types of oil which are cococut oil, rice bran oil and used palm oil. Other than that, it also reported by Sherby et. al (2010) where they comparing the biodiesel production from jatropha oil by using conventional and microwave irridation. The results obtained are the conventional heating gained 99.8% yield in 60min while microwave irradiation gained 97.4% yield in just within 20 minutes [15].

2.6 Phase Transfer Catalyst (PTC) Assisted Transesterification Reaction

The use of phase transfer catalysis (PTC) appeared as a reasonable and promising approach to such mass transfer limitations during synthesis of organic products. PTC is a phase transfer agent in catalytic amount used to transfer one of the reactants to the location where it can rapidly react with another reactant. The fundamental mechanism of PTC as described above depends on the ability of a phase transfer agent to facilitate the transport of one reagent from one phase into another immiscible or sparingly miscible phase with the previous phase where the other reacting reagent exists. The reaction between the two reagents is made possible by bringing them together which are originally in different phases. During application of PTC, it is also necessary to note that the transferred reagent is in its active state for effective catalytic action [8,9].

Even though PTC has been widely applied to enhance the reaction of two or more immiscible or sparingly miscible reactants for the synthesis of many organic chemicals, it has not been exploited as a rate enhancement agent for the synthesis of biodiesel except an investigation conducted by Hailegiorgis et al.(2011, 2012, 2013), and Zhang et al. 2009. It was also reported that use of PTC has substantially increased the rate of reaction as compared to the reaction conducted without PTC. However, due to the remarkable ability of PTC to increase the solubility of two insoluble or slightly soluble reactants, it can be used in catalytic amount, its wide availability, environmentally friendly nature, the use of PTC to enhance the rate of transesterification reaction needs detail research works to develop appropriate reaction mechanisms and reaction properties [8,9].

2.7 Feedstock for Transesterification Reaction

The feedstock for biodiesel production is commonly from vegetable oils and animal fats. Currently, vegetable oils are promising feedstock for production of biodiesel. Vegetable oils consists of edible and non-edible oils. In biodiesel production edible oils such as rapeseed, soybean, sunflower, palm and coconut oil are widely used. More than 95% of biodiesel is made from edible sources [4]. However, this causes competitiveness in edible oil market as it is extensively used in food processing industries thus resulting in rising of edible oils together with biodiesel price.

Moreover, 75% of the overall biodiesel production cost comes from feedstock alone [2]. Thus, the use of non-edible oil such as jatropha curcas, karanja and sea mango is seen as economically viable as it is cheaper than edible oils. Furthermore, the potential of using jatropha curcas as biodiesel feedstock has getting worldwide attention. In 2007 Goldman cited that the best vegetable oil for future biodiesel production is jatropha curcas oil and it is the cheapest feedstock to produce biodiesel. Table 1 shows the price comparison between biodiesel feedstocks [2].

Table 1: Price comparison between biodiesel feedstock [2]

Feedstock	Price of crude vegetable oil (USD/tonnes	Price of B100 Biodiesel (USD/tonnes)
Rapeseed	815-829 (Ex-Dutch Mill)	940-965 (FOB NEW)
Soybean	735 (FOB Rosario)	800-805 (FOB Rosario)
Palm oil	610 (Del. Malaysia)	720-750 (FOB SE Asia)
Waste cooking oil	360	600 (estimated)
Animal Tallow	245	500 (estimated)
Jatropha	N/A	400-500 (estimated)

2.8 *Jatropha curcas L.* as Source of Biodiesel Feedstock

Jatropha curcas is a succulent type of plant with a small or large shrub tree (5-7 m tall). It is belongs to the family of Euphorbiaceae which consists of around 800 species. It has many vernacular names such as physic nut or purging nut and also known as Ratan-jayot. In Malaysia, jatropha curcas is called as Jarak Pagar. The life expectancy for jatropha curcas is 50 years [2]. As compared with soybean, linseed and palm kernel that is the edible oil source, jatropha curcas was reported has more oil contents which are 66.4% [2]. Soybean, linseed and palm kernel only consists of 18.35%, 33.33% and 63.16% of oil contents [2]. Meanwhile, amongst non-edible oils, jatropha curcas has found to give highest yield of 1892 liters per hectare as shown the Table 2. Nowadays, planting jatropha curcas has drawn worldwide attention especially in tropical and subtropical countries. This is due to their characteristics which are easy to propagate, drought resistant, can adapt to wide agro-climate conditions and consists of high oil content. Besides that, it also can be adapted for marginal land and has a potential to grow in sand, saline or infertile soil. This shown that jatropha curcas can be grown with a very low cost [2].

Table 2: Oil yield for major non-edible oil crops [4,12,13,14]

Type of oil	Oil yield (litre/ha)	Oil yield (%)
Jatropha curcas	1893	Seed: 35-40, kernel:50-60
Castor	1413	45-50
Pongamia pinnata	225-250	30-40
Rubber seed	80-120	40-50
Sea mango	N/A	54
Cotton	325	18-25
Karanja	27-39	
Moringa oleifera	N/A	35-40

CHAPTER 3

METHODOLOGY

3.1 Introduction

Overall process flow diagram of the research methodology to investigate transesterification of jatropha curcas oil with preheating using microwave energy in the presence of PTC in the present study is presented in Table 3. Materials to be used are presented in section 3.3. Experimental methodology is presented in section 3.4. Statistical design of the experiment for transesterification of jatropha curcas oil is discussed in section 3.4.3.

3.1 Project activities

Table 3: Project activities

Literature Review
• For FYPII, further understanding on the process of esterification and transesterification reaction is carried out. • More review on the literature is done to understand the mechanisms and effects of microwave energy and phase transfer catalyst on transesterification reaction
Experiment
• Experiment is designed for a transesterification experiment with three (3) different conditions. The conditions are as follows: i) Base catalysed transesterification reaction. ii) Microwave energy pretreated transesterification with alkali catalyst (without PTC) iii) Microwave energy pretreated transesterification in the presence of alkali PTC. • In order to optimize the biodiesel yield, the experiment is designed by using the Design Expert software.
Data Collection
• From the experiments conducted, biodiesel yield is calculated. • The data is then transferred into the design expert software in order to develop the model that predicts the yield of biodiesel at designed reaction.
Conclusion
• The experiments will be concluded based on the results obtain at the end of the project. • Report thesis of the project is prepared.

3.2 Gantt Chart and Key Milestones

Table 4: Gant Chart and Key Milestones

No	Detailed work	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Jatropha oil characterization	■	■	■	■	■									
2	Preliminary experiment			■	■	■	■	■							
3	Design of Experiment							■							
4	Main experiment							■	■	■	■	■			
5	Acid value, viscosity, specific gravity				■										
6	Submission of progress report								■						
7	Pre-Sedex											■			
8	Submission of draft report												■		
9	Submission of dissertation (softbound)													■	
10	Submission of technical paper													■	
11	Oral presentation														■
12	Submision of dissertation (hard bound)														■

3.3 Materials and Chemicals

Jatropha curcas oil produced in Malaysia was purchased from supplier BIONAS, Malaysia, a local jatropha curcas seeds and oil trading company. Chemicals used for transesterification reaction, pro-analysis chemicals, alkaline catalyst, and phase transfer catalysts and standard chemicals were purchased from local suppliers.

Table 5: Chemicals used in the present research work

Description	Purity	Supplier
Alcohol		
Methanol	≥ 99.7%	N/A
Catalyst		
Sulphuric Acid	≥ 95%	N/A
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%	

3.4 Experimental approach

3.4.1 Characterization of Jatropha Curcas 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. In this present work, the acid value, calorific value, viscosity and specific gravity of jatropha curcas oil was determined.

