SYNTHESIS AND CHARACTERIZATION OF TITANIUM DIOXIDE (TiO_2) NANOMATERIALS FOR BIODIESEL PRODUCTION

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Dissertation submitted in partial fulfillment of the requirements for the
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CERTIFICATION OF APPROVAL

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Approved by,

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(   )

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September 2014

CERTIFICATION OF ORIGINALITY

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

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TENGKU SYAZA AMALINA BT TENGKU AZAM

ABSTRACT

This project studies the optimization for parameters affecting the biodiesel production and synthesized the mixed metal oxides catalyst which is CeO_2-TiO_2. The feedstock used is crude palm oil which undergone the oil analysis prior the transesterification process. The FFA of crude palm oil is 0.11%, which is readily below 2%. Therefore, one-step transesterification is applicable. Based on the optimization using Response Surface Methodology (RSM), the optimized conditions are reaction temperature is 55°C, methanol to oil ratio is 11.05:1, 1.0 wt% catalyst concentration and reaction time is 60 minutes using NaOH as catalyst. The yield is 53.2%. The transesterification of palm oil is repeated under the same conditions using synthesized catalyst which yield 59.7% biodiesel. The CeO_2-TiO_2 is characterized using FTIR, SAP, VPFESEM and Raman Spectrometer. The reusability of the catalyst also is tested which shows that it can be recycled for about 5 runs with the decrement of yield not more than 3% for every run. This proves the ability of heterogeneous catalyst to be reused in more than one cycle. Besides, the catalyst dosage and reaction time effect on biodiesel yield are also tested. The results show that as the dosage of catalyst and reaction time increase, the yield also increases. In addition, experimental-simulation comparison is done by using ASPEN HYSYS software which shows slight different of 2.3%.

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First and foremost, I would like to express my greatest gratitude to The Almighty for blessing a good health and assistance throughout my four year studies in Universiti Teknologi PETRONAS (UTP) especially in completing this Final Year Project.

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CHAPTER 1

INTRODUCTION

1.1 Background

Biodiesel is a renewable and biodegradable alternative fuel to diesel from petroleum. Currently, biodiesel is produced by transesterification reaction from vegetable oils or animal fats to produce fatty acid methyl esters (FAME). However, the major obstacle for biodiesel from vegetable oils to survive in market is due to high cost of raw materials. Furthermore, oil is significant element in the human food supply chain, thus their long term conversions to biodiesel may not be sustainable. The use of cheap feed stocks, such as, waste cooking oil, soap stock (byproduct of vegetable oil refinery) and non-edible oils may improve the economic feasibility of biodiesel [1, 2].

Homogeneous alkali or acid are the general catalysts in biodiesel industry because of their high catalytic activity. However, majority of low-cost biodiesel feed stocks are easily saponified by alkali catalyst due to their high free fatty acid, FFAs content. These oils are usually catalyzed by sulfuric acid in biodiesel production. Plus, it also caused the equipment corrosion and environmental problem. Moreover, high purification cost and time-consuming process in separating the catalysts from the product is one of the disadvantages. Li et al. stressed that the development of heterogeneous and high-performance catalysts is vital to enhance the efficiency of process and yield of the product in economical way and environmentally safe [3].

Titanium Dioxide, the transition metal oxides has four commonly known polymorphs which are anatase (tetragonal), brookite (orthorhombic), rutile (tetragonal), and TiO2 (B) (monoclinic) [4]. The functional properties such as surface area, defects quantity, temperatures of phase transition, and the stability of the different phases are determined by the size and shape of the Titanium Dioxide particles. Besides, the crystalline phase, the crystallite size, and the porosity also affecting the optical, textural, and catalytic properties of Titanium Dioxide. Therefore, the preparation of nanomaterials of Titanium Dioxide with specific properties for several applications including biodiesel industry is of interest due to the new properties expected [5].

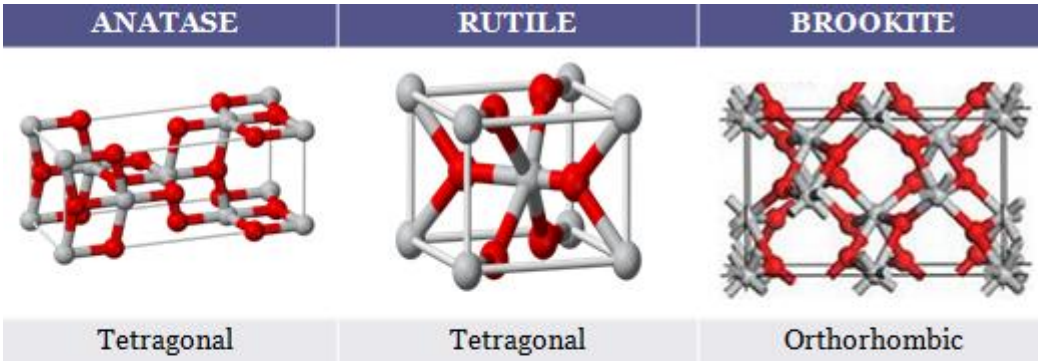


Figure 1Titanium Dioxide Morphologies

In this study, the activity of cerium oxide doped Titanium Dioxide nanomaterials as catalysts in biodiesel production is investigated. This method is done to enhance its catalytic properties to improve the production of biodiesel. Both Titanium Dioxide nanomaterials and biodiesel prepared are characterized using various analytical equipment to determine several properties which vital in enhancing biodiesel yield. In addition, parametric optimization using response surface methodology also is performed.

1.2 Problem Statement

Recently, environmental pollutions especially due to the use of fuels have gathered the great world concern. These issues have encouraged more research in finding the alternatives of renewable energy including the production of biodiesel. Biodiesel can be synthesized by transesterification of several feed stocks for instance vegetable oils and animal fats with alcohol using either homogenous or heterogeneous catalysts. However, the application of homogenous catalysts in the production process is costly due to separation process of catalysts from reaction mixture. Hence, the substitution of common homogenous catalysts with heterogeneous catalysts solves numerous problems related to economic and environmental aspects as this type of catalyst is ecological friendly and less expensive. Besides, this catalyst is easier to be extracted from liquid products and can be manipulated to increase the activity and selectivity. The development of new active materials in transesterification and esterification for instance Titanium Dioxide is highly feasible to be used in biodiesel production due to its improved catalytic activity.

