TRANSESTERIFICATION OF NON-EDIBLE OIL USING PHASE TRANSFER CATALYST VIA RESPONSE SURFACE METHODOLOGY

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CERTIFICATION OF APPROVAL

TRANSESTERIFICATION OF NON-EDIBLE OIL USING PHASE TRANSFER CATALYST VIA RESPONSE SURFACE METHODOLOGY

by

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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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MAY 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.

(AHMAD FAEZ SYAZWAN BIN CHE MOHD AZMI)

Table of Contents

List of Figures

List of Table

Abbreviations and Nomenclature

NaOH	- Sodium Hydroxide
CTMAB	- Cetyltrimethylammonium Bromide
BTAMOH	- Benzyltrimethylammonium Hyroxide
H_2SO_4	- Sulphuric Acid
GC	- Gas Chromatography
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

ABSTRACT

With the increasing demand for energy from the fossil fuels, the oil reserves are getting depleted and raising a serious concern over the future rising energy demand. Use of fossil fuels are becoming the environmental issue as the environment and its ecosystems are getting polluted by the emission of greenhouse gases such as carbon dioxide generated from use of fuels. Use of renewable alternative energy and chemical resources can reduce the problem. One such option is biodiesel. However, use of edible oil as a source of raw material for biodiesel directly competes with food processing industries affecting the cost of biodiesel and food industries. Use of non-edible oils can reduce the high cost of edible oil. Besides that, due to limited solubility between oil and alcohol phase leads to an increase of the cost of biodiesel. Use of reaction rate enhancement agent and microwave energy can reduce the processing costs. In the present project work, Caster oil as a source of non-edible oil sources was used to produce biodiesel. Alkaline cetyltrimethylammonium bromide (CTMAB) as a phase transfer catalyst (PTC) was utilized to enhance the rate of transesterification reaction. Optimum reaction condition was established using statistical tools of response surface methodology (RSM) central composite design (CCD) technique. At optimum condition, 89.85% w/w of fatty acid methyl esters (FAME) was produced in 25.91 minutes of reaction time as compared to 76.8% w/w FAME yield produced without the use of PTC in 31.3 minutes of reaction time. It can be observed that by the use of CTMAB as PTC about 13.05 wt% additional yield increment is achieved while reducing the reaction time. Model equation that predicts the yield of biodiesel was also developed using RSM of CCD. Model predicted yield compares well with experimentally observed FAME yield indicating that developed model equation is adequate enough to predict the yield of biodiesel.

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CHAPTER 1: INTRODUCTION

1.1 BACKGROUND STUDY

Global energy consumption is rising rapidly with increasing population and standard of living. About 88% of the world energy consumption is based on fossil fuels. 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. Increasing use of fossil fuel has negatively affecting the environment due to the emission of pollutants 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 demanding environmental friendly alternative source of energy and chemical feed stocks [1, 2]. One such option is biodiesel. Biodiesel is gaining increasing attention as it can substitute effectively for petro diesel. Biodiesel can be produced by transesterification of a wide range of feedstocks such as vegetable oils, animal fats, used frying oils, etc. with alcohols [3, 4]. 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 [3, 5].

Transesterification is a chemical reaction between triglycerides present in the oils or fats and alcohols such as methanol or ethanol to form esters and glycerol in the presence of a catalyst or non-catalyst, at high pressure and temperature [6, 7]. 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. 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 [8, 9]. Theoretically, one mole of triglycerides reacts with three moles of alcohol and gives three moles of biodiesel and one glycerol as shown in the Figure 1.

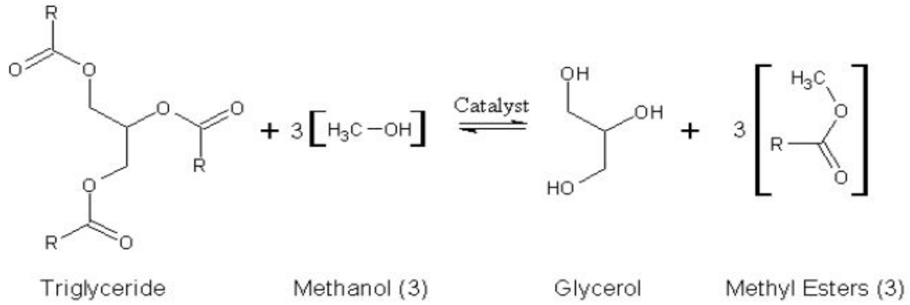

Figure 1: Schematic represents ion of transesterification reaction

As vegetable oils are sparingly soluble in lower alcohols, the transesterification reaction is slow due to limited mass transfer rate between the oil phase and alcohol phase [10]. Several techniques such as mixing, co-solvent addition, higher temperature, higher pressure, super critical alcohol, ultrasonication and microwave irradiation have been investigated to enhance the reaction rates [11- 13].

Currently, more than 95% of biodiesel in this world is made from edible oil sources such as rapeseeds, soybeans, sunflower and palm. The capacity for biodiesel production increased from 2.2 million tons per year in 2002 to 46.5 million tons per year in 2011; however, biodiesel production was only 1.9 million tons per year in 2002 and 18.3 million tons per year in 2011 [1, 2, 14, 15]. Biodiesel industry had to compete with food processing industry for its main raw material (edible oils). This resulted in the rise of edible oil prices affecting the economics of biodiesel production as well as food prices. For this critical reason, currently, it was reported that feedstock cost alone accounts for 75% of the biodiesel production cost [4].

Production of biodiesel from non-edible oil sources such as Castor oil (Ricinus communis) can potentially reduce the high edible oil feedstock costs for biodiesel production. Castor or also known as castor bean or castor ricin is identified as a potential alternative non-edible oil bearing plant source to edible oils in different parts of the world. Planting castor as a source of oil for biodiesel production is gaining more attention particularly in tropical and subtropical countries such as Malaysia because the plant can tolerate to variable weather conditions and soil types [16]. Besides that, due to its type as a perennial crop, it can provides soil support hence reducing erosion effects. The seeds of castor plant contain oils up to 60% which have high amount of triglycerides, mainly ricinolein [17].

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. Natural gas (43.4%), crude oil (38.2%), coal (15.3%) and the renewable resources (3.1%) contribute to the required energy mix [18]. 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 [18, 19]. With the high cost of feedstock (edible oil source-Palm oil) biodiesel producers in Malaysia will continue to face a difficult environment. However, Malaysian government modified its biodiesel oil feedstocks strategy to include alternative non- edible feedstocks such as castor plant. Malaysia has about 1.5 million ha of estimated marginal land that can be used for castor plantation even though its current plantation is at a gradual level [20]. Forest Research Institute Malaysia (FRIM) has conducted a research work for exploring alternative non-edible feedstocks to complement palm oil for the production of biodiesel. Therefore, the current initiatives to use castor plant as a source of biodiesel need to be supported by rigorous research work.

In the present project work, castor oil is used as a source of non-edible oil sources to substitute edible oil sources such as palm oil in order to produce biodiesel. To enhance the limited solubility of oil and alcohol and increase the mass transfer rate between the two reactants so as to promote transesterification reaction, alkaline phase transfer catalyst (PTC) will be employed.

1.2 PROBLEM STATEMENT

Biodiesel is an attractive renewable option to complement dependence on petro diesel. Biodiesel can be produced by transesterification of vegetable oils with methanol in presence of a suitable catalyst. Presently, more than 95% of biodiesel is made from edible oil sources such as rapeseeds, soybeans, sunflower and palm which are available in large scale from the agricultural industry. Usage of edible oils has an adverse effect on its price due to its demand by food processing industry. Limited solubility of oils in alcohols reduces reaction rates. It is necessary to keep the cost of production under control to make the biodiesel technology viable by using alternative cheap feedstock and effective reaction pathways. The general review presented suggests that transesterification of non-edible seeds as feedstock is a possibility that can keep the cost of feedstock and processing low. Application of phase transfer catalysis can enhance the reaction rates. In the present work, it is proposed to use transesterification of castor oil as a non-edible oil sources. To enhance the slow reaction rate of transesterification due to limited solubility of alcohol and oil, it is proposed to investigate phase transfer catalysts (PTC) as reaction rate enhancement agent.