3.4.1.1 Determination of Acid Value and Acid Number

Acid value is the measure of the free fatty acid (FFA) present in the oil. According to ASTM D 974-06, acid number is defined as the quantity of base expressed in milligrams of potassium hydroxide per gram of sample to a specified end point. 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 jatropha curcas oil and the corresponding biodiesel produced was 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 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 6:

Table 6: 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 number is calculated as;

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

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 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 MSDS given by BIONAS the highest percentages of FFA in a sample of jatropha curcas 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

3.4.1.2 Determination of viscosity

The viscosity of jatropha curcas 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 jatropha curcas 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

3.4.1.3 The specific gravity of jatropha curcas oil

The procedure are as follows:

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

$$Density = \frac{Mass\ of\ beaker\ with\ oil - \ Mass\ of\ beaker\ without\ oil}{Volume\ of\ oil}$$

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

3.4.1.4 The calorific value of jatropha oil

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

3.4.2 Two-steps transesterification reaction

3.4.2.1 Purification of jatropha curcas oil (esterification)

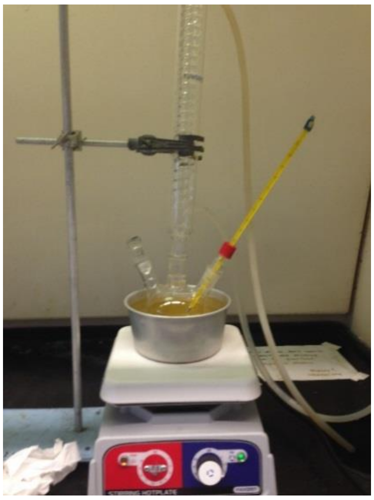

Figure 3: Main experiment set-up

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 jatropha curcas oil 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 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 methanol 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 methanol sulphuric acid and impurities while the bottom layer containing the purified jatropha curcas oil.
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 jatropha curcas oil can be further use for transesterification reaction.

3.4.2.2 Transesterification reaction experimental approach

1. A two neck round bottom flask reactor equipped with a reflux condenser (to prevent loss of alcohol), a magnetic stirrer and a thermometer is used.
2. 10g of jatropha oil is prepared and placed in the round bottom flask reactor.
3. The jatropha curcas oil is preheated in microwave at the desired duration of time *(for microwave energy pretreated transesterification)*
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 the desired temperature. The flask is immersed in an oil bath immediately to maintain the reaction temperature.
6. Then, the prepared of catalyst 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 and diluted with distilled water to arrest further reactions. The separation processes requires several hours to form a clear phase separation between the top layer that contains mixture of alkyl ester while the bottom layer containing glycerol, methanol, sodium hydroxide, PTC, water and unspent oil.
8. The top layer is recovered and then be washed with warm (50 - 60^{o}C) water several times to remove contaminants
9. The recovered alkyl ester is weighed and stored in a screw capped bottle. The details experimental flow diagram is shown in Figure 4.

3.4.2.3 Catalyst Preparation procedure

a) Sodium hydroxide (NaOH)
   1. NaOH tablets is crushed into fine grains.
   2. Based on the w/wt% of NaOH to oil, NaOH grains is measured on a weighing balance and placed into a beaker.
   3. Based on the methanol to oil molar ratio, methanol weight is measure and poured into the beaker mix with NaOH.

4. The mixture is now ready to be used in transesterification reaction.

b) Alkali Phase Transfer Catalyst - Cetyltrimethylammonium bromide $C_{19}H_{42}BrN$) -CTMAB

1. 1w/wt% of NaOH grains is weighed and place into a beaker.
2. Based on CTMAB/NaOH molar ratio, CTMAB is measure on weighing balance and placed into a beaker.
3. Based on the methanol to oil molar ratio, methanol is weight is measure and pour into the beaker with with NaOH and CTMAB.
4. The mixture is then ready to be used in transesterification reaction.

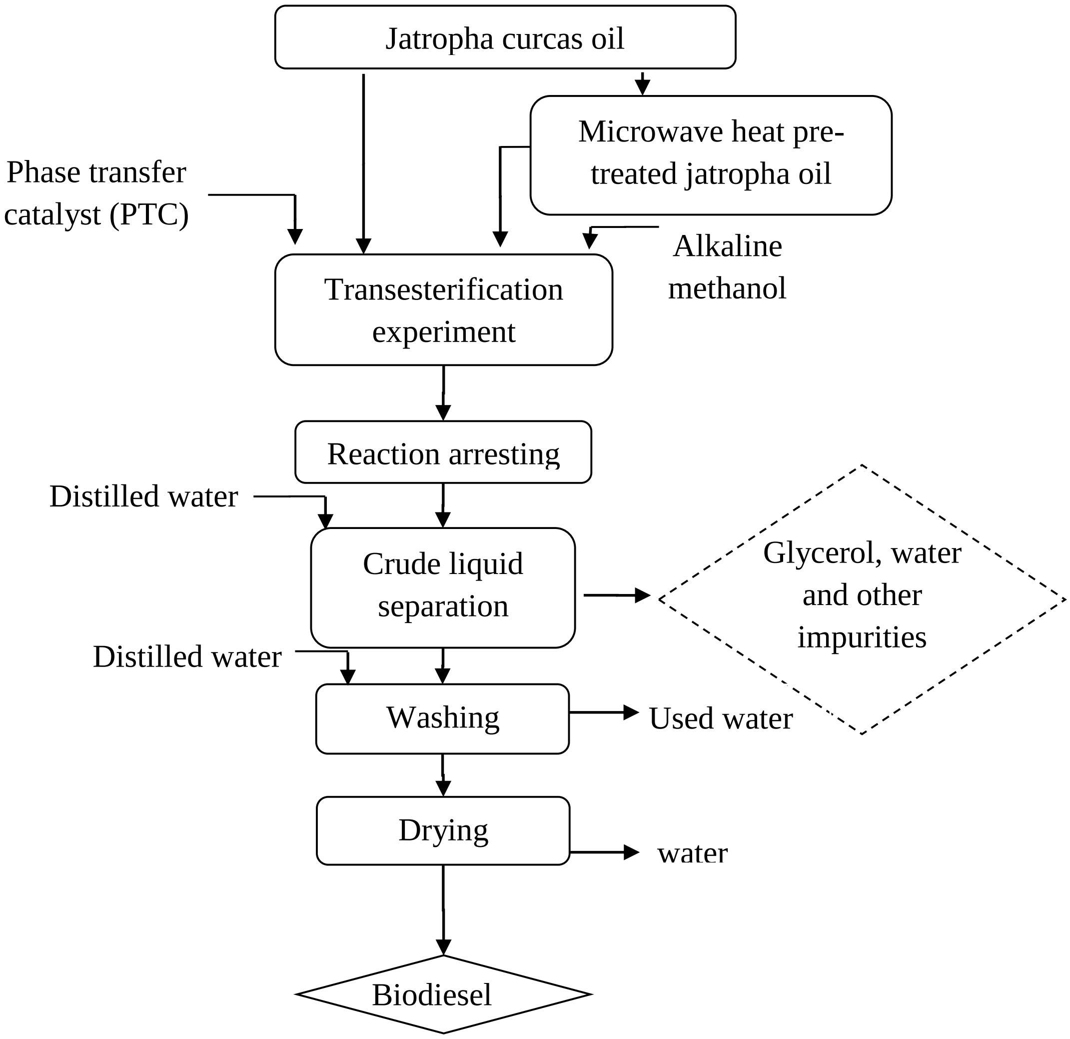

Figure 4: Process flow of transesterification of jatropha curcas oil of the present study

3.4.3 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.

Therefore, in this present studies Central Composite (CCD) technique of RSM was used for the experimental design to investigate the individual and interaction effects of reaction variables and determine the optimum reaction condition for transesterification of jatropha curcas oil. There were five parameters used for the based design which involved methanol to oil ratio, amount of catalyst used, microwave heating time, reaction temperature and time taken for the reaction. From the software, three (3) models of experiments were investigated. One of the models of experiment is transesterification reaction without microwave heating and presence of PTC. The second model is microwave energy pretreated transesterification reaction without the presence of PTC and the third model is microwave energy pretreated transesterification reaction with the presence of alkali PTC. A total of 54 experiments are genererated with 18 experiments with different parameters condition for each model of experiment. Hence, 54 transesterification experiment was conducted in order to identify the optimum reaction for transesterification reaction.