1.3 Objectives and Scope of Study

The objectives of the project are as the following:

- To synthesis the cerium oxide doped Titanium Dioxide (TiO_2) nanomaterials catalyst.
- To characterize the synthesized cerium oxide doped Titanium Dioxide (TiO_2) nanomaterials catalyst.
- To perform the parameters optimization for transesterification reactions of Palm Oil.
- To investigate the activity of Titanium Dioxide (TiO_2) nanomaterials as catalyst in transesterification reactions of Palm Oil to produce biodiesel.
- To study the utilization and conversion of biodiesel byproduct into value added chemical.

The scopes of study covered for this project include:

- Synthesizing of cerium oxide doped Titanium Dioxide (TiO_2) nanomaterials.
- Characterization of cerium oxide doped Titanium Dioxide (TiO_2) nanomaterials by various analytical tools to identify the structural properties.
- Analyzing the effect of cerium oxide doped Titanium Dioxide (TiO_2) nanomaterials as catalyst in biodiesel production.
- Performing parametric optimization by response surface methodology using Design Expert Software.
- Constructing brief process on converting glycerol into 1,2-propanediol.

CHAPTER 2

LITERATURE REVIEW AND THEORY

Biodiesel can be defined as monoalkyl esters made up of long chain fatty acids, derived from the feedstock used. One of the alternatives to the usage of fossil fuels is the crude oils and fats extracted from vegetable and animal sources. However, according to Dupont *et. al*., these extractions cannot undergo direct combustion in modern diesel engines because of their high viscosity and density [6]. These types of oils are made up of triglycerides which can be converted into biofuel or biodiesel by several techniques. The techniques are pyrolysis (cracking), micro emulsification and also transesterification [7]. Biodiesel is a promising alternative due to its environmental-friendly properties. This type of diesel is non-toxic and biodegradable renewable fuel comprised of mono-alkyl esters of long chain fatty acids. It is characterized by excellent properties as diesel engine fuels and can be used in compression–ignition engines with little or without any modifications. Apart from that, it emits low emission of CO, SO_x and particulate matter during the combustion [8].

There are numerous advantages of biodiesel compared to diesel derived from petroleum in many aspects. Besides environmentally friendly as it emits less air pollutants and greenhouse gases, it is safer to handle compare to petroleum derived diesel [9]. Biodiesel also applicable to be used in most of diesel engines including the new ones. Besides, biodiesel has high flash point, make it available to blend with normal diesel fuel. Plus, it also can be used in its original or pure form [10]. The application of biodiesel allows the balancing in many aspects which are economic, agriculture and environment. Transesterification is the most common method in biodiesel production. Fan et al. define transesterification as chemical reaction involving triglycerides and alcohol, normally methanol or ethanol, in the presence of either homogeneous or heterogeneous catalyst to form esters and glycerol [11]. The glycerol produced as byproduct can be utilized and converted to other products for industrial applications. Figure 1 shows a general scheme for free fatty acid esterification and triglyceride transesterification.

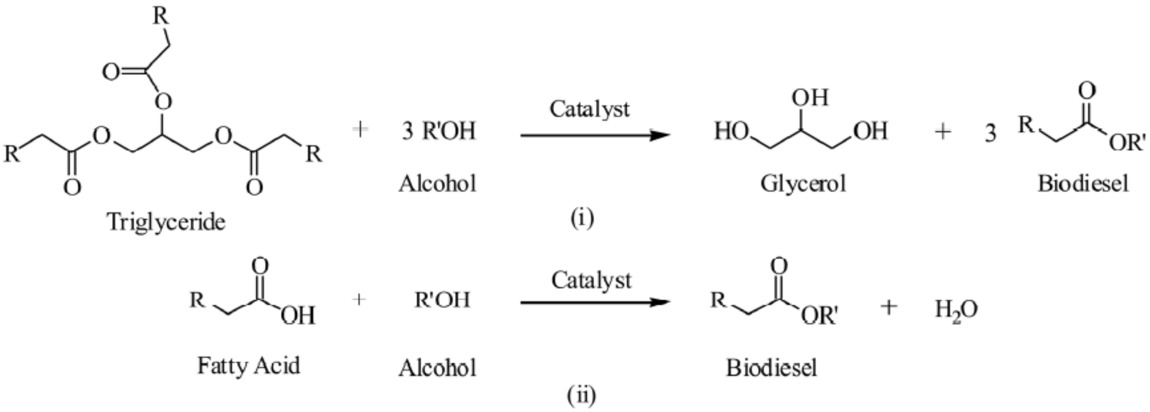


Figure 2 Schematic of (i) triglyceride transesterification and (ii) free fatty acid esterification.

In producing biodiesel, generally, homogeneous catalysts possess advantages including high activity and mild reaction. However, the use of homogeneous catalysts can cause soap production which will affect the quality of biodiesel yield. Besides, in the homogeneous process, the catalyst is consumed which means, its quantity decreasing along the reaction, thus reducing the catalytic efficiency, causing the increase in viscosity and gels are formed. In addition, the removal of the catalyst after reaction is difficult and uses a lot of cost. Therefore, the cost of biodiesel production using homogeneous catalysts are still not competitive compared to cost of diesel produced from petroleum. Because of this scenario, the usage of heterogeneous catalysts gained the attention as they solve many drawbacks of traditional homogeneous catalysts. However, the efficiency of the heterogeneous process still depends on variables of type of oil, molar ratio alcohol to oil, temperature and catalyst type [12].

Metal oxides are important class of materials used in industrial processes including the conversion of fuel cells. One of them is mixed metal oxides generated by the doping of nanoparticles of an oxide on top of the surface of another oxide. This activity enhance the combination of structural and electronic properties to the oxide nanoparticles, also the interfacial region between the oxide and the metal. Theoretically, these doping could expose the molecules to unique structures which will enhance the catalytic ability. When considering the CeO_x/TiO_2 system, the two oxides are prototypical lanthanide (CeO_2) and transition metal (TiO_2) oxides. According to previous researches, a unique mixture of ceria morphologies on titania has a significant impact on the performance of the mixed-metal oxide in catalytic processes[13].