1.3 OBJECTIVES

The objectives of this research work are:

1. To investigate alkaline transesterification of castor oil with methanol in the presence of phase transfer catalysts.
2. Investigation of the catalytic effect of phase transfer catalysts such as cetyltrimethylammonium bromide (CTMAB).
3. Study the individual and interaction effect of reaction variables on transesterification reaction of castor oil.
4. Optimization of reaction parameters by statistical experimental design technique of response surface methodology (RSM).

1.4. SCOPE OF STUDY

To achieve the abovementioned objectives, castor oils will be used and characterized for their physical and chemical properties. Effects of alkaline and phase transfer catalysts, parametric effect of reactant ratio (methanol to castor oil), reaction time, and reaction temperature on transesterification of castor oil as well as, alkaline catalyst and PTC concentration will be investigated in a batch reactor. Optimum operating conditions will be established using response surface methodology (RSM). Conversions of triglycerides with time at different reaction conditions will be measured to investigate the rate of reaction and order of reaction equations.

1.5 FEASIBILITY OF THE PROJECT

Based on the Gantt chart table provided, this project work can be completed in the given time frame because all equipment that are needed in conducting the experiment are available in UTP. Even though some of the equipment requires time to understand the equipment operating procedure, it still manageable. In addition, the non-edible oil to be used as feedstock (castor oil) is already available and project can be start as soon as possible. Besides that, with the assistance from the supervisor, this project can be completed within the given time frame with success.

CHAPTER 2: LITERATURE REVIEW

2.1 BIODIESEL TO REPLACE FOSSIL FUELS

Biodiesel 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 [21]. 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 [22]. 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.

2.2 CASTOR OIL (RICINNUS COMMUNIS)

For this present research project, the non-edible vegetable oil that is used is castor oil. Castor oil is extracted from its seed from a plant of the Euphorbiceae species [17]. It is the only member of the genus Ricinus and of the sub-species Ricininae. The seeds contain up to 60% oil, which is rich in triglycerides, mainly ricinolein. The top producers of castor oil country are China, India and Brazil because the castor plant is suitable to be plant in tropical and subtropical countries. The reasons why castor oil is chosen for this present research project because castor oil has lower cost compared to the on obtained from other vegetable oils due to its solubility in alcohol and thus the transesterification reaction can occur under the ambient temperature [23]. Besides that, according to Ramezani et al. it has greater cetane number, which indicates a better quality of ignition, and it has more oxygen, making its combustion more complete. A study of neutralization of castor oil by Sousa et al. indicates that yield of methyl esters obtained from neutralized castor oil was higher than the yield obtain from raw oil under the same operating condition. Previous studies have shown that castor has improved lubricity over other oils with similar carbon chain-length fatty acids. The hypothesis was that the hydroxylated fatty acids of ricinoleic acid in castor oil impart it better performance as lubricity enhancer than other common vegetable oil esters[23].These are the reasons why castor oil is used for this present research work. By having this research project carried out, more information on castor oil properties will be collected to be used as feedstock in biodiesel production

2.3 TRANSESTERIFICATION METHOD

Non-edible vegetable oil, for example castor oil is not suitable to be used as fuel for internal combustion because of their high viscosity, lower volatility and high reactivity due to its unsaturated hydrocarbon. Therefore, in order for vegetable oil to be used as a fuel, several methods has been used to change its chemical and physical properties. Examples of these methods are dilution, micro-emulsion and transesterification [24].Among these methods, the most preferable method is transesterification process to lower the viscosity of vegetable oil and commercially established process to convert vegetable oils or animal fats to biodiesel [9].The down side of this process is that it has a very slow reaction time because insolubility of methanol and vegetable oil mixture. Transesterification process is the reaction of triglycerides (fat/oil) with an alcohol to form esters and glycerol. A triglyceride has a glycerine molecule as its base with three long chain fatty acids attached. During the esterification process, the triglyceride is reacted with alcohol in the presence of a catalyst, usually a strong alkaline like sodium hydroxide. The alcohol reacts with the fatty acids to form the mono-alkyl ester, or biodiesel, and crude glycerol. Triglycerides are converted to glycerol sequentially via diglycerides and monoglycerides, with one methyl ester molecule being formed at each step [25].

2.4 PHASE TRANSFER CATALYST (PTC)

Phase Transfer Catalysts are used in heterogeneous reaction mixtures to facilitate movement of a reactant from one phase to another. Phase transfer catalysts are known to sometimes accelerate reaction rates and minimize solvent waste, since the reactions tend to be heterogeneous. PTC functions like a detergent for solubilizing the salts into the organic phase. Besides that, PTC also refers to the acceleration of the reaction upon the addition of PTC in a reaction process. By using PTC, a reaction of heterogeneous phase can achieve faster reactions, obtain higher conversions or yields, fewer byproducts produced, eliminating the need of 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. In biodiesel production, the used of PTC is to facilitate anion transfer between polar methanol/glycerol phase and non-polar oil phase to speed up transesterification [25].

A previous research has been conducted by Zhang et al regarding the present of phase catalyst in transesterfication process. Zhang et al, has used different types of PTC to enhance the reaction of transesterification of soybean oil with methanol in the presence of base catalyst as deprotonating agent. It was reported that, with the presence of PTC, the rate of reaction increase compared to reaction conducted without PTC. Hence, further research need to be conducted in order to develop appropriate reaction mechanisms and reaction properties. Therefore, Cetyltrimethyammonium bromide (CTMAB) will be used as the phase transfer catalyst and act as an enhancement agent for transesterification reaction.

Chapter 3: Research Methodology

3.1 PROJECT ACTIVITIES

Litreature Review

- For FYPII, further understanding on the concept of esterification and transesterification reaction is carried out.
- More review on the litreature is done to understand the mechanisms and efeects of phase transfer catalyst on transesterification reaction

Experiment

- Experiment is designed for a transesterication experiment with the presence of phase transfer catalyst and without the presence of phase transfer catalyst.
- In order to optimize the biodiesel yield, the experiment is designed by using the Design Expert software.
- Transesterification experiments with and without the presence of phase transfer catalyst is conducted and the results for both of the experiments in collected

Data Collection

- From the experiments conducted, biodiesel produced is withdrawn, measured and the biodiesel yield is calculated.
- The data is then keyed into the design expert software in order to develope 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 1: Gantt chart and key milestones of the project

No	Detail Work	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Preliminary transesterification experiment	🟨	🟨	🟨	🟨	🟨									
2	Preliminary transesterification experiment completed					√									
3	Transesterification Experiment						🟨	🟨	🟨	🟨					
	Transesterification Experiment completed									√					
3	Statistical Experiment Design										🟨	🟨			
4	Statistical experiment design completed											√			
5	Analysis of Biodiesel Sample										🟨	🟨			
6	Biodiesel analysis completed											√			
7	Submission of Progress Report							√							
8	Pre-SEDEX										🟨				
9	Submission of Final Draft Report											🟨			
10	Submission of Dissertation (soft bound)												🟨		
11	Submission of technical paper												🟨		
12	Viva													🟨	
13	Submission of Project Dissertation														🟨

Legends:

√ – Achieved key milestone of the project

🟨 – Project work progress

3.3 EXPERIMENT METHODOLOGY

3.3.1 The properties of Castor Oil

a) Determination of acid value for Castor Oil

This test is to determine the FFA content in castor oil samples before it is used for transesterification reaction. The FFA must be below 3% to ensure no soap or water will formed during the transesterification process. The standard procedure for this test is according Acid Value test AOCS Official method Cd 3d-63.

1. 3g of castor oil is dissolved in iso-propanol in conical flask
2. Phenolphthalein is added into the flask
3. The solution is titrated with a 0.1M of potassium hydroxide until the mixture turn light pink
4. The volume of KOH used is recorded and calculated

Acid value is calculated using the formula:
AN= (v-b) x N x 56.1 / w
v= the titaration volume in mL
b= the blank in ml
N=the normality of the KOH solution
w= the weight of sample in g

b) The calorific value of castor oil

This test is to determine the calorific value of castor oil by using the bomb calorimeter equipment. The procedure are as follows:

1. Sample is placed into the decomposition vessel
2. The start button is activated, the cell cover closes and the decomposition vessel is filled with oxygen. Next, inner vessel is filled with water.
3. The sample is ignited and the change in temperature over time is recorded.
4. The system then display the result of the experiment.
5. The data is collected.

c) The density of castor oil

This test is used to determine the density of castor oil. The procedure are as follows:

1. A 50 mL beaker is weigh on the weighing machine and the weight is recorded.
2. 10 mL of castor oil is pour into beaker.
3. The beaker is now weigh and the weight is recorded.
4. The density is of oil is then calculated.