The experimental results was fitted using a polynomial quadratic equation in order to correlate the response variables. The general form of the polynomial quadratic equation shown in equation (1) is used to develop a model that predicts (estimates) the yield of alkyl esters (FAME) at designed reaction variable combination. The variable Xi was coded according to equation (2).

$$\mathrm{Y_i} = \beta_o + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} X_i X_j \quad \text{(eqn 1)} \quad , \qquad x_i = \frac{X_i - X_i^*}{\Delta X_i} \quad \text{(eqn2)}$$

Where: Yi is the predicted response and Xi is the input variables for BTMAOH concentration, NaOH concentration, and volume of alcohol, reaction temperature and time. The term βo is the offset term (intercept), βi is the linear terms, βii is the squared terms and βij is the interaction terms and Xj is the cross term to represent two-parameter interactions

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Jatropha curcas oil characterization

4.1.1 Acid number determination

The result for the acid determination value is as follows:

Table 7: Acid number determination

Run	1	2
Mass of Jatropha oil	20.0534	10.6805
Titration starting point	0	0
Titration end point	164	80.9
Volume KOH used (ml)	164	80.9
Blank titration starting point	27.85	30.9
Blank titration end point	28.35	32.4
Volume KOH used (ml)	0.5	0.5
Acid value(mg KOH/g)	45.74	42.23
Average	43.99	
%	15.65	

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 7 above, it was determined that the free fatty acid (FFA) content was very high which is 15.65%. 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 catalyzed 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 jatropha curcas oil is high, thus two-step transesterification reaction is required. The jatropha curcas oil need to be undergo acid catalyzed transesterification (esterification) to reduce the FFA content before can proceed to alkali catalyzed transesterification.

4.1.2 Specific Gravity Determination

The result calculated for specific gravity is as follows:

$$Density\ of\ jatropha\ oil = \frac{52.3732g - 42.0058g}{11.50ml}$$

$$= 0.9015 \text{ g/ml}$$

Mass of measuring cylinder = 42.0058g

Mass of measuring cylinder with jatropha curcas oil = 52.3732g

Mass of jatropha curcas oil = 10.2674

Volume of jatropha curcas oil = 11.50ml

Density of water = 1 g/ml

From the data above, the specific gravity for jatropha curcas oil is 0.9015.

4.1.3 Calorific Value Determination

The calorific value of jatropha curcas 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, jatropha curcas oil is considered as a feasible fuel.

4.1.4 Viscosity Determination

The result obtained for viscosity determination is as follows:

Temperature = 40 ℃
Speed = 250 rpm

Table 8: Viscosity determination

Spindle	cP	%
1	40.5	5.4
2	52	3.5
3	87	2.9
4	96	1.6
5	132	1.1
6	180	0.6

The value of viscosity was taken at the highest percentage. Based on the result tabulated above, at 5.4% the viscosity of jatropha curcas oil is 40.5 cP. This value is higher as compared to petroleum based diesel fuel which is 1 cP at 40 ℃ [19]. Therefore, jatropha curcas 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.

4.1.5 Jatropha oil properties

The properties of jatropha curcas such as FFA content, viscosity, calorific value and specific gravity are tabulated in the Table 9 below:

Table 9: Jatropha curcas oil properties

Properties of jatropha curcas oil	Value
Specific gravity	0.9015
Viscosity (cP)	40.5
Calorific Value (kJ//g)	39.70
FFA content (%)	15.65
Molecular weight (g/mol)	878.6 [a]

[a] Source: Hailegiorgis [8,9]

4.2 Preliminary Experiment Result

4.2.1 Esterification reaction

The FFA content of jatropha curcas oil is high. Thus, it is required to undergo two-step transesterification reaction which is acid-catalyzed esterification to reduce the FFA content in the oil followed by alkaline catalyzed transesterification to produce biodiesel.

The result in esterification is tabulated in the Table 8 below:

Table 10: Esterification reaction results

Run	1	2
Mass of Jatropha curcas oil	10.1381	10.0406
Titration starting point	0	0
Titration end point	3.2	3.75
Volume KOH used (ml)	3.2	3.75
Blank titration starting point	3.2	3.75
Blank titration end point	3.7	4.25
Volume KOH used (ml)	0.5	0.5
Acid value(mg KOH/g)	1.49	1.82
Average	1.66	
%	0.59	

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 10 above, it is shown that the FFA content in oil has reduced to 0.589%. It is consider as a good condition to undergo transesterification reaction as the FFA content is below than 3% [17,18]

4.2.2 Transesterification Reaction

Three 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:

Jatropha curcas oil : 10g

Stirring speed : 350 rpm

Weight percent of NaOH : 1.5 w/w %

Reaction time : 60 minutes

Table 11: Preliminary experiment

Methanol to oil molar ratio	**Reaction Temperature (℃)**	**FAME yield w/w %**
6	50	72.23
9	60	70.56
12	40	65.11

The FAME yield is calculated by using the following formula:

$$FAME\ yield = \frac{weight\ of\ oil\ after\ transesterification}{weight\ of\ oil\ used} \times 100$$

From the Table 11 above, it shows that at 6:1 methanol to oil molar ratio at temperature 50 **(**℃) give the highest biodiesel yield which is 72.23 w/w%.

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

Table 12: Range of variables for design experiment RSM

Variables	**Range**
Methanol to oil ratio	6 - 9
NaOH concentration (w/w%)	0.75 – 2.0
Reaction temperature (℃)	30 - 60
Reaction time (min)	30 - 60

4.3 Base catalyzed transesterification

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

4.3.1 Optimization of base catalyzed transesterification of jatropha curcas oil

In this section, yield of FAME produced is mainly depends on four independent variables: - Methanol to oil molar ratio (A), NaOH concentration (B), reaction temperature (C), and reaction time (D). In all the experiment, 10 g of jatropha curcas 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 13 below:

Table 13: Experimental range and level of the independent variables

Variables	**Coded symbol**	**Range and levels**				
		-2	-1	0	1	2
Methanol	A	4.977	6	7.5	9	10.02
NaOH	B	0.323	0.75	1.375	2	2.426
Temperature	C	19.77	30	45	60	70.23
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 biodiesel yield for base transesterification are presented in Table 14.

Table 14: Experimental design matrix by CCD technique for base catalysed transesterification along with experimental and model predicted yields

No	Methanol to oil Molar Ratio	NaOH concentration (%w/w)	Reaction Temperature (℃)	Reaction time (min)	Experimental yield (%)	Predicted yield (%)
1	7.5(0)	2.426(2)	45(0)	45(0)	55.23	58.31
2	6(-1)	0.75(-1)	45(0)	30(-1)	44.66	43.0
3	7.5(0)	1.375(0)	19.773(-2)	45(0)	48.2	54.17
4	9(1)	2(1)	30(-1)	30(-1)	53.7	50.18
5	4.977(-2)	1.375(0)	45(0)	45(0)	46.3	49.39
6	6(-1)	2(1)	30(-1)	60(1)	60.3	56.78
7	7.5(0)	1.375(0)	45(0)	45(0)	65.53	61.97
8	7.5(0)	1.375(0)	70.227(2)	45(0)	55.02	54.61
9	9(1)	2(1)	60(1)	30(-1)	61.4	60.57
10	7.5(0)	1.375(0)	45(0)	19.773(-2)	65.77	68.85
11	10.023(2)	1.375(0)	45(0)	45(0)	50.67	53.75
12	9(1)	0.75(-1)	30(-1)	60(1)	71.25	67.73
13	6(-1)	0.75(-1)	30(-1)	30(-1)	50.44	47.75
14	9(1)	0.75(-1)	60(1)	60(1)	60.3	59.47
15	6(-1)	2(1)	60(1)	60(1)	71.43	70.60
16	7.5(0)	1.375(0)	45(0)	45(0)	65.03	61.97
17	7.5(0)	0.324(-2)	45(0)	45(0)	35.2	38.28
18	7.5(0)	1.375(0)	45(0)	70.23(2)	80.11	83.19