Figure 3 Cerium Oxide Morphology

There are several researches done before on transesterification of vegetable oils using mixed metal oxides. Among the metal oxides used, cerium oxide is widely used to be mixed with other metal catalysts in order to increase the catalytic activity in transesterification reactions. In 2011, Yu et. al used CaO-CeO_2 for transesterification of Pistacia Chinensis oil in yielding biodiesel. The results show that the addition of cerium improved the stability of the solid base catalyst. This is due to Ce ions substitutes Ca ions on the surface of the heterogeneous catalyst. The best catalyst for this research is CaO-CeO^2 with ratio of Ce/Ca 0.15 and the catalyst is calcinated at 700 ^oC [14]. Other research using cerium oxide is done by Manríquez et. al. MgO-CeO_2 is used as solid base catalyst in converting waste cooking oil into biodiesel. Under the conditions of temperature of 60 ^oC, methanol to oil ratio of 4 : 1 and 1 hour reaction time, the conversion shows more than 50%, which is better than MgO catalyst without CeO_2 deposition with only 44% conversion. This shows that CeO_2 improved the catalytic ability of MgO [15]. Another example of CeO_2 application is done by Soares et. al. Transesterification of soybean oil is done under condition of methanol to oil ratio is 9 : 1, temperature is maintained at 67^oC

and reaction time of 4 hours, Ce-Mg-Al catalyst gives yield of more than 90% of biodiesel compare to without cerium ions. These findings proved that CeO_2 improved the stability and catalytic ability of metal oxides catalyst used in transesterification reactions. [16].

Various of edible and non-edible oils for example soybean, palm, rapeseed, sunflower seed, peanut, cottonseed, coconut, palm kernel, olive, jatropha, castor and rubber has been identified for the production of biodiesel [17]. Nowadays, soybean is the common feedstock used in USA while in Europe, rapeseed oil is used. For Asian countries, crude palm kernel oil and crude coconut oil are explored and used as FAME feed stocks [18]. However, palm oil is identified as the world’s cheapest vegetable oil, which gathers the attention of utilizing this oil as feedstock for biodiesel production.

Table 1 General Properties of Palm Oil

Fatty acids	**Percentage (%)**
Lauric, C-12 :0	0.1
Myristic, C-14 : 0	1.0
Palmitic, C – 16 : 0	42.8
Stearic, C -18 : 1	4.5
Oleic, C – 18 : 1	40.5
Linoleic, C – 18 : 2	10.1
Linolenic, C – 18 : 3	0.2
Other/ Unknown	0.8

Previously, many researches shows the potential of palm oil to be converted into high quality biodiesel. Bo et. al. used palm oil as feedstock in producing biodiesel in the presence of KF/AL_2O_3 as base catalyst. The conditions of the reaction are temperature of 65^oC, catalyst concentration of 4 wt%, methanol to oil ratio is 12 : 1 and reaction time is 3 hours. This reaction gives the FAME yield over 90% [19]. Another research is done by Fei et. al using palm oil as feedstock to produce biodiesel. This research focus on optimizing the parameters value in order to increase the yield or conversion of methyl esters. From the range inserted in the software for every parameters, it is found that the optimum conditions for palm oil transesterification are methanol to oil ratio of 8 wt% of catalyst which is sulphated zirconia alumina, a very high temperature of 127^oC and reaction time of 3 hours. The FAME yield is found to be more than 80% [17].

CHAPTER 3

METHODOLOGY AND PROJECT WORK

3.1 Materials and Equipment

The analytical equipment used for cerium oxide doped Titanium Dioxide (TiO_2) nanomaterials catalyst and biodiesel characterizations are as follows:

Table 2 Analytical Equipment

No	Analytical Equipment	Functions
1	Fourier Transform Infrared Spectroscopy (FT-IR)	Organic functional group
2	Scanning Electron Microscopy (SEM)	Surface topography
3	Gas Chromatography (GC)	Relative amount of components determination
4	Surface Area and Pore Size Analyzer (SAP)	Surface are and pore size of the catalyst
5	Raman Spectrometers	Active side of catalyst

In order to perform the acid esterification and base transesterification to produce biodiesel from palm oil, the following chemicals are needed:

1. Raw Palm Oil
2. Potassium Hydroxide, KOH
3. Phosphoric Acid, H_3PO_4
4. Nitric Acid, HNO_3
5. Sodium Hydroxide, NaOH
6. Isopropanol

7 Toluene

8. Phenolphthalein

3.2 Procedures

The procedures in this project can be divided into two parts which are synthesizing and characterization of CeO_2-TiO_2 nanomaterials and biodiesel production.

3.2.1 Catalyst Preparation

To prepare the catalyst, Cerium Nitrate Hexahydrate powder is used as cerium precursor.

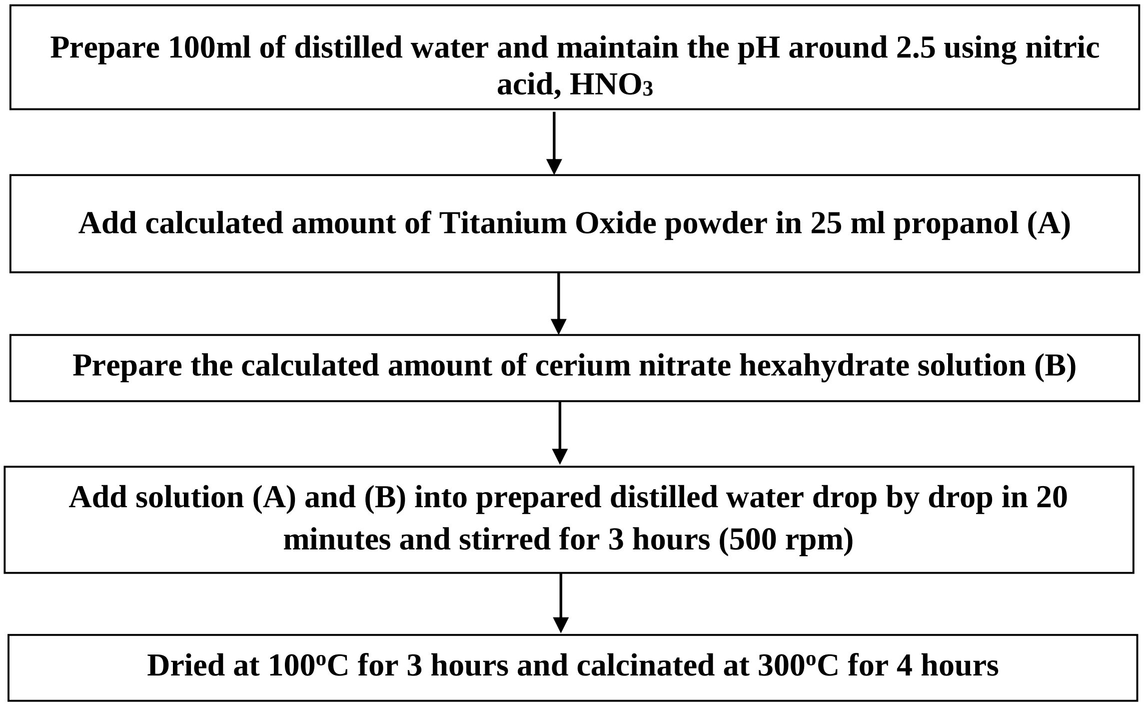
To prepare 0.4 wt% of CeO_2/TiO_2 catalyst:

Molecular weight of Cerium Nitrate Hexahydrate = 434.22 g/mol

Molecular weight of Cerium Oxide (CeO_2) = 172.11 g/mol

$$\frac{434.22}{172.11}\, X\ 0.4 = 1\ g\ of\ Cerium\ Nitrate\ Hexahydrate$$

Titanium Oxide = 1.5 g



Prepare 100ml of distilled water and maintain the pH around 2.5 using nitric acid, HNO_3

Add calculated amount of Titanium Oxide powder in 25 ml propanol (A)

Prepare the calculated amount of cerium nitrate hexahydrate solution (B)

Add solution (A) and (B) into prepared distilled water drop by drop in 20 minutes and stirred for 3 hours (500 rpm)

Dried at 100°C for 3 hours and calcinated at 300°C for 4 hours

Figure 4 General procedures for synthesizing CeO_2-TiO_2

3.2.2 Biodiesel Production

As for the biodiesel production, the general procedures are as follow:

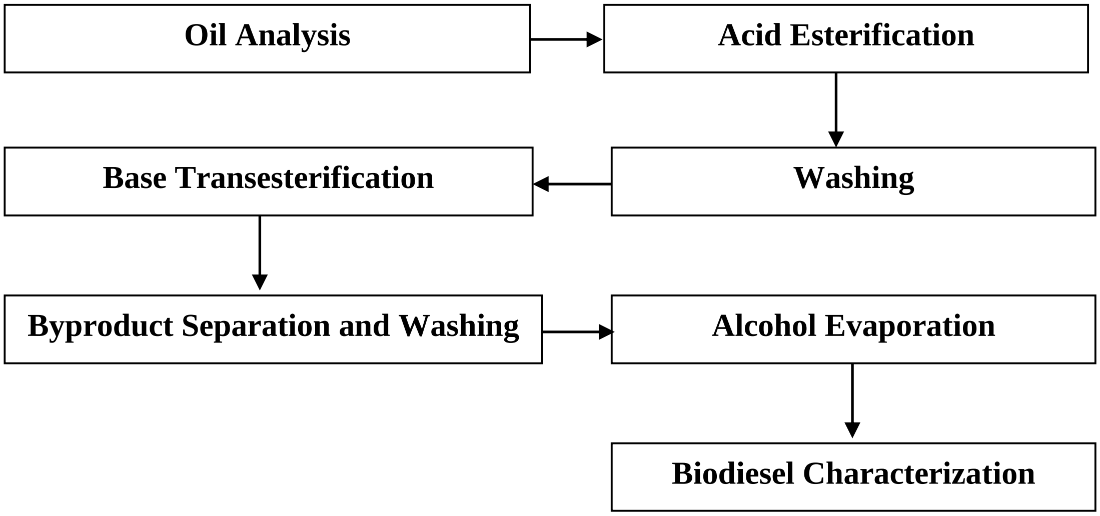


Figure 5 General procedures for biodiesel production.

3.2.2.1 Oil Analysis

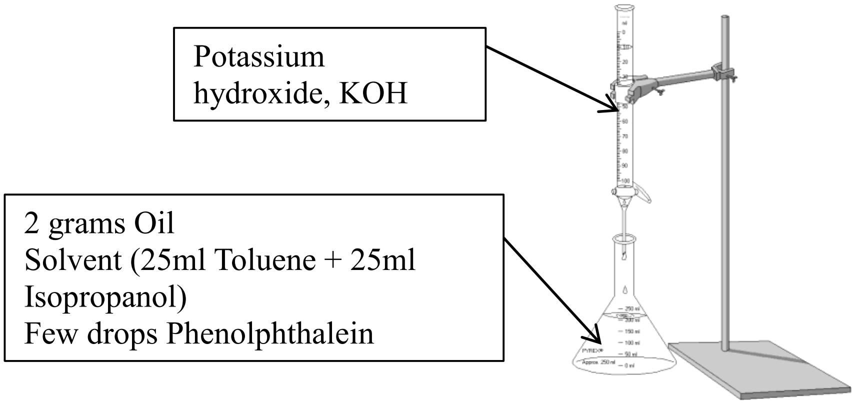


Figure 6 Titration for oil analysis

The basic oil analysis is to be performed on the crude palm oil following the American Oil Chemists' Society (AOCS) method [20]. This analysis is done to detemine the acid value and the free fatty acid (FFA) content in the oil. High FFA can lead to saponification of the oil instead of producing biodiesel. Hence, to obtain high yield of biodiesel, it is important to have as low FFA content as possible.

To determine the FFA content, titration is done by using potassium hydroxide as titrate and is titrated to a mixture of 25 ml isopropanol and 25 ml toluene with phenolphthalein as the indicator. A blank sample is first titrated and proceed to the second titration with 2 grams of oil added to the conical flask.

The acid value is then calculated by using the equation

$$Acid\ value = \frac{(V_a - V_b) \times N \times \rho}{W}$$

Equation 1 Acid Value Determination

whereby ,

V_a : volume of potassium hydroxide used against sample

V_b : Volume of potassium hydroxide used against blank

N : Normality of oil

ρ : Density of oil

W : Weight of sample used

For the determination of FFA content, titration is done by using potassium hydroxide as titrate and is titrated to a mixture isoprpylene and toluene with phenolphthalein as the indicator.

The FFA value is calculated from the acid value

$$FFA = \frac{Acid\ value}{2}$$

Equation 2 Free Fatty Acid (FFA) Determination

3.2.2.2 Acid Esterification

The oil undergoes acid esterification in which it reacts with lower alcohol such as methanol with the presence of acid catalyst in order to lower the acid and free fatty acid values. The acid catalyst used is sulphuric acid, H_2SO_4. The acid value is the number of milligrams of potassium hydroxide needed to neutralize the free acid in 1 gram of sample. The experiment is conducted by using a triple neck round bottom flask set with a reflux condenser. This is to avoid any methanol loss. Each experimental run requires 50 grams of oil to be heated to the desired temperature. Methanol and sulphuric acid is then added in a specific amount and stirred for a specific time. The reaction is stopped and the sample is put into the separating funnel to separate the pretreated oil and excess of methanol and catalyst. The treated oil is separated and collected for base transesterification process next. The free fatty acid amount should be less than 2% before proceeding to the base transesterification else the acid esterification should be repeated with different parameter values.