The density of oil is calculated by:

$$density = \frac{mass\ of\ beaker\ with\ oil - \ mass\ of\ beaker\ without\ oil}{the\ volume\ oil}$$

d) The viscosity of castor oil

This experiment is to find the viscosity of castor oil by using the viscometer equipment. 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 castor oil is placed onto the plate. The handled is lowered and locked.
4. The spindle is allowed to equilibrate to the temperature control setting.
5. The run time is for rotating is set and the run key is pressed.
6. The result is the collected.

3.3.2 Catalyst preparation procedure

a) Sodium hydroxide (NaOH) - 1.5 % w/wt to oil

1. NaOH tablets is crushed into fine grains.
2. 0.15g of NaOH grains is measured on a weighing balance and placed into a beaker.
3. Based on 1:9 methanol oil ratio, 4.24 mL of methanol is poured into the beaker and mix with 0.15g of NaOH.
4. The mixture is now ready to be used in transesterification experiment.

b) Cetyltrimethylammonium bromide ($C_{19}H_{42}BrN$) – 0.5% molar ratio to NaOH
   1. 0.456g of cetyltrimethylammonium bromide is weigh and mix with 1% w/wt of NaOH catalyst
   2. The mixture is then ready to be used in transesterification experiment.

3.3.3 Designed experiment for preparation of biodiesel

The experiment was designed by using the Designed Expert software, which is a response surface methodology software. This software is a statistical tool for experimental design and identification of optimal condition. In this project central composite design (CCD) technique of RSM will be used for experimental design to investigate the individual and interaction effects of reaction variables and determine the optimum reaction condition for transesterification of castor oils in the presence of alkaline PTC. There are four parameters used for the base design which are methanol to oil ratio, amount NaOH used, the temperature and time taken for the reaction. From the software, two models of experiment were designed. One of the models of experiment is transesterification reaction with the presence of phase transfer catalyst and the other one is transesterification reaction without the presence of phase transfer catalyst. A total of 42 experiments are generated 21 experiments with different parameters condition with PTC and another 21 experiments without the presence of PTC. Hence, 42 transesterification experiment need to be conducted in order to identify the optimum reaction condition for transesterification reaction.

a) Transesterification process without phase transfer catalyst

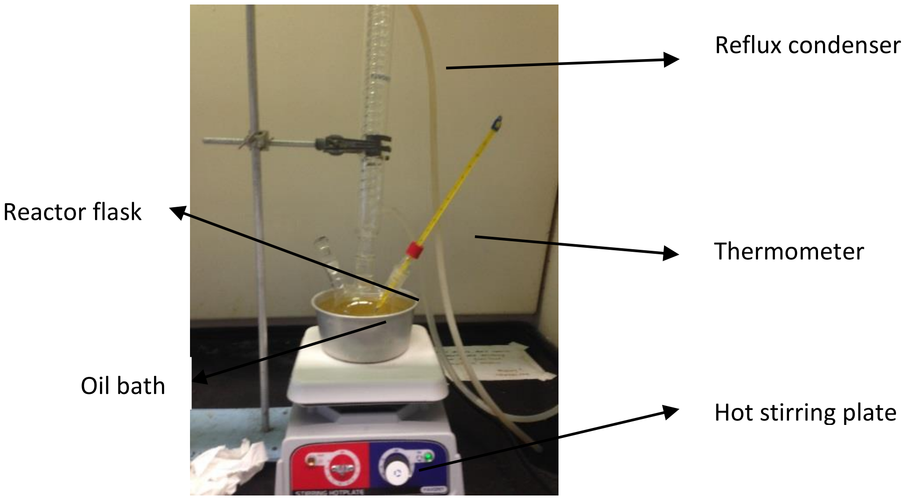

Figure 2: Set-up of experiment for transesterification

1. The experiment was setup according to the figure above.
2. The reaction is carried out in a 100mL of three neck flask, where the neck is for a reflux condenser, thermometer and a sampling port.
3. 10g of castor oil by is placed into the reactor flask.
4. A magnetic stirrer is placed into the reactor flask and set to 350 rpm.
5. The heat is turned on and allowed for the oil bath to reach 50^{0}C (based of the desired temperature).
6. Then, the prepared NaOH catalyst is placed into the reactor flask and the reaction is started.
7. The reactor is left for 30 minutes (based on the desired time) till the reaction is completed.
8. After the reaction, the reacted oil is the placed into the separation funnel for separation.
9. The biodiesel is washed with warm water (50°C) until a clear solution is seen at the bottom of the biodiesel layer.
10. The lower layer which contain water is removed from the separation funnel.
11. The biodiesel produced is then extracted and heated up to 120°C in a dryer for 30 minutes.
12. The FAME yield of the dried biodiesel oil is then calculated by weight weight.

13. The experiment is repeated according to the response surface methodology experiment that was designed.

b) Transesterification process without phase transfer catalyst

1. The experiment was setup according to the figure above.
2. The reaction is carried out in a 100mL of three neck flask, where the neck is for a reflux condenser, thermometer and a sampling port.
3. 10g of castor oil by is placed into the reactor flask.
4. A magnetic stirrer is placed into the reactor flask and set to 350 rpm.
5. The heat is turned on and allowed for the oil bath to reach 50^{0}C (based of the desired temperature)
6. Then, the prepared PTC catalyst is placed into the reactor flask and the reaction is started.
7. The reactor is left for 30 minutes (based on the desired time) till the reaction is completed.
8. After the reaction, the reacted oil is the placed into the separation funnel for separation.
9. The lower layer which contain water is removed from the separation funnel.
10. The biodiesel is washed with warm water (50°C) until a clear solution is seen at the bottom of the biodiesel layer.
11. The biodiesel produced is then extracted and the yield is calculated.
12. The experiment is repeated according to the response surface methodology experiment that was designed.

Chapter 4: Results and Discussion

4.1 Properties of Castor oil

4.1.1 Acid number determination

The results of the acid value is as follows:

Run	A=Volume, mL of standard alkali used in the titration	B=Volume,mL of standard alkali used in titrating the blank	normality of standard alkali	W= mass, grams of sample	Acid Value
1	12.5	0.2	0.1	2.5	3.38
2	2.1	0.15	0.1	2.5	4.38
3	1.9	0.15	0.1	2.5	3.93

From the table above, the average of the acid value calculated is 3.9. According to AOCS Official Method Cd 3d-63, acid value need to be divided by 1.99 to obtain the free fatty acid (FFA) value. FFA calculated from the average acid value calculated is 1.96. Therefore, the FFA content is less than 3% and base transesterification reaction can be proceed.

4.1.2 Viscosity determination

The results obtained from the viscosity experiment is a follows:

	Spindle 1	Spindle 2	Spindle 3	Spindle 4	Spindle 5	Spindle 6
cP	548.3	358	0		84	60
%	73.1	23.9	-22.9	12.9	0.7	0.2

Based on the procedure of the experiment, the value for the viscosity is taken with the highest percentage. According to the above table, the viscosity of castor oil is 548.3 cP equivalent to 54.8 Pa.s which is higher than petroleum based diesel. Therefore, castor oil need to undergo transesterification reaction to reduce its viscosity.

4.1.3 Determination of castor oil calorific value

The calorific value of castor oil is obtained from bomb calorimeter experiment which is 33.72 kJ/g. this is comparable when considering the energy content of diesel which is at 43.1 kJ/g. The heating energy of castor oil is considered feasible as a fuel.