Based on the Table 14, it is observed run 18 has the highest FAME yield which is 80.11% and 83.19% predicted yield at at 7.5 methanol to oil molar ratio, 1.375 % wt/wt of NaOH concentration, 45 °C reaction temperature and 70.23 minutes reaction time. . The FAME yield is calculated by using the following formula:

Table 15: Regression Coefficient for FAME yield (base catalyzed transesterification)

Coefficient	**Estimate**
constant	-32.862
A:Methanol to oil molar ratio	25.5957
B:NaOH concentration	55.9828
C:Reaction Temperature	-0.172362
D:Reaction Time	-2.31785
AA	-1.63516
AB	-3.87957
AC	0.0177373
AD	0.096313
BB	-12.3782
BC	0.631369
BD	-0.260659
CC	-0.0119049
CD	0.00558484
DD	0.0220757

FAME yield obtained during base transesterification were statistically analyzed by ANOVA in order to determine the constants of the quadratic equation which is shown in the Table 15. 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.

$$\textbf{FAME yield} = -32.862 + 25.5957A + 55.9828B - 0.172362C - 2.31785D - 1.63516A^2 - 3.87957AB + 0.0177373AC + 0.096313AD - 12.3782B^2 + 0.631369BC - 0.260659BD - 0.0119049C^2 + 0.00558484CD + 0.0220757D^2$$

Where A is methanol 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 5 compares the observed experimental FAME yield with the predicted values obtained using quadratic model equation. Linear trend are shown between the experimental values versus predicted values of the FAME yield. This indicate that the experimental values are nearly same to the predicted values. Apart from that, the R-Squared statistic ($R^2 = 0.92$) indicates that the model as fitted explains 92.23% of the variability in FAME yield. This implies that, 92.23% of the experiment values for base catalyzed transesterification is reliable.

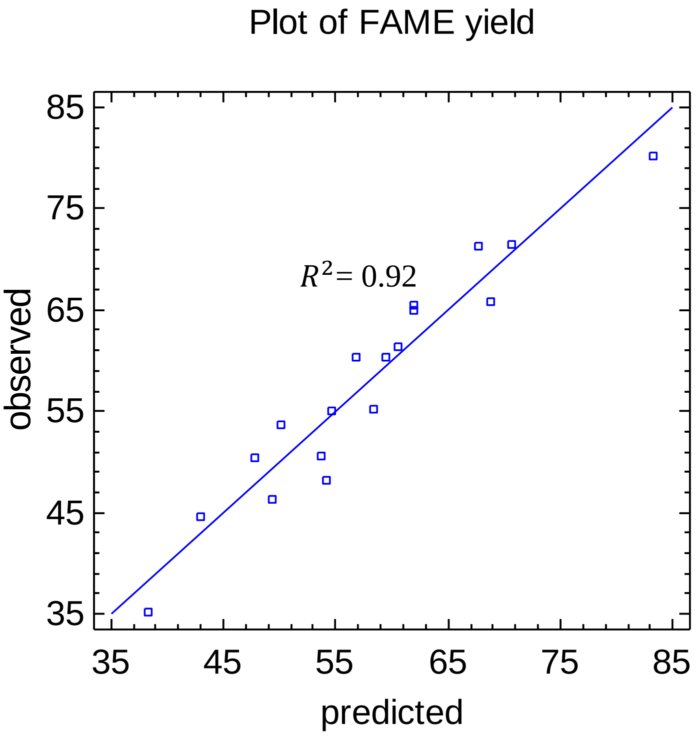

Figure 5: The diagnostic plot of experimental FAME yield (observed) versus predicted FAME yield for base catalyzed transesterification

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

The response surface plots for the yield of FAME as a function of two factors at a time while keeping the other three factors at their center point level were plotted in the three dimensional surface with the contour plot at the bottom as shown in Figure 6 . 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 [8,9].

Figure 6(a) depicts the interaction effects of methanol to oil molar ratio and catalyst concentration (NaOH w/wt%). Both of these parameters has a good interaction effect. From the contour plot, it was observed that the increasing volume of methanol can increase the FAME yield. However, the FAME yield started to decrease when the methanol volume reaches to a certain marginal level which is about 7.5 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. From the contour plot, the maximum yield gained is in the range of 62% to 65% with 6.5 to 8.5 methanol to oil molar ratio and 1 to 1.9% w/wt of NaOH concentration.

Figure 6(b) presents the yield of FAME as a function of methanol to oil molar ratio and reaction temperature. Increase the temperature also effect the FAME yield. Increased the temperature increase the FAME yield up to a certain level which is about 50℃ . Further increase the temperature caused the reduction of FAME yield. This is because, transesterification under high temperature promotes saponification reactions.

Figure 6(c) presents the effects of methanol to oil molar ratio and reaction time towards the FAME yield. It is expected that increasing the reaction time can increased the FAME yield. Further longer the reaction time beyond its optimum value reducing the FAME recovery process due the saponification reaction favors at longer duration reaction time. However, the contour plot depicts that high yield is gained at short reaction time and further increase the reaction time reducing the FAME yield until a certain value which is in the range of 35 to 40 minutes. Increasing the reaction time up to that value, the FAME yield is increasing. This problem might be due to the human error while conducting the experiments.

Figure 6(d) 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 65% to 70% FAME yield with 1.6 to 2 w/wt (NaOH concentration) and 50 to 55 ℃ (reaction temperature).

Figure 6(e) illustrates the effects of of NaOH concentration and reaction time towards the FAME yield. Increasing the NaOH concentration can give positive effects on FAME yield up until 1.9 w/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 60 minutes.

Figure 6(f) depicts FAME yield as a function of reaction temperature and reaction time. Reaction temperature give slightly positive effects on FAME yield. High reaction temperature promotes the saponification reaction.

4.3.3 Optimum reaction conditions for base catalysed transesterification

Table 16: Optimum Condition of Base Catalyzed Transesterification

Factor	Low	High	Optimum
Methanol to oil molar ratio	4.98	10.02	7.92
NaOH Concentration (w/wt%)	0.32	2.43	1.96
Reaction Temperature (℃)	20	70	65
Reaction Time (min)	20	70	70

From the design expert, RSM analyzation, it was observed that the maximum optimum FAME yield is 86.62% for base catalysed transesterification of jatropha curcas oil.