Conditions used in this project:

Oil amount = 50 gram

Time = 2 hours

Temperature = 60 ^{o}C

Methanol amount = $\frac{50\ g\ oil}{MW\ of\ oil}\ X\ MW\ of\ methanol\ X\ ratio = x\ gram$

$$V = \frac{x\ gram\ of\ methanol}{density\ of\ methanol} = y\ ml\ of\ methanol$$

Sulphuric Acid amount = 5% of oil amount

3.2.2.3 Base Transesterification

Similar to acid esterification, the oil or triglycerides undergoes esterification but this time with the presence of base catalyst. The base catalyst used is the homogeneous catalyst, sodium hydroxide. For this part, 50 grams of pre-treated oil is mixed together with methanol and the catalyst then is heated and stirred for a specific time. Water bath is used to promote even heating. Then the sample undergo separation in the separating funnel and will be left for 24 hours. Two layers will form; the upper layer is methyl ester (biodiesel) while the lower layer is glycerol, methanol and other impurities. The condition for every runs of the experiment are obtained using Response Surface Methodology from Design Expert Software. From the software, there are 21 runs of experiment should be done in order to obtained the optimized conditions.

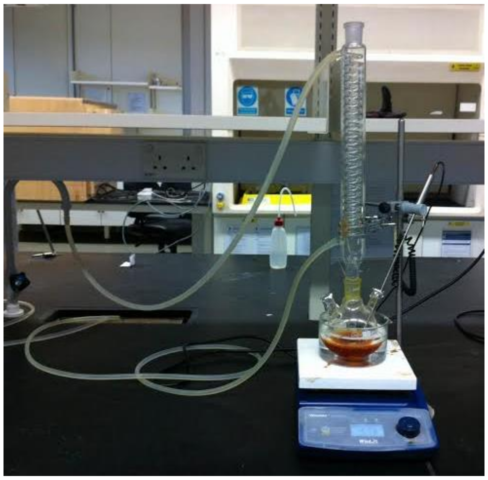


Figure 7 Experiment set up

3.2.2.4 Parameters Optimization

The optimization of base transesterification process is performed and optimized using the Response Surface Methodology (RSM) from the software Design Expert 6.0.8. To investigate the effects of four parameters on the yield, the total number of experiments needed are 21 runs. The process parameters and its ranges of values are shown in Table 3. The low values are denoted as -1 while the high values are denoted as +1. These parameters are randomized to reduce the unexpected variability on the response yield.

Table 3 Value ranges for parameters

Parameters	**-1**	**0**	**+1**
A : Time (min)	30	60	90
B : Temperature (^oC)	45	55	65
C : Catalyst concentration (wt%)	0.5	1.0	1.5
D : Oil to methanol ratio	3	6	9

From the 21 runs, the optimized conditions are then determined and used for experiment with heterogeneous catalyst for biodiesel production. Taking these values, the experiment is repeated by using CeO_2- TiO_2. The yield is compared to determine the effect of catalyst towards the yield of biodiesel. The Response Surface Methodology gives formulation of a second order equation that describes the process. The general equation is as follows:

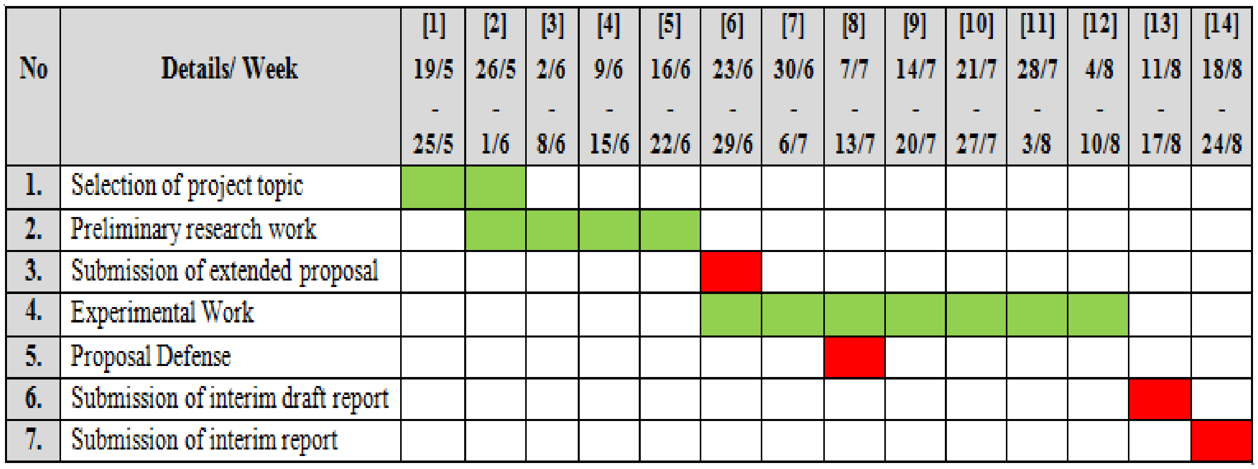
$$\mathbf{Y = \beta_0 + \beta_1 X_1 - \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 - \beta_{11} X_1^2 + \beta_{22} X_2^2 - \beta_{33} X_3^2 - \beta_{44} X_4^2}$$
$$\mathbf{+\beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 - \beta_{14} X_1 X_4 + \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4 - \beta_{34} X_3 X_4}$$

Equation 3 General Equation for Transesterification

where Y is the methyl ester yield percentage, β_0 is the intercept term, $\beta_1, \beta_2, \beta_3$ and β_4 are linear coefficients, β_{11}, β_{22}, β_{33}, β_{44} are quadratic equations, β_{12}, β_{13}, β_{14}, β_{23}, β_{24}, β_{34} are interactive coefficients and X_1, X_2, X_3, X_4 are the independent variables. The optimized conditions are then determined and used for further study with synthesized catalyst for biodiesel production.