The properties of biodiesel such as the viscosity, density, calorific value and acid value were measured by standard method and tabulated in the table below:

Table 2: Properties of castor oil

Properties of castor oil	Value
Density	0.81 g/ml
Viscosity	54.83 Pa.s
Calorific value	33.724 kJ/g
FFA content	1.96%
Molecular weight*	850 g/mol

*molecular weight was assumed to the normal molecular weight of oil

4.2 Design of experiments

Transesterification of castor oil with methanol is carried out with (i) in the presence of base catalyst NaOH, (ii) in the presence of both catalyst NaOH and cetyltrimethylammonium bromide as a PTC to investigate the effects of each catalyst with different parameters by using response surface methodology. In this project there are four selected process variables namely A: oil to methanol molar ratio, B: catalyst (with and without PTC), C: Temperature and D: reaction time. Central Composite Design (CCD is used to perform the experimental design. Table 1 and 2 shows the experimental design for transesterification without the presence of phase transfer catalyst and with the presence of cetyltrimethylammonium as PTC.

Table 3: Experimental design for transesterification without PTC with FAME conversion

Standard order #	**A:oil to methanol molar ratio**	**B:NaOH (catalyst) (w/wt.%)**	**C:Temperature (°C)**	**D:Reaction Time (min)**	**Yield %**	**Predicted value %**
1	9	1.5	50	20	55.4	58.91
2	9	1.5	30	20	53.1	53.05
3	9	0.5	50	40	54.8	58.31
4	6	1.5	30	40	51.1	51.05
5	9	0.5	30	40	48.5	48.45
6	6	0.5	50	20	44.2	47.71
7	6	1.5	50	40	51.6	55.11
8	6	0.5	30	20	30.6	30.55
9	4.98	1	40	30	51.7	49.25
10	10.02	1	40	30	64.5	62.05
11	7.5	0.16	40	30	31.5	29.05
12	7.5	1.84	40	30	40.5	38.05
13	7.5	1	23.18	30	59	60.79
14	7.5	1	56.82	30	83	76.32
15	7.5	1	40	13.18	61	58.55
16	7.5	1	40	46.82	71	68.55
17	7.5	1	40	30	66	67.25
18	7.5	1	40	30	64	67.25
19	7.5	1	40	30	68.5	67.25
20	7.5	1	40	30	67	67.25
21	7.5	1	40	30	65	67.25

Table 4: Experimental design of transesterification without PTC with FAME conversion

Standard order #	A:oil to methanol molar ratio	B:NaOH (catalyst) (w/wt.%)	C:Temperature (°C)	D:Reaction Time (min)	Experimental Value %	Predicted Value %
1	9	0.75	50	20	60.74	57.32
2	9	0.75	30	20	13.4	13.91
3	9	0.25	50	40	57.1	53.68
4	6	0.75	30	40	83.3	83.81
5	9	0.25	30	40	34.5	35.01
6	6	0.25	50	20	43.1	39.68
7	6	0.75	50	40	28.84	25.42
8	6	0.25	30	20	47.2	47.71
9	4.98	0.5	40	30	47.32	49.38
10	10.02	0.5	40	30	82.8	84.86
11	7.5	0.08	40	30	56.55	58.61
12	7.5	0.92	40	30	47.9	49.96
13	7.5	0.5	23.18	30	21.7	19.07
14	7.5	0.5	56.82	30	10.5	17.24
15	7.5	0.5	40	13.18	62.4	64.46
16	7.5	0.5	40	46.82	91	93.06
17	7.5	0.5	40	30	88.52	78.74
18	7.5	0.5	40	30	75.8	78.74
19	7.5	0.5	40	30	79.7	78.74
20	7.5	0.5	40	30	78.8	78.74
21	7.5	0.5	40	30	75.7	78.74

Biodiesel yield is selected as the response for the combination of the selected process variables. The biodiesel yield is calculated using the following formula:

$$Biodiesel\ yield = \frac{weight\ oil\ after\ base\ transesterfication}{weight\ of\ oil\ before\ transesterification} \times 100$$

There are 21 experiments for each model, as generated by the software. Out of the 21 experiments for the model of transesterification without the presence of PTC, run 14 has the highest biodiesel yield at 83%. As for another 21 experiments with the model of transesterification with PTC, run 16 has the highest biodiesel yield at 91%.

4.3 ANOVA analysis for transesterification

The data obtained from independent variables were statistically analyzed by ANOVA in order to confirm the significance of the output response variable. Table shows the ANOVA for transesterification of castor oil with and without the presence of PTC. The P-value must be less than 0.05 in order for the variables to have significance effect on the response values. Therefore, the reliability and the variance of the output response of the model is indicated by the F-value. The higher the F–value for the specific independent variables, the higher will be the effects on that variable. Table 4 and 5 shows the ANOVA for transesterification of castor oil with and without PTC. For both of the models, the P-value is less than 0.05 which are 0.0064 for transesterification without PTC and 0.0006 for transesterification with PTC. Hence, both of the models is significance. The temperature is the most influencing process variables for the output response as compared to the other three variables for transesterification without PTC. As for transesterification with PTC, oil to methanol molar ratio is the most influencing process variable for the output response.

The perturbation plot for both of the models is shown in figure 3 and 5. The steepest curve shows the most influencing factor towards the FAME yield. The most influencing factor for biodiesel conversion from castor oil without PTC is the reaction temperature followed by oil to methanol molar ratio (figure 3). However, the most influencing factor for biodiesel conversion from castor oil with PTC is the oil to methanol molar ratio followed by reaction time (figure 5).

The trend between predicted values against actual values is illustrates in figure 4 and 6. From the plot of both experiment models, it is clearly shown that most of the points are linear, which indicates that the predicted value close to the experimental values.