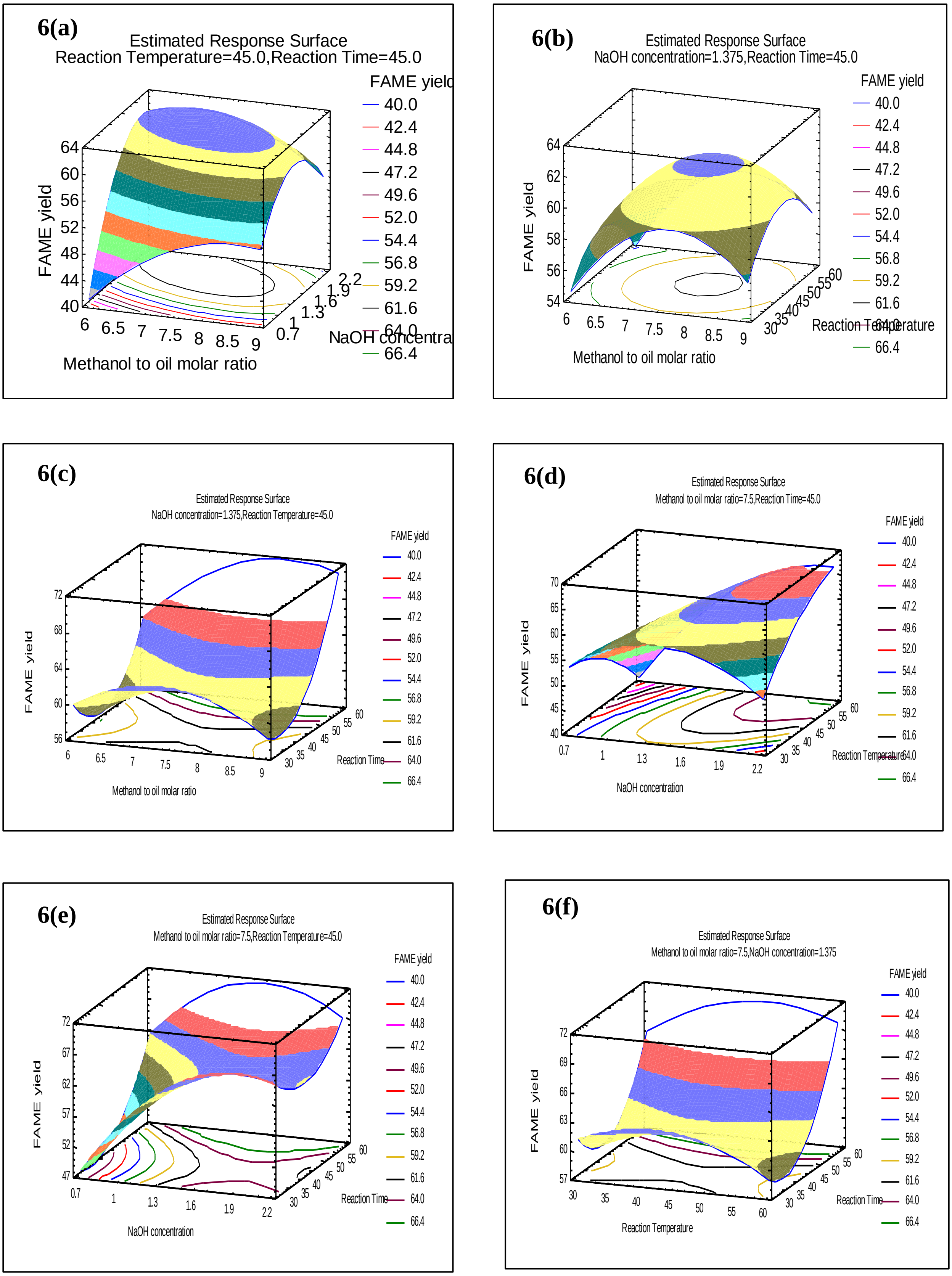

Figure 6: Contour plots for base catalysed transesterification

4.4 Microwave energy pretreated transesterification with alkali catalyst

In this section, the reaction of base catalyzed transesterification of jatropha curcas oil was enhanced by microwave energy pretreated at the beginning of the experiment.

4.4.1 Optimization of Microwave Energy Pretreated Transesterification with alkali catalyst

FAME yield produced is mainly depends on four independent variables: - Microwave heating time (A), methanol to oil molar ratio (B), NaOH concentration (C), and reaction time (D). In all the experiment, 10 g of jatropha curcas 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 FAME 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 17 below:

Table 17: Experimental range and level of the independent variables

Variables	**Coded symbol**	**Range and levels**				
		-2	-1	0	1	2
MWHT	A	1.318	2	3	4	4.682
Methanol	B	4.977	6	7.5	9	10.023
NaOH	C	0.323	0.75	1.375	2	2.426
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 FAME yield for microwave energy pretreated transesterification of jatropha curcas oil) are presented in Table 18.

Table 18: Experimental design matrix by CCD technique for microwave energy pretreated transesterification (without PTC) along with the experimental and model predicted yields

No	MHWT (min)	Methanol to oil molar ratio	NaOH Concentration (%w/wt)	Reaction Time (min)	Experimental yield (%)	Predicted yield (%)
1	3(0)	7.5(0)	1.375(0)	70.227(2)	71.04	72.76
2	4(1)	9(1)	2(1)	30(-1)	67.49	66.64
3	3(0)	7.5(0)	0.324(-2)	45(0)	69.32	71.91
4	2(-1)	6(-1)	2(1)	30(-1)	56.22	55.37
5	3(0)	7.5(0)	1.375(0)	19.773(-2)	80.97	82.70
6	3(0)	7.5(0)	1.375(0)	45(0)	87.67	84.85
7	2(-1)	9(1)	2(1)	60(1)	57.73	56.88
8	4(1)	6(-1)	2(1)	60(1)	54.06	53.21
9	4(1)	9(1)	0.75(-1)	30(-1)	89.69	90.11
10	3(0)	7.5(0)	1.375(0)	45(0)	86.05	84.85
11	3(0)	10.023(2)	1.375(0)	45(0)	65.62	67.34
12	4(1)	6(-1)	0.75(-1)	60(1)	57.13	55.55
13	1.318(-2)	7.5(0)	1.375(0)	45(0)	82.7	84.42
14	4.682(2)	7.5(0)	1.375(0)	45(0)	66.5	68.23
15	2(-1)	9(1)	0.75(-1)	60(1)	80.18	78.60
16	3(0)	4.977(-2)	1.375(0)	45(0)	60.59	62.31
17	3(0)	7.5(0)	2.426(2)	45(0)	50.73	51.58
18	2(-1)	6(-1)	0.75(-1)	30(-1)	59.77	58.19

Based on the Table 18, it was observed run 9 has the highest FAME yield which is 89.69% with predicted yield of 90.11% at at 4 minutes MWHT, 9 methanol to oil molar ratio, 0.75%w/wt NaOH concentration and 30 minutes reaction time.

Table 19: T and P values for the regression coefficients in the second order model equation

Coefficient	Estimate	F-Ratio	P-Value
constant	-365.273		
A:MHWT	33.7659	8.29	0.0636
B:Methanol to oil molar ratio	68.2952	0.8	0.4372
C:NaOH Concentration	85.2825	31.51	0.0112
D:Reaction Time	4.41299	3.11	0.1758
AA	-3.0143	6.75	0.0805
AB	0.0376961	0	0.981
AC	0.146	0	0.9524
AD	-0.466219	10.24	0.0493
BB	-3.14594	37.22	0.0088
BC	-5.07067	11.42	0.0431
BD	-0.294447	9.19	0.0563
CC	-20.9084	49.56	0.0059
CD	0.00306667	0	0.985
DD	-0.0111891	4.71	0.1185

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.

$$\textbf{FAME yield} = -365.273 + 33.7659A + 68.2952B + 85.2825C + 4.41299D - 3.0143A^2 + 0.0376961AB + 0.146AC - 0.466219AD - 3.14594B^2 - 5.07067BC - 0.294447BD - 20.9084C^2 + 0.00306667CD - 0.0111891D^2$$

FAME yields predicted by this second order model equations were tabulated in the Table 18 together with the experimental observation.

The second order model equations were evaluated statistically in order to study the significance of the model terms. Table 19 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 pretreated transesterification with alkali catalyst (without PTC), 5 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, NaOH concentration is the most significantly influenced the FAME yields as it has the low P-value and high T-value as compared to the other variables.

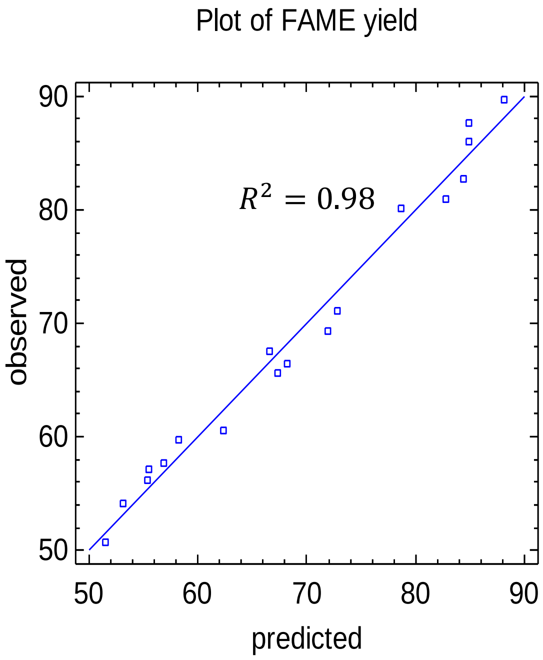

Figure 7: The diagnostic plot of experimental FAME yield (observed) versus predicted FAME yield for microwave energy pretreated transesterification

Figure 7 shows the diagnostic plot of experimental FAME yield (observed) versus the predicted FAME yield for microwave energy pretreated transesterification (without PTC). Linear trend are shown between the experimental values versus predicted values of the FAME yield. This indicate that the experimental values are nearly same to the predicted values. Apart from that, the R-Squared statistic ($R^2 = 0.98$) indicates that the model as fitted explains 98.24% of the variability in FAME yield. This implies that, 98.24% of the experiment values for microwave energy pretreated transesterification (without PTC) is reliable.