3.3 Project Timeline

Table 4 Project Gantt Chart (May - August)



No	Details/ Week	[1] 19/5 - 25/5	[2] 26/5 - 1/6	[3] 2/6 - 8/6	[4] 9/6 - 15/6	[5] 16/6 - 22/6	[6] 23/6 - 29/6	[7] 30/6 - 6/7	[8] 7/7 - 13/7	[9] 14/7 - 20/7	[10] 21/7 - 27/7	[11] 28/7 - 3/8	[12] 4/8 - 10/8	[13] 11/8 - 17/8	[14] 18/8 - 24/8
1.	Selection of project topic	🟩	🟩												
2.	Preliminary research work		🟩	🟩	🟩	🟩									
3.	Submission of extended proposal						🟥								
4.	Experimental Work						🟩	🟩	🟩	🟩	🟩	🟩	🟩		
5.	Proposal Defense								🟥						
6.	Submission of interim draft report													🟥	
7.	Submission of interim report														🟥

Table 5 Project Gantt Chart (September- Disember)

No	Details/ Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Project Work														
	Catalyst Synthesis	🟩	🟩												
	Catalyst Characterization							🟩	🟩	🟩	🟩				
	Oil Analysis			🟩											
	Acid Esterification				🟩										
	Base Transesterification					🟩	🟩	🟩							
	Characterization of biodiesel							🟩	🟩	🟩	🟩				
2	Submission of Progress Report								🟥						
3	Pre-SEDEX											🟥			
4	Submission of Final Report Draft												🟥		
5	Submission of Dissertation (Soft Bound)													🟥	
6	Submission of Technical Paper													🟥	
7	Viva														🟥
8	Submission of Dissertation (Hard Bound)														🟥

🟥 Submission 🟩 Process

3.4 Key Milestones

Table 6 Project Key Milestones

TASK	DATE	WEEKS	REMARKS
Selection of project topic	19/5 – 1/6	1-2	**DONE**
Preliminary research work	26/5 – 22/6	1-4	**DONE**
Completion and submission of extended proposal	23/6-29/6	5	**DONE**
Experimental work	23/6 – 10/8	1-8	**DONE**
Proposal Defense	9/7/2014	8	**DONE**
Submission of interim draft report	11/8 – 17/8	13	**DONE**
Submission of interim report	18/8 – 24/8	14	**DONE**
Continuation in Semester 2			
Project Work	22/9/2014 – 30/11/2014	1-10	**DONE**
Submission of Progress Report	12/11/2014	8	**DONE**
Pre-SEDEX	3/12/2014	11	**DONE**
Submission of Final Report Draft	9/12/2014	12	**DONE**
Submission of Dissertation (Soft Bound)	15/12/2014	13	**DONE**
Submission of Technical Paper	15/12/2014	13	**DONE**
Viva	22/12/2014 - 24/12/2014	14	**DONE**
Submission of Dissertation (Hard Bound)	31/12/2014	14	**DONE**

CHAPTER 4

RESULTS AND DISCUSSION

All the results from all parts of experiment are recorded and analyzed in this chapter.

4.1 Oil Analysis

Prior to esterification and transesterification process, 3 types of oil are tested to identify the acid value and free fatty acid (FFA) amount. Therefore, the oil analysis is done to all three types of oil which are Palm oil, Castor Oil and Kapok Seed Oil. Based on the analysis, the FFA value for the respective oils are as follows:

Table 7 Free fatty acid (FFA) amount for untreated oils

Type of Oil	Acid Value (mgKOH/g)	FFA amount
Palm Oil	0.22	0.11 %
Castor Oil	3.40	1.70%
Kapok Seed Oil	15.48	7.74%

For this project, Crude Palm Oil is used as the feedstock.

4.2 Acid Esterification

Acid esterification is done for the crude palm oil to identify the change of the free fatty acid (FFA) content. Low FFA is vital in preventing saponification during the base transesterification process. The parameters used and the results of the acid esterification is as Table 8.

Table 8 Result of acid esterification of palm oil

Run	**Time (min)**	**Temperature (ºC)**	**Oil to methanol ratio**	**Catalyst comcentration (wt%)**	**Acid value (mgKOH/g)**	**FFA**
1	120	60	9	5	0.5	0.25

For this project, the FFA value should be lower than 2% to proceed with base transesterification process. Based on Table 8, the result obtained shows that the FFA is increased after the acid esterification, which is more that the FFA of untreated palm oil as shown in Table 7. This shows that the acid content of the oil has not decreased, instead it slightly increases. This happened due to the acid catalyst is not fully separated within the mixture. To obtain the correct result without being affected by the acid catalyst, the washed off water should be of the same pH before and after washing the biodiesel. A large amount of water is needed and this is not economically preferable. Therefore, for this project, the crude palm oil is used for the base transesterification as the FFA amount is already below 2%.

4.3 Base Transesterification

The parameter tested for this project are reaction time, temperature, catalyst concentration and methanol to oil ratio. The range of value for each parameter is tabulated in Table 3. This part of experiment is done according to the conditions tabulated in Design Expert software as shown in Table 9. The yield percentage is calculated using the formula:

$$\text{Biodiesel yield} = \frac{\text{Weight of oil after base transesterification}}{\text{Weight of oil before base transesterification}} \text{ x } 100\%$$

Equation 4 Biodiesel Yield

Table 9 Yield percentage for every experimental run

Run	A : Time (min)	B : Temperature (°C)	C : Catalyst concentration (wt %)	D: Methanol to Oil Ratio	Yield (%)
1	110.45	55.00	1.00	6.00	40.9
2	90.00	65.00	1.50	3.00	40.5
3	90.00	65.00	0.50	3.00	24.2
4	30.00	65.00	0.50	9.00	20.1
5	60.00	55.00	1.00	11.05	53.2
6	90.00	45.00	1.50	9.00	30.3
7	30.00	45.00	0.50	3.00	15.3
8	60.00	71.82	1.00	6.00	40.7
9	60.00	55.00	1.00	6.00	40.1
10	60.00	55.00	1.84	6.00	42.0
11	9.55	55.00	1.00	6.00	0.0
12	60.00	55.00	1.00	6.00	40.1
13	60.00	38.18	1.00	6.00	45.6
14	60.00	55.00	1.00	6.00	40.1
15	60.00	55.00	1.00	0.95	0.0
16	60.00	55.00	1.00	6.00	40.1
17	60.00	55.00	1.00	6.00	40.1
18	30.00	45.00	1.50	3.00	17.7
19	90.00	45.00	0.50	9.00	28.4
20	30.00	65.00	1.50	9.00	21.7
21	60.00	55.00	0.16	6.00	13.2

Based on the tabulated data, it is found that Run 5 has the highest biodiesel yield which is 53.2%. Therefore, the parameters of this run is considered as the optimum conditions which will be used to test the catalyst synthesized, which are as follows:

A. Time (min) = 60 minutes
B. Temperature (^{o}C) = 55 ^{o}C
C. Catalyst Concentration (wt%) = 1.0 wt%
D. Methanol to Oil Ratio = 11.05 : 1

There are two runs which did not give any yield as all the treated oil and other mixture in separating funnel turn into solid after being left for separation for 24 hours. This happened due to amount of glycerol produced as the byproduct of transesterifcation reaction to produce biodiesel.