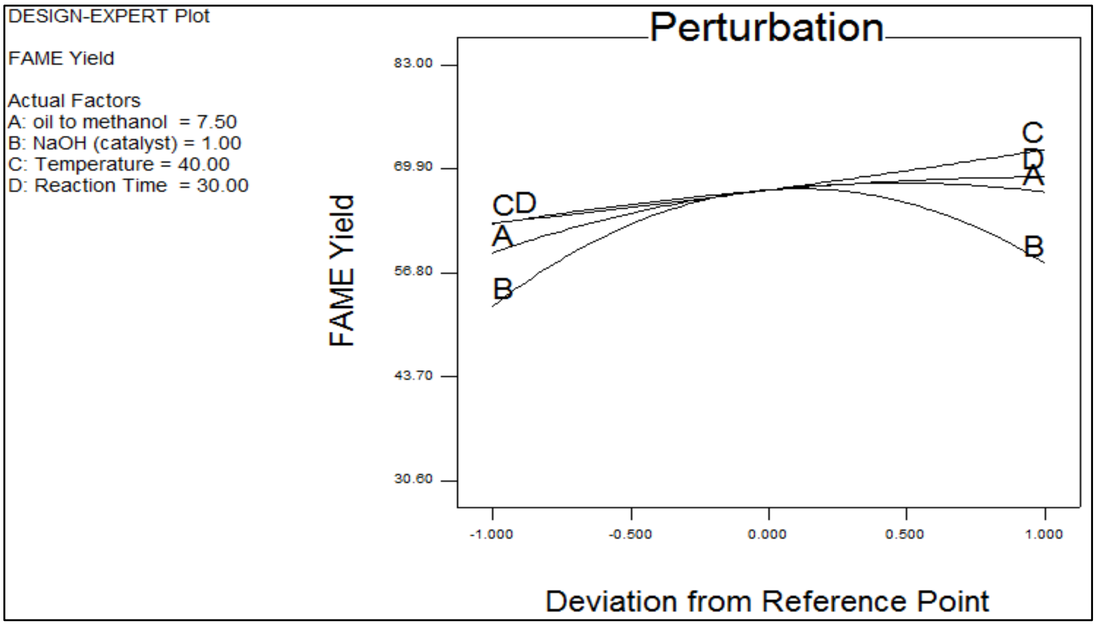

Figure 3: Perturbation plot of transesterification of castor oil without PTC

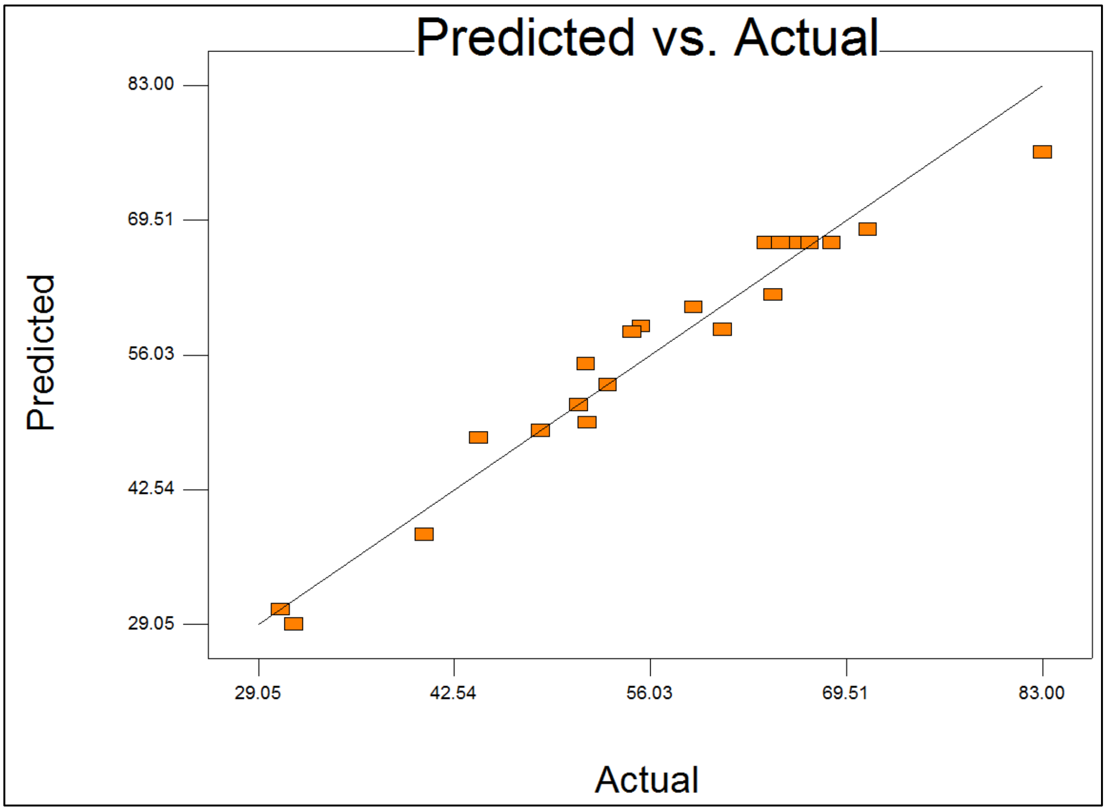

Figure 4: Predicted versus actual value plot for transesterification of castor oil without PTC

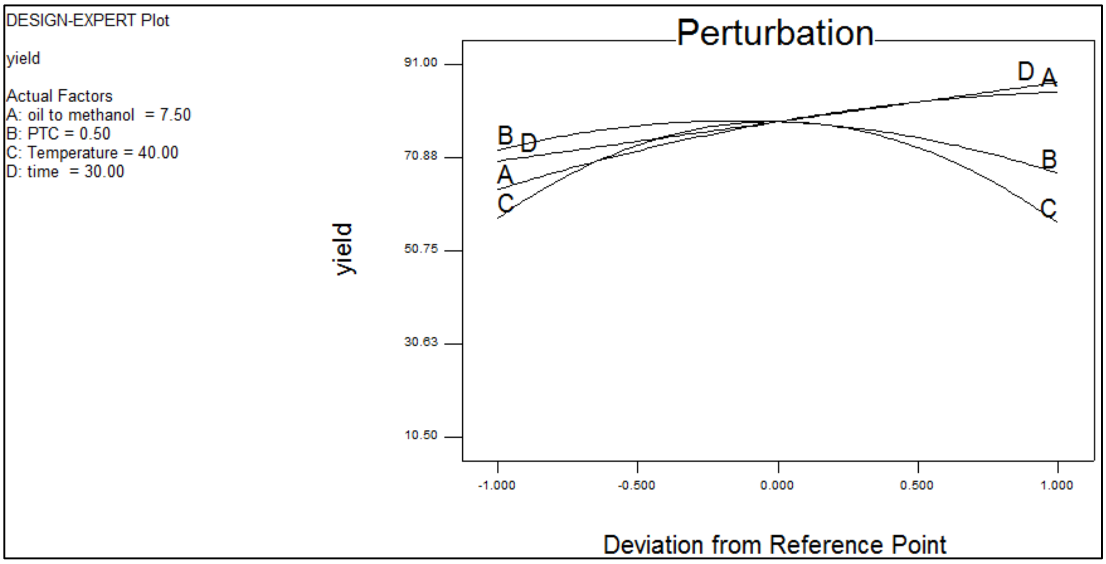

Figure 5: Perturbation plot for transesterification of castor oil with PTC

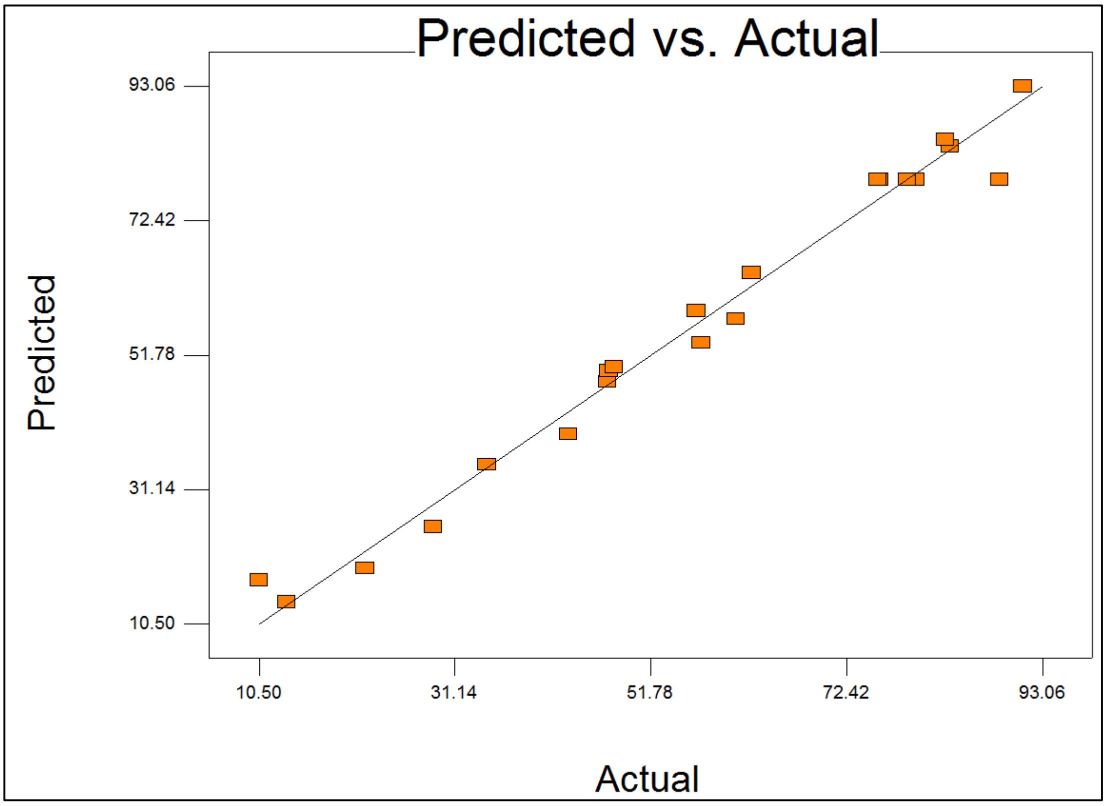

Figure 6: Predicted versus actual value plot for transesterification of castor oil with PTC