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

The response surface plots for the yield of FAME yield as a function of two factors at a time while keeping the other three factors at their center 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 [8,9].

Figure 8(a) presents the effects of methanol to oil molar ratio to FAME yield with the microwave energy pretreated transesterification. Maximum yield was observed at volume of methanol between 7 to 8 molar ratios of methanol to jatropha 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.

Figure 8(b) presents the effects of alkali catalyst (NaOH) on the microwave pretreated transesterification on jatropha oil. The maximum FAME yield can be seen at range of 0.75 to 1.375 w/wt % of NaOH concentration to oil. From the figure, increasing the NaOH concentration can increase the FAME yield up to a certain marginal value (0.94 w/wt%). 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 8(c) depicts the interaction between reaction time and FAME yield on microwave energy pretreated transesterification on jatropha curcas oil. Increasing the reaction time 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 45 to 60 minutes.

Figure 8(d) shows the interaction effects between methanol to oil molar ratio and reaction time towards FAME yield. The maximum FAME yield was observed at range of 7.5 to 9 methanol to oil molar ratio and at 30minutes 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 8(e) depicts the interaction effects between methanol to oil molar ratio and NaOH concentration towards the FAME yield. The maximum FAME yield was observed at a range of 7.5 to 8.5 methanol to oil molar ration and 0.75 to 1.375 w/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 favoring saponification reaction.

Figure 8(f) 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 to 1.3 w/wt% and 30 to 40 minutes reaction time.

4.4.3 Optimum reaction conditions for Microwave Energy Pretreated Transesterification with alkali catalyst

Table 20: Optimum Condition of Microwave Energy Pretreated Transesterification

Factor	Low	High	Optimum
MHWT(min)	1.3	4.7	4.2
Methanol to oil molar ratio	4.98	10.02	9.20
NaOH Concentration(w/wt%)	0.32	2.43	0.94
Reaction Time (min)	20	70.	20

From the RSM analyzation, it was observed that the maximum optimum FAME yield is 95.95% for microwave energy pretreated transesterification of jatropha curcas oil.

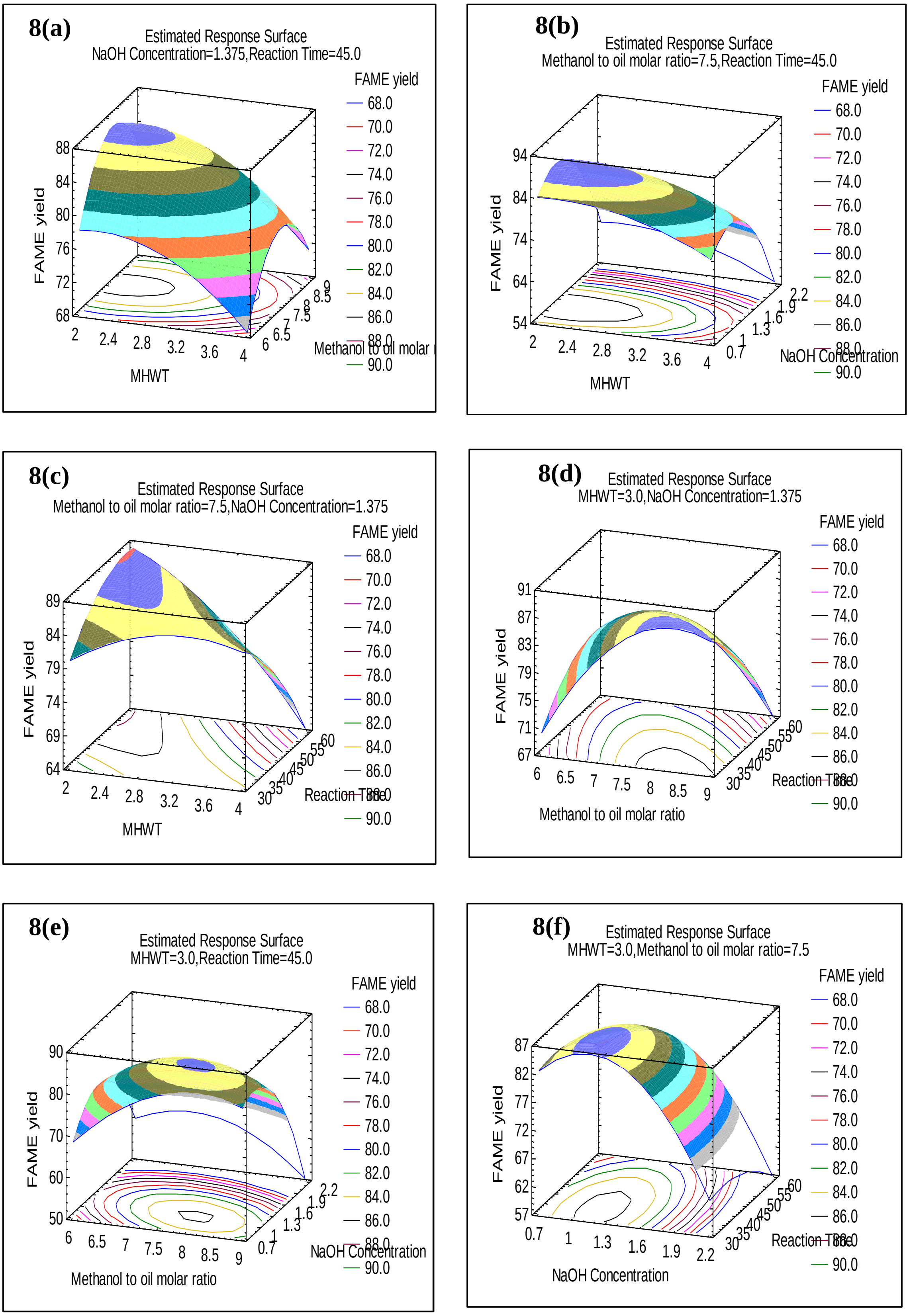

Figure 8: Contour Plot for Microwave Energy Pretreated Transesterification with alkali catalyst

4.5 Microwave energy pretreated transesterification of jatropha curcas oil in the presence of alkali Phase Transfer Catalyst (PTC)

In this section, the reaction of microwave energy pretreated transesterification of jatropha oil was further enhanced by the presence of PTC which is Cetyltrimethylammonium Bromide (CTMAB).

4.5.1 Optimization of Microwave Energy Pretreated Transesterification in the presence of PTC.

FAME yield produced is mainly depends on four independent variables: - Microwave heating time (A), methanol to oil molar ratio (B), CTMAB/NaOH molar ratio (PTC Concentration) (C), and reaction time (D). In all the experiment, 10 g of jatropha curcas oil, stirrer speed of 400 rpm,1.0 w/wt% of NaOH concentration and reaction temperature at 30 **(**℃) 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). 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 21 below:

Table 21: Experimental range and level of the independent variables for microwave energy pretreated transesterification in the presence of PTC

Variables	**Coded symbol**	**Range and levels**				
		-2	-1	0	1	2
MWHT	A	1.318	2	3	4	4.682
Methanol	B	4.977	6	7.5	9	10.023
CTMAB	C	0.33	0.5	0.75	1	1.17
Time	D	13.18	20	30	40	46.82

Experiments was 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 FAME yield for microwave energy pretreated transesterification of jatropha oil in the presence of PTC are presented in Table 22.