4.4 Model Fitting and Statistical Analysis

Analysis of variance or ANOVA is used to study the significance of the output obtained from the input tested. The output which is the yield of biodiesel (%) is in the range of 0-53.2%. The second order model equation in terms of coded factors are as follow:

$$\mathbf{Yield = 40.15 + 12.16A - 1.46B + 5.17C + 15.82D - 7.01A^{2} + 1.02B^{2} - 4.48C^{2} - 4.83D^{2} + 15.47AB + 1.77AC - 3.31AD + 1.70BC + 6.08BD - 1.90CD}$$

Equation 5 Second Order Model Equation

The ANOVA also gave the statistical analysis for the quadratic model as shown in Table 10. The R^2 value indicates whether the model fits the data of the experiment. The best fitting between the model and the experimental dat ais shown through the value of 1.0000. The closer the R^2 value to 1.0000, the better the fitting is. Based on the analysis, the R^2 value is 0.9749. This justifies the given equation is acceptable and reliable to be used in simulating the reaction. The Model F-value of 16.66 shows that the model is significant. There is only a 0.12% chance that a "Model F-Value" this large could occur due to noise.Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, C, D, A^2, C^2, D^2, AB, BD are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. Parameter D which is methanol to oil ratio shows the highest F-value, which indicates that it is the most influencing parameter for the base transesterification as compared to the other three parameters.

Table 10 ANOVA Analysis

Source	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**
Model	4319.97	14	308.57	16.66	0.0012 significant
A	836.40	1	836.40	45.15	0.0005
B	12.01	1	12.01	0.05	0.4515
C	365.34	1	305.34	10.72	0.0044
D	1415.12	1	1415.12	76.30	0.0001
A^2	733.61	1	733.01	30.60	0.0008
B^2	15.52	1	15.52	0.84	0.3953
C^2	200.74	1	200.74	16.18	0.0060
D^2	348.03	1	348.03	18.83	0.0040
AB	702.68	1	702.08	42.79	0.0006
AC	25.20	1	25.20	1.36	0.2877
AD	36.23	1	36.23	1.96	0.2115
BC	23.12	1	23.12	1.25	0.3067
BD	122.08	1	122.08	0.02	0.0421
CD	28.88	1	28.88	1.50	0.2583
Residual	111.15	6	18.53		
Lack of Fit	111.15	2	55.58		
Pure Error	0.000	4	0.000		

4.5 Optimization of Parameter Values

The optimization of parameter values are conducted by using the Design Expert 6.0.8. Perturbation plot compares all factors influencing the yield of biodiesel. Figure 8 shows the perturbation plot for base transesterification for palm oil biodiesel based on studies conducted. The steepest plot shows the most significant and influential factor towards the response, which is parameter D, methanol to oil ratio. The second most influencing factor is parameter A, reaction time. Figure 9 shows the comparison between actual values of FFA% with the predicted values base transesterification respectively. The graph shows that the points are scattered in linear, which means that the experimental values are close to the predicted values. In addition, the graph shows that the actual values indicated by the colored dots lie near the predicted line thus these results are reliable.