Table 5: ANOVA analysis of transesterification of castor oil without PTC

Source	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**
Model	3182.22	14	227.30	8.98	0.0064
A(alcohol)	81.92	1	81.92	3.24	0.1220
B(catalyst)	40.50	1	40.50	1.60	0.2527
C(temperature)	291.21	1	291.21	11.51	0.0146
D(time)	50.00	1	50.00	1.98	0.2094
A2	251.04	1	251.04	9.92	0.0198
B2	2120.56	1	2120.56	83.82	< 0.0001
C2	3.19	1	3.19	0.13	0.7346
D2	25.47	1	25.47	1.01	0.3544
AB	0.06	1	0.06	0.00	0.9625
AC	3.78	1	3.78	0.15	0.7124
AD	7.08	1	7.08	0.28	0.6158
BC	36.55	1	36.55	1.44	0.2746
BD	0.77	1	0.77	0.03	0.8672
CD	10.35	1	10.35	0.41	0.5460
Residual	151.79	6	25.30		
Lack of Fit	139.59	2	69.79	22.88	0.0065
Pure Error	12.20	4	3.05		
R^2=0.95		Adj-R^2=0.84		adequate precision=11.1	

Table 6: ANOVA analysis of transesterification of castor oil with PTC

Source	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**
Model	12073.25	14	862.38	21.56	0.0006
A(alcohol)	629.42	1	629.42	15.73	0.0074
B(catalyst)	37.41	1	37.41	0.94	0.3709
C(temperature)	4.07	1	4.07	0.10	0.7605
D(time)	408.98	1	408.98	10.22	0.0187
A2	252.42	1	252.42	6.31	0.0458
B2	1117.56	1	1117.56	27.94	0.0019
C2	6856.47	1	6856.47	171.40	< 0.0001
D2	0.00	1	0.00	0.00	0.9974
AB	42.72	1	42.72	1.07	0.3413
AC	2064.03	1	2064.03	51.60	0.0004
AD	32.24	1	32.24	0.81	0.4039
BC	82.05	1	82.05	2.05	0.2021
BD	759.14	1	759.14	18.98	0.0048
CD	705.00	1	705.00	17.62	0.0057
Residual	240.02	6	40.00		
Lack of Fit	130.21	2	65.10	2.37	0.2093
Pure Error	109.81	4	27.45		
R^2=0.98		Adj-R^2=0.94		adequate precision= 14.8	

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.

$$FAME_{without\ PTC} = +67.52+3.81*A+2.68*B+4.62*C+2.97*D-4.10*A^2-11.91*B^2+0.46*C^2-1.31*D^2+0.14A*B-0.69*A*C-1.46*A*D-2.14*B*C-0.48*B*D-1.14*C*D$$

$$FAME_{with\ PTC} = +78.74+10.55*A-2.57*B-0.55*C+8.50*D-4.11*A^2-8.65*B^2-21.42*C^2+0.006*D^2+3.59A*B+16.06*A*C-3.12*A*D-3.20*B*C+15.14*B*D-9.39*C*D$$

Results of ANOVA for the fitted polynomial models is reliable with high regression coefficients of (R^2=0.95 and 0.98). This implies that, 96% of the experimental data for transesterification without PTC confirm capability with the data predicted by the model. Determination coefficient R^2 value means that the model shows positive predicted results with respect to output response within the range of acceptable precision. The adjusted determination coefficient i.e. Adj-R^2. The value of adjusted R^2 for both of the model is 0.87 and 0.68 which are in good agreement with R^2 value.

4.4 Effects of the variables on FAME yield

The response surface plots for the yield of FAME as a function of two factors at a time by keeping the other two factors at their center point level were plotted in three dimensional surface with the contour plot at the bottom as shown in figure 7 to 16. If the contour plot have an elliptical shape, it indicates a good interaction of the two variables on the response. If the contour plot have a circle shape, it indicates less interaction effects between the variables to affect the response.

4.4.1 Effects of the variables on FAME yield without PTC

Figure 7 presents yield of FAME as a function of oil to methanol molar ratio and base catalyst NaOH to castor oil. Maximum yield was observed with oil to methanol molar ratio of 8.3 and base catalyst NaOH of 1.13 w/wt. %. Increase in concentration of methanol to oil ratio and NaOH helped in promoting the catalytic reaction. However, further overloading of NaOH decreased the FAME yield due to saponification reaction was favored at high concentration of NaOH.

Figure 8 shows the effect of base catalyst NaOH and reaction temperature on the FAME yield. NaOH has a positive effect on the yield of FAME up to a certain value of oil to methanol molar ratio (8.3). If there is an increasing of NaOH loading, will result in high saponification reaction. However, there is no interaction between NaOH and reaction temperature.

Figure 9 depicts the interaction between base catalyst NaOH and reaction time on the yield of FAME. It is observed that yield of FAME increased up to a certain reaction time (39 minutes) beyond which it is decreased slightly. The decrease in yield is due to formation of soap as the soap was observed during the experiment.

Figure 10 illustrates the interaction between oil to methanol molar ratio and reaction time on the yield of FAME. Maximum FAME yield is observed at reaction time (39 minutes) and oil to methanol molar ratio (8.3).

Beyond these values, FAME yield decreased slightly because by increasing the value of oil to methanol molar ratio will result in higher FAME yield up to a marginal value (8.3). Overloading of methanol would dissolve the product biodiesel into the glycerol phase and could affect the biodiesel recovery process which leads to reduction of FAME yield.

Figure 11 shows the interaction between oil to methanol molar ratio and the reaction temperature. Increasing the value of oil to methanol molar ratio will result in higher FAME yield up to a marginal value (8.3). Overloading of methanol would dissolve the product biodiesel into the glycerol phase and could affect the biodiesel recovery process which leads to reduction of FAME yield. However, there is no interaction between methanol and reaction temperature.