Table 22: Experimental design matrix by CCD technique for microwave energy pretreated transesterification in the presence of PTC together with the experimental and model predicted yields (4.5)

No	MHWT (min)	Methanol to oil molar ratio	CTMAB/NaOH molar ratio	Reaction Time (min)	Experimental Yield (%)	Predicted Yield (%)
1	2(-1)	6(-1)	1(1)	20(-1)	59.1	57.77
2	4.682(2)	7.5(0)	0.75(0)	30(0)	83.5	84.72
3	2(-1)	9(1)	1(1)	40(1)	81.41	80.08
4	3(0)	10.023(2)	0.75(0)	30(0)	79.33	80.55
5	3(0)	7.5(0)	0.75(0)	46.818(2)	86.96	88.18
6	3(0)	7.5(0)	0.75(0)	13.182(-2)	74.78	76.00
7	4(1)	6(-1)	1(1)	40(1)	69.15	67.82
8	3(0)	7.5(0)	0.329(-2)	30(0)	95.97	96.09
9	2(-1)	9(1)	0.5(-1)	40(1)	91.45	91.05
10	4(1)	9(1)	1(1)	20(-1)	71.7	70.37
11	4(1)	9(1)	0.5(-1)	20(-1)	90.14	89.74
12	1.318(-2)	7.5(0)	0.75(0)	30(0)	81.12	82.34
13	4(1)	6(-1)	0.5(-1)	40(1)	72.19	71.79
14	3(0)	4.977(-2)	0.75(0)	30(0)	62.85	64.07
15	2(-1)	6(-1)	0.5(-1)	20(-1)	89.3	88.90
16	3(0)	7.5(0)	0.75(0)	30(0)	86.91	87.02
17	3(0)	7.5(0)	1.170(2)	30(0)	66.27	68.59
18	3(0)	7.5(0)	0.75(0)	30(0)	89.99	87.02

Based on the Table 22, it was observed run 8 has the highest FAME yield which is 95.97% with predicted yield of 96.09% at 3 minutes MWHT, 7.5 methanol to oil molar ratio, 0.75 CTMAB/NaOH molar ratio and 30minutes reaction time.

Table 23: T and P values for the regression coefficients in the second order model equation

Coefficient	Estimate	F-Ratio	P-Value
constant	57.3815		
A:MHWT	-12.4006	0.28	0.6362
B:Methanol to oil molar ratio	24.5526	13.19	0.0359
C:CTMAB/NaOH molar ratio	-86.4052	88.72	0.0025
D:Reaction Time	-1.19395	7.21	0.0748
AA	-1.2327	1.74	0.2792
AB	2.08409	3.15	0.1742
AC	9.38	4.27	0.1306
AD	-0.0720445	0.17	0.7101
BB	-2.31091	30.9	0.0115
BC	1.58667	0.28	0.6362
BD	0.197839	2.84	0.1908
CC	-26.4546	3.12	0.1753
CD	1.778	15.36	0.0295
DD	-0.0174182	3.47	0.1595

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.

$$\textbf{FAME yield (PTC)} = 57.3815 - 12.4006A + 24.5526B - 86.4052C - 1.19395D - 1.2327A^2 + 2.08409AB + 9.38AC - 0.0720445AD - 2.31091B^2 + 1.58667*BC + 0.197839BD - 26.4546C^2 + 1.778CD - 0.0174182D^2$$

FAME yields predicted by this second order model equations were tabulated in the Table 22 together with the experimental observation.

The second order model equations was evaluated statistically in order to study the significance of the model terms. Table 23 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 pretreated transesterification of jatropha oil in the presence of PTC, 4 effects have P-values less than 5% indicating that they are significantly different from zero at the 95.0% confidence level. In this experiment, methanol to oil molar ratio (B) and CTMAB/NaOH (C) molar ratio significantly influenced the FAME yields as it has the low P-value and high T-value as compared to the other variables.

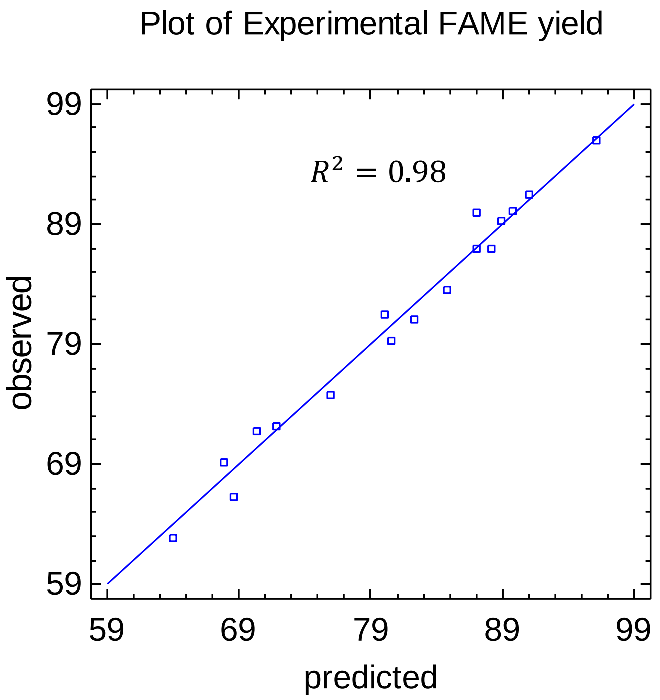

Figure 9: Diagnostic plot of experimental FAME yield (observed) versus the predicted FAME yield for microwave energy pretreated transesterification in the presence of PTC

Figure 9 shows the diagnostic plot of experimental FAME yield (observed) versus the predicted FAME yield. Similar to microwave energy pretreated transesterification (without PTC) where linear trend are shown between the experimental values versus predicted values of the FAME yield. This indicates that the experimental values are nearly same to the predicted values. Apart from that, the R-Squared statistic ($R^2 = 0.98$) indicates that the model as fitted explains 98.44% of the variability in FAME yield. This implies that, 98.44% of the experiment values for microwave energy pretreated transesterification in the presence of PTC is reliable.

4.5.2 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 center point level were plotted in a three dimensional surface with the contour plot at the bottom as shown in Figure 10.

Figure 10(a) presents the yield of FAME as a function of MWHT and methanol to oil molar ratio. The maximum FAME yield was observed at a range 3.6 to 4 minutes MWHT with 8 to 9 methanol to oil molar ratio. The increasing MWHT give good results on FAME yield up until certain marginal value (3.6 to 4 minutes). Continue increased the MWHT time caused the FAME yield slightly decreased. Similar to methanol to oil molar ratio variable where increasing the volume of methanol can improve the biodiesel production process. However further increased the volume of methanol beyond the marginal value (8 to 9 molar ratio) reduces the biodiesel yield slightly. This is due to the solubility problem where biodiesel dissolve into the glycerol phase thus some of biodiesel may lost with the byproduct glycerin.

Figure 10(b) presents the yield of FAME as a function of MHWT and CTMAB/NaOH molar ratio (PTC concentration). Both of the parameters give positive effect on FAME yield. Adding CTMAB in transesterification does helped the catalytic reaction as the FAME yield is improved. However, overloading of CTMAB/NaOH molar ratio cause the biodiesel yield to decrease. This is because, further increase of catalyst favors the saponification reaction. The maximum yield observed is between 92% to 96% with MWHT from 2 to 3.5 minutes and CTMAB/NaOH molar ratio below than 0.5.

Figure 10(c) depicts the interaction between MWHT and reaction time towards FAME yield. The maximum FAME yield was observed at 32 to 40 minutes reaction time and 2 to 4 minutes MWHT. The longer the reaction time, the higher the biodiesel yield. However, further increase the reaction time beyond at the maximum yield obtained causes the biodiesel yield to decrease slightly. This is because longer duration of transesterification favor saponification reaction too.

Figure 10(d) shows the interaction effects of methanol to oil molar ratio and CTMAB/NaOH molar ratio. Increased the methanol does give positive effect on FAME yield. However, further increased the methanol value up to a certain value cause the FAME yield to decrease due to solubility problem. For CTMAB/NaOH molar ratio, it presence does increased the biodiesel yield. Overloading more than 0.5 molar ratio of CTMAB/NaOH consequences on the reduction of biodiesel yield.

Figure 10(e) depicts the interactions between the methanol to oil molar ratio and reaction time. The maximum yield obtained is at 90% to 92% with the 8 to 9 molar ratio of methanol to oil and 36 to 40 minutes of reaction time.