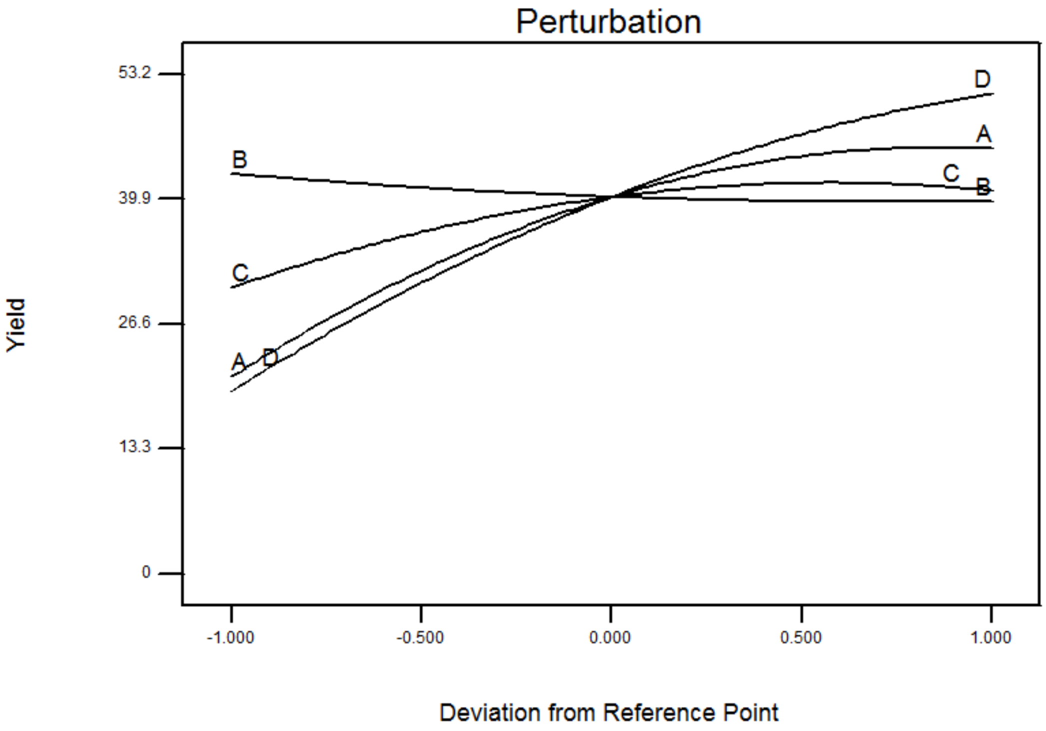


Figure 8 Perturbation plot for Base Transesterification

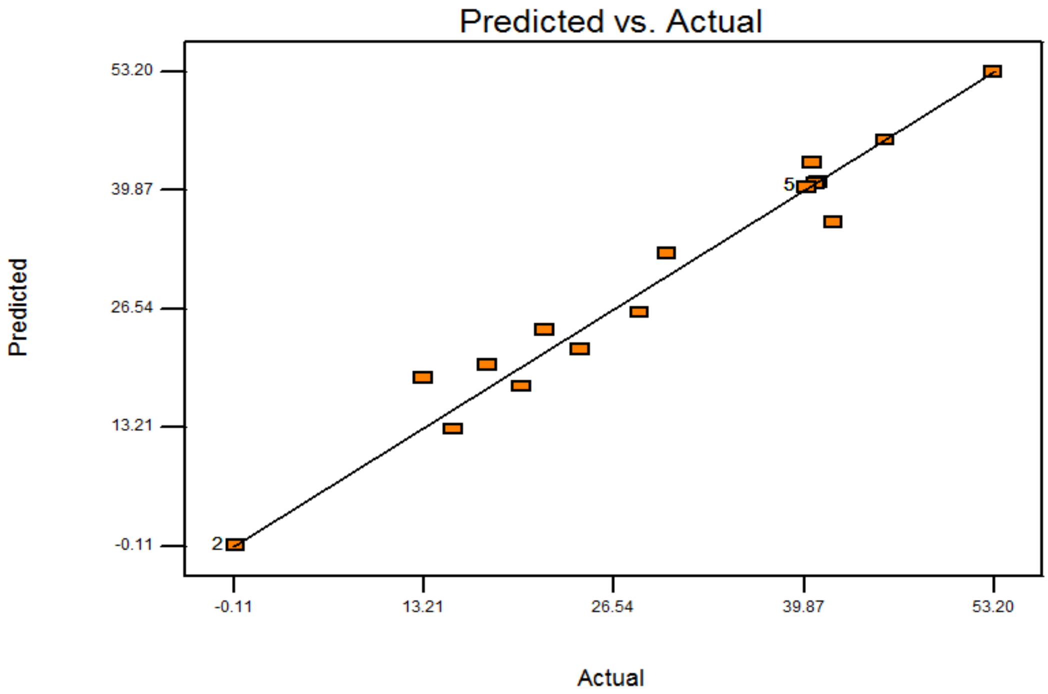


Figure 9 Predicted versus experimental values for base transesterification

4.5.1 The effect of individual parameter

The individual effects of all four parameters labeled A, B, C and D on biodiesel yield are shown in Figure 10, 11, 12 and 13 respectively. Based on the second order model equation, parameter D which is oil to methanol ratio is the major variable affecting the yield of biodiesel as it has the largest coefficient magnitude. Figure 10 shows the graph of yield against time (min). It can be observed that as the reaction time increase, biodiesel also will increase. This can be explained as longer reaction time will give the reactants and catalyst sufficient time to fully react in producing biodiesel.

Figure 11 indicates the effect of temperature on biodiesel yield. The optimum temperature is 55°C which yield the highest amount of biodiesel. However, as the temperature increases, the yield of biodiesel decreases. This happens due to the condensation of methanol which affecting the transesterification reaction. For this reaction, excess methanol is needed to force the reaction towards biodiesel production.

The effect of methanol to oil ratio towards biodiesel yield is shown in Figure 13. The conversion of triglycerides to methyl ester is a reversible reaction. Therefore, the amount of methanol should be in excess for instance, for this project, the optimum ratio is 11.0:1. The last parameter affecting the yield of biodiesel in catalyst concentration. As for catalyst concentration, Figure 12 shows that the highest biodiesel yield is obtained from the run with 1.0 wt% catalyst. The total number of available active catalytic sites for the transesterification reaction increased with higher catalyst loading, which subsequently leads to the higher yield of biodiesel.

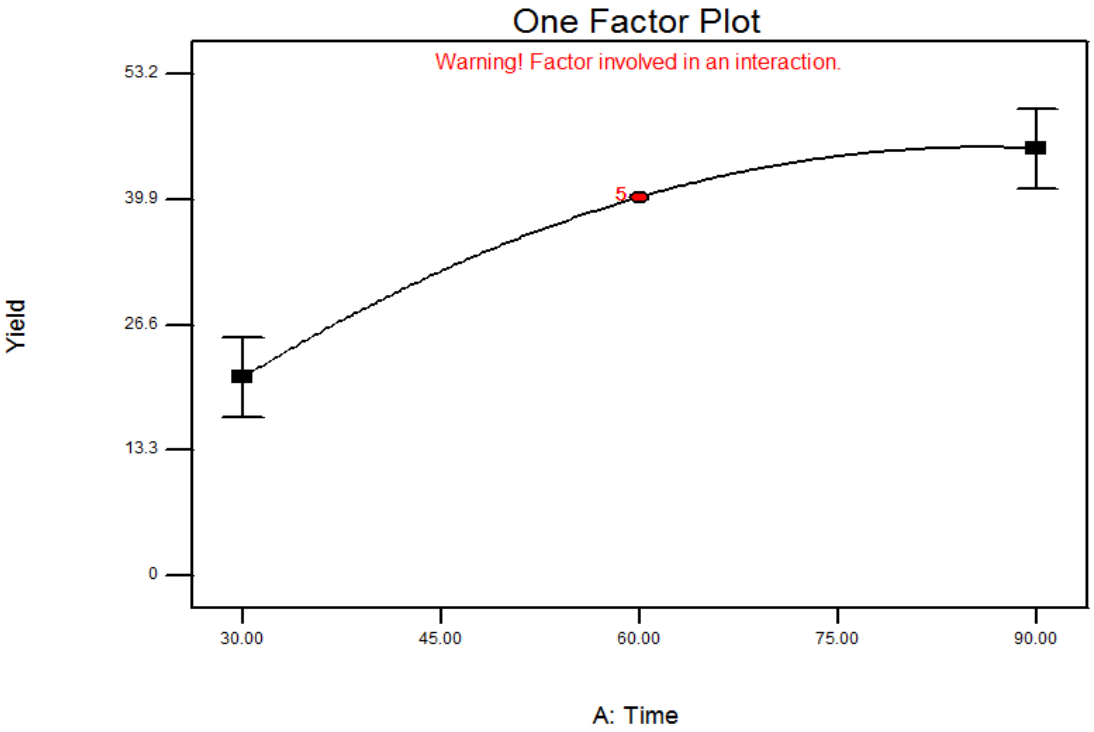


Figure 10 The individual effect of reaction time on the biodiesel yield