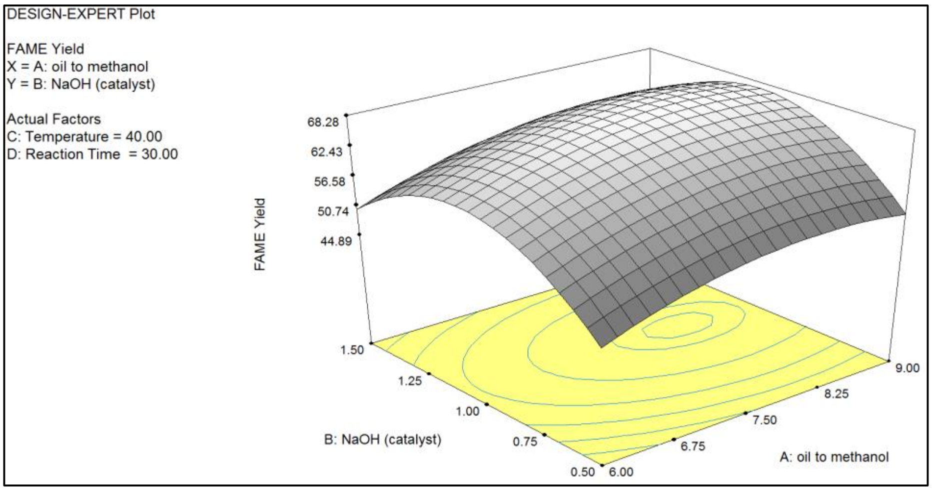

Figure 7: NaOH and oil to methanol molar ratio

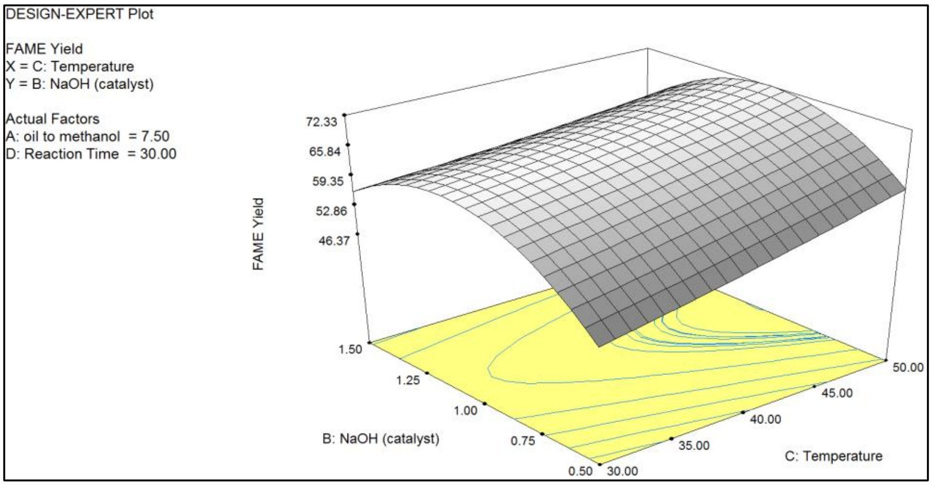

Figure 8: NaOH and Temperature

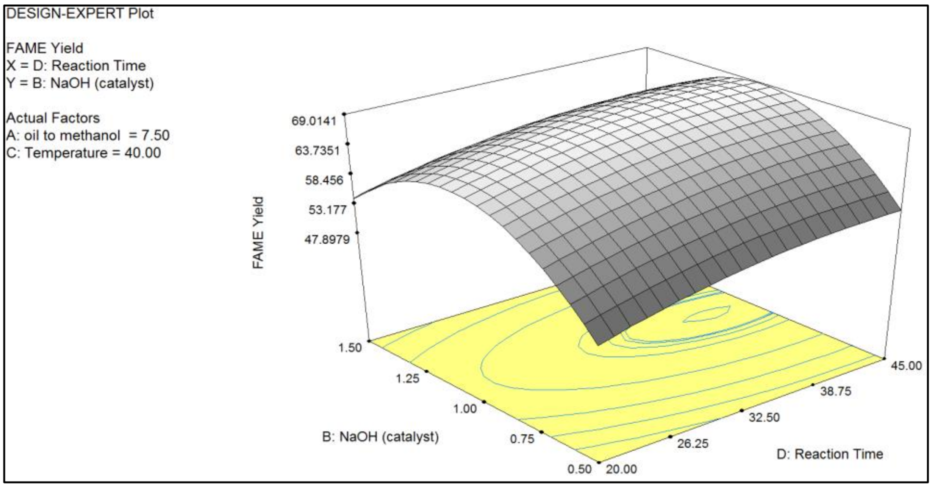

Figure 9: NaOH and Reaction time

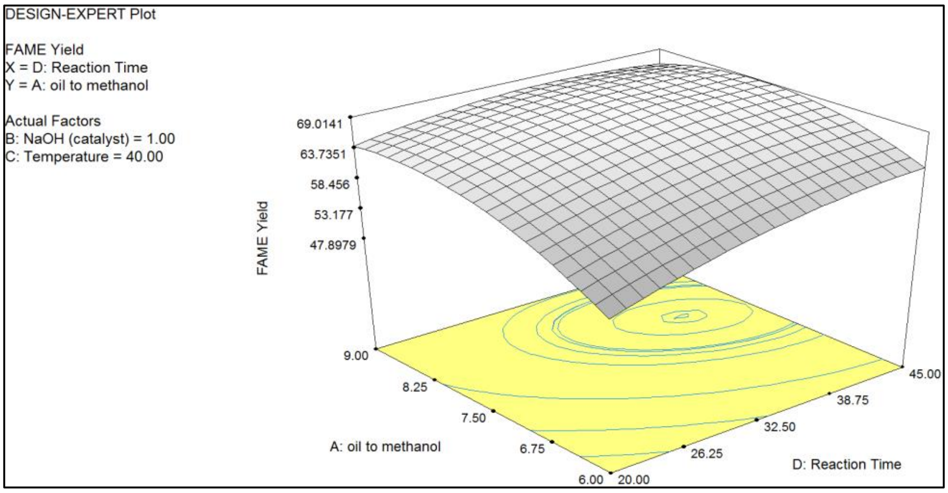

Figure 10: Oil to methanol molar ratio and reaction time

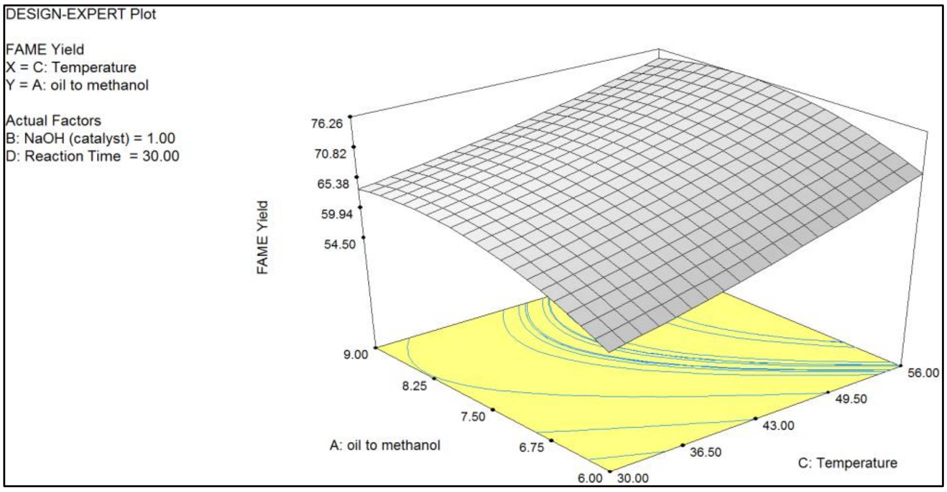

Figure 11: Oil to methanol and temperature

4.4.2 Effects of variables on FAME yield with PTC

Figure 12 illustrates interaction of PTC and reaction temperature to FAME yield. Increasing of PTC loading to (0.4) and temperature to 39°C results in maximum FAME yield. Further loading of PTC above 0.4 result in decreasing FAME yield because saponification value was favored.

Figure 13 shows the reaction between PTC and oil to methanol molar ratio. FAME yield is maximum at PTC (0.5) and oil to methanol molar ratio of 8.3. However, above these values, the FAME yield is decreasing. The reason is when the value of oil to methanol is very high, methanol would dissolve the product biodiesel into the glycerol phase and could affect the biodiesel recovery process which leads to reduction of FAME yield.

Figure 14 depicts the interaction between PTC and reaction time. Higher value of PTC will favors saponification value which may result in reduction of FAME yield. However, there is no interaction between these two variables.

Figure 15 presents oil to methanol molar ratio and reaction temperature. Increasing the value of oil to methanol molar ratio will result in higher FAME yield up to a marginal value (8.3). Overloading of methanol would dissolve the product biodiesel into the glycerol phase and could affect the biodiesel recovery process which leads to reduction of FAME yield. However, there is no interaction between methanol and reaction temperature.

Figure 16 illustrates FAME yield with the function of oil to methanol molar ratio and reaction time. The contour plot is not