Figure 10(f) presents the FAME yield as a function of CTMAB/NaOH molar ratio and reaction time. Both of the parameters give positive effects on the biodiesel yield. The maximum yield was observed at PTC concentration below than 0.5 molar ratio of CTMAB/NaOH and reaction time between 20 to 30 minutes. Further increase the value of both parameters reduced the biodiesel yield due to the saponification reaction.

4.5.3 Optimum reaction conditions for Microwave Energy PretreatedTransesterification in the presence of PTC

Table 24: Optimum Condition of Microwave Energy Pretreated Transesterification in the presence of PTC

Factor	Low	High	Optimum
MHWT(min)	1.3	4.7	1.5
CTMAB/NaOH to oil molar ratio	4.98	10.02	7.11
NaOH Concentration(w/wt%)	0.33	1.17	0.33
Reaction Time (min)	13	47	26

From the RSM analyzation, it is observed that the maximum optimum FAME yield is 99.22%.

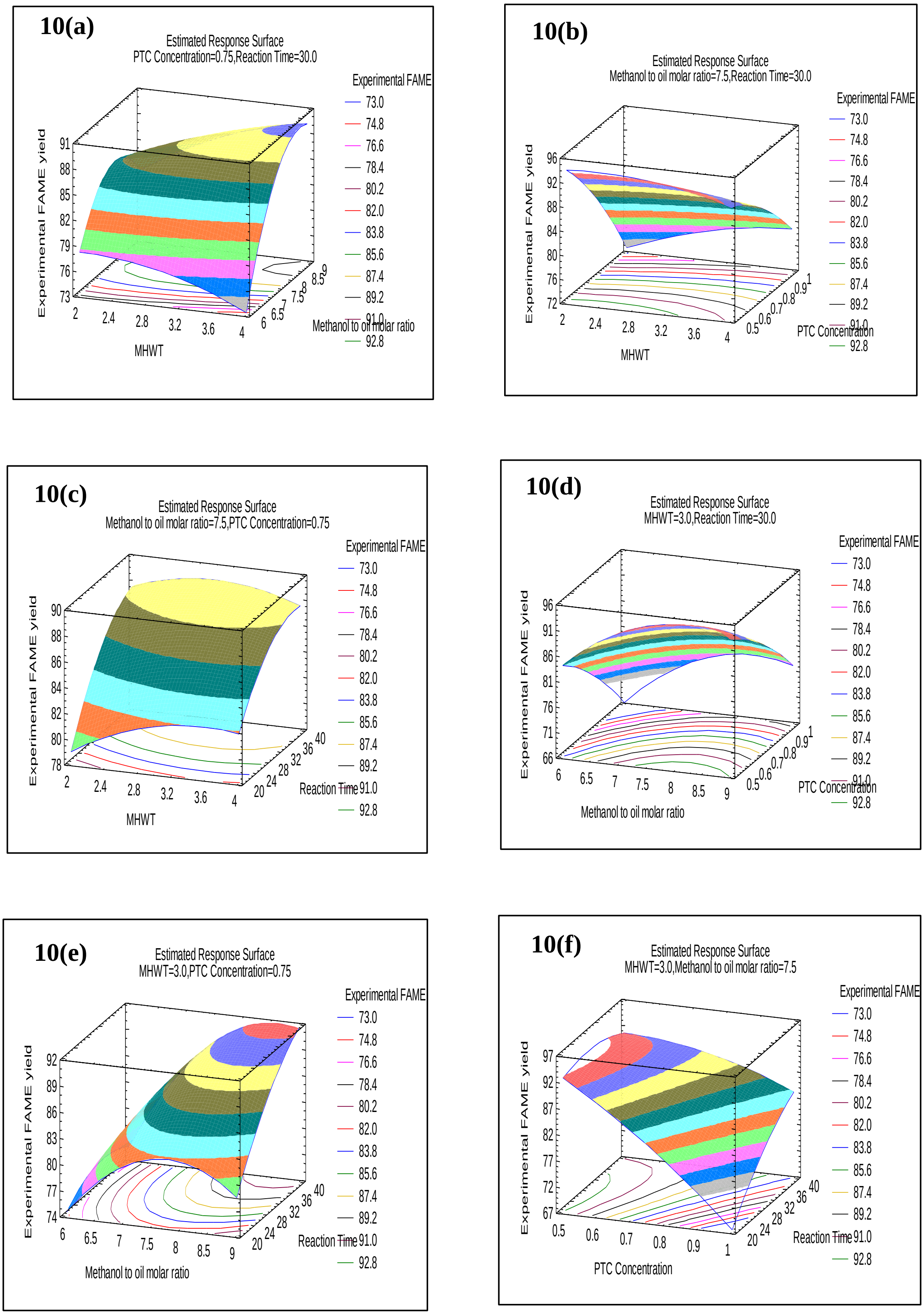

Figure 10: Contour plot for microwave energy pretreated transesterification in the presence of PTC

4.6 Summary for optimization of FAME yield

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

Optimization 1:	Base catalyzed transesterification
Optimization 2:	Microwave energy pretreated transesterification with alkali catalyst
Optimization3:	Microwave energy pretreated transesterification in the presence of alkali PTC.

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

Table 25: Optimization summary

Conditions **Reaction parameters**	**Optimization 1**	**Optimization 2**	**Optimization 3**
MWHT (min)	-	4	1.5
Methanol to oil molar ratio	7.92	9.20	7.11
NaOH Concentration (w/wt %)	1.96	0.94	1.0 *(constant)*
CTMAB/NaOH molar ratio	-	-	0.33
Reaction Temperature (℃)	66	50 *(constant)*	30
Reaction Time (min)	70	20	26
FAME yield (w/wt%)	86.62	95.65	99.22

From Table 25, it can be seen that optimization of microwave energy pretreated transesterification of jatropha oil curcas in the presence of phase transfer catalyst has the highest FAME yield. Followed by the microwave energy pretreated transesterification. Base transesterification has the least FAME yield. Results shows that 99.22% w/wt of FAME yield can be obtained within 26 minutes reaction time for transesterification reaction that pretreated with microwave irradiation in the presence of PTC. As compared to the microwave energy pretreated transesterification with the absence of PTC the highest FAME yield obtained was only 95.65% w/. This shows that in the presence of PTC, there was an increment of FAME yield which is 3.57%. On the other hand, as compared with base transesterification, the microwave energy pretreated oil transesterification assisted by PTC has obtained an increment of 12.6% of FAME yield. .Thus, it can be conclude that microwave energy can improve the transesterification reaction and the reaction has better improvement in the presence of PTC.

CHAPTER 5

CONCLUSION AND RECOMENDATION

5.1 Conclusion

In this present studies, the non- edible oil source, jatropha oil curcas L. was used as the raw material for transesterification reaction to produce biodiesel. Base transesterification, microwave energy pretreated transesterification and microwave energy pretreated transesterification in the presence of PTC were investigated. Results shows that at optimum condition, 99.22%w/wt within 26 minutes reaction time of FAME yield was observed when the reaction was conducted with microwave heat pretreated oil in the presence of PTC. It was also demonstrated that a gain of 3.57% of FAME yield for a reaction conducted using microwave energy pretreated oil transesterification reaction assisted by PTC as compared to microwave untreated transesterification reaction in the absence of PTC (FAME yield=95.65% w/wt). As compared to base catalyzed transesterification, the reaction conducted by using microwave energy pretreated oil transesterification assisted by PTC has an increment 12.6% of FAME yield. Thus, it can be conclude that microwave energy can improve the transesterification reaction and the reaction has better improvement in the presence of PTC. Hence, use of microwave pretreatment of oil and alkaline PTC as a catalyst has a promosing future in enhance transesterification and increase yield of biodiesel.

5.2 Recommendation for future work

As for future works and recommendation, microwave energy pretreated transesterification in the presence of phase transfer catalyst should be done with other non-edible oil for example, Kapok oil, Margosa oil, Neem oil and etc in order. Besides that, difference type of PTC can also be used as an enhance agent in tranesterification 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. 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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