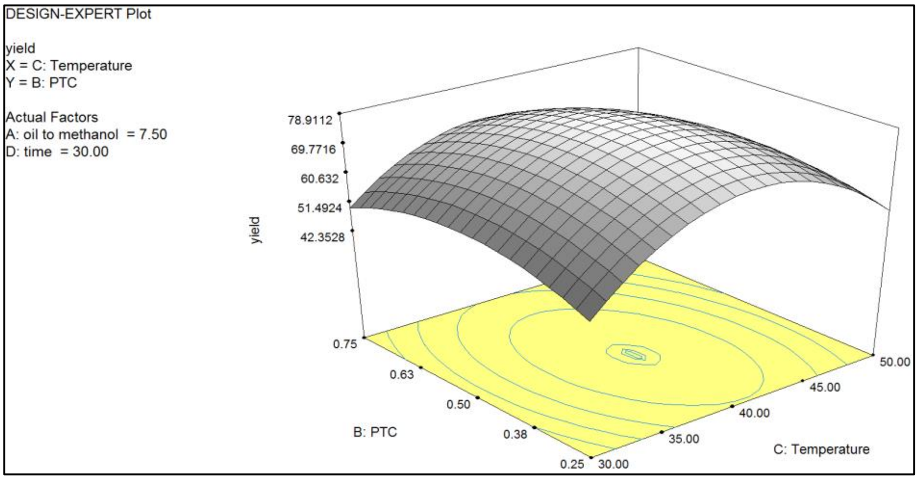

Figure 12: PTC and Reaction temperature

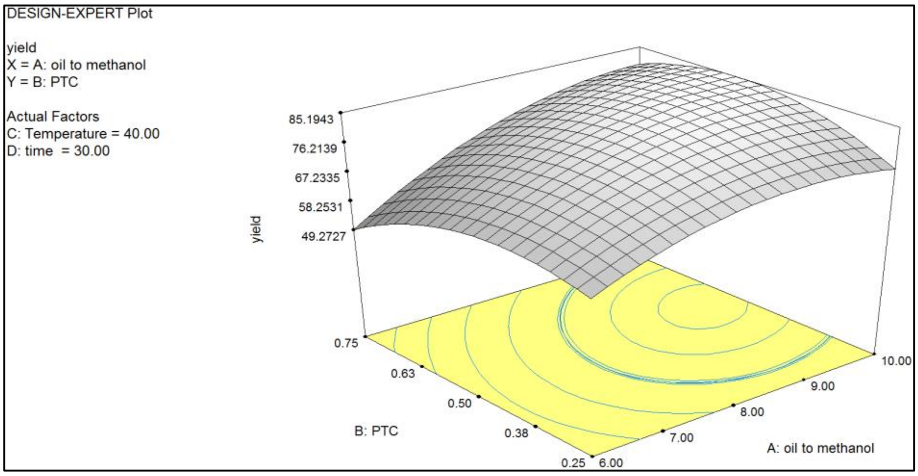

Figure 13: PTC and Oil to methanol molar ratio

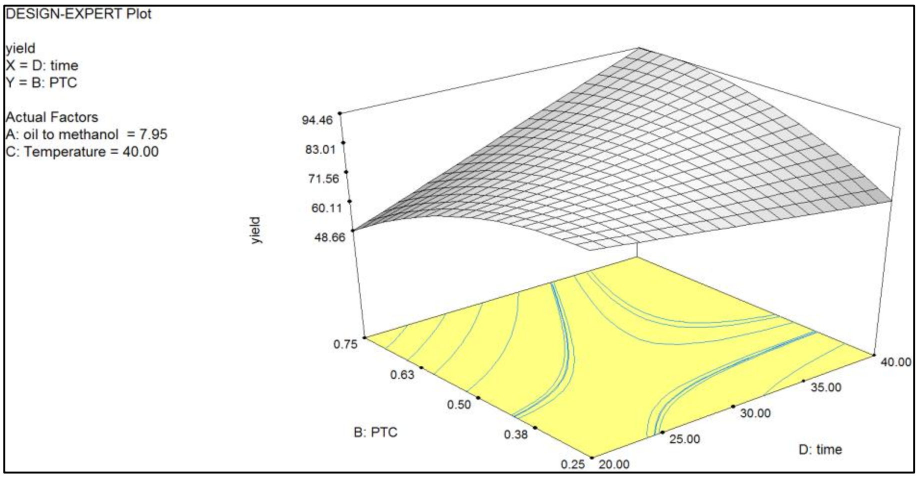

Figure 14: PTC and reaction time

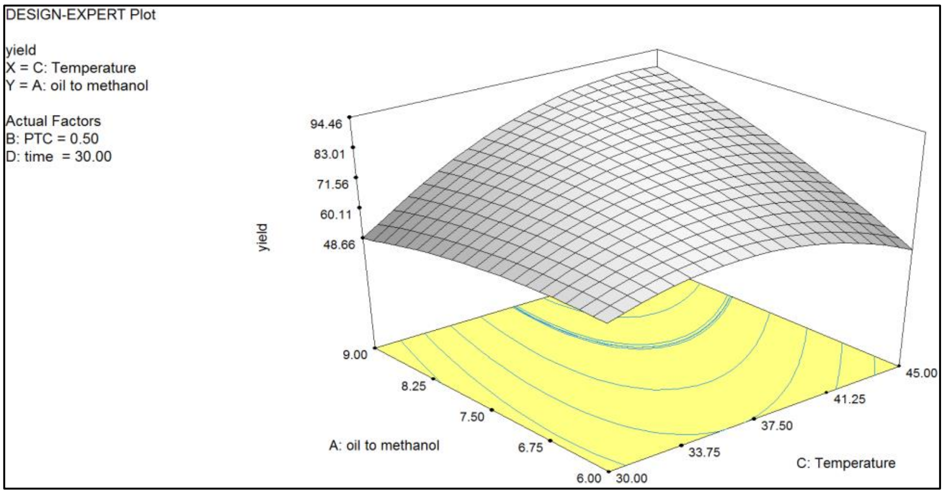

Figure 15: Oil to methanol molar ratio and reaction temperature

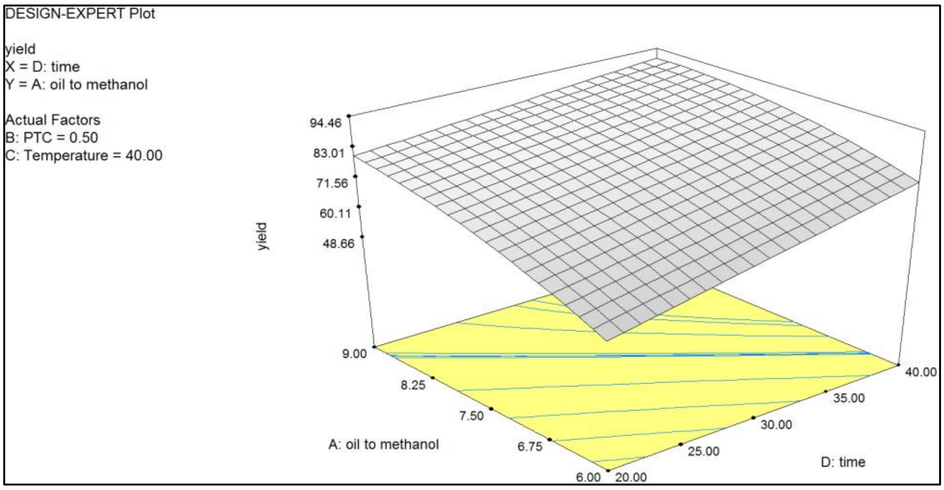

Figure 16: Oil to methanol molar ratio and reaction time

4.5 Optimization of FAME yield with and without PTC

The optimization of FAME yield with and without PTC is established by using the response surface methodology optimizer and are presented in table 6. Experiments were conducted by implementing the optimal condition to test the significance of the model predictions. 76.8% of FAME yield without PTC is obtained as the experimental value. The expected yield suggested by the model is 78.76 which is close enough to the experimental value with error of 2.4%. Similar to FAME yield with PTC, the experimental value obtained was 89.85% which come close agreement with the suggested model predictions 91.05% with an error of 1.31%. From the results, it shows that higher FAME yield is obtained by transesterification with the presence of phase transfer catalyst. Hence, the objective is achieved.

Table 7: Optimum operating condition of FAME yield with and without PTC by transesterification

Factor	**Optimum value for FAME yield without PTC**	**Optimum value for FAME yield with PTC**
Castor oil to methanol molar ratio	7.91	9.43
Mass of NaOH to mass of castor oil	0.97g	-
PTC to NaOH molar ratio	-	0.46
Reaction Temperature	60°C	45.3°C
Reaction Time	31.23min	25.91min
Predicted FAME value	78.76%	91.05%
Experimental FAME value	76.8%	89.85%

Chapter 5: Conclusion and Recommendations

5.1 Conclusion

Transesterification of castor oil with the presence of cetyltrimethylammonium bromide as phase transfer catalyst and without the presence of phase transfer catalyst were investigated. Transesterification reaction with the presence of cetyltrimethylammonium bromide as PTC gave higher FAME yield 91.05, after optimization compared to transesterification reaction conducted without PTC which gives 76.08%. At optimum reaction condition, a good agreement was observed between yield of biodiesel obtained experimentally and by predicted model equation. The biodiesel obtained by transesterification with the presence of phase transfer catalyst is higher compared to the biodiesel produced by transesterification without the presence of phase transfer catalyst. Therefore, the objective of this project is achieved successfully

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5.2 Recommendations

As for future works and recommendation, phase transfer catalyst should be used with other non-edible oil for example, Kapok oil, Margosa oil, Neem oil and any other non-edible oil in order to investigate the effects on biodiesel yield with the presence of phase transfer catalyst. 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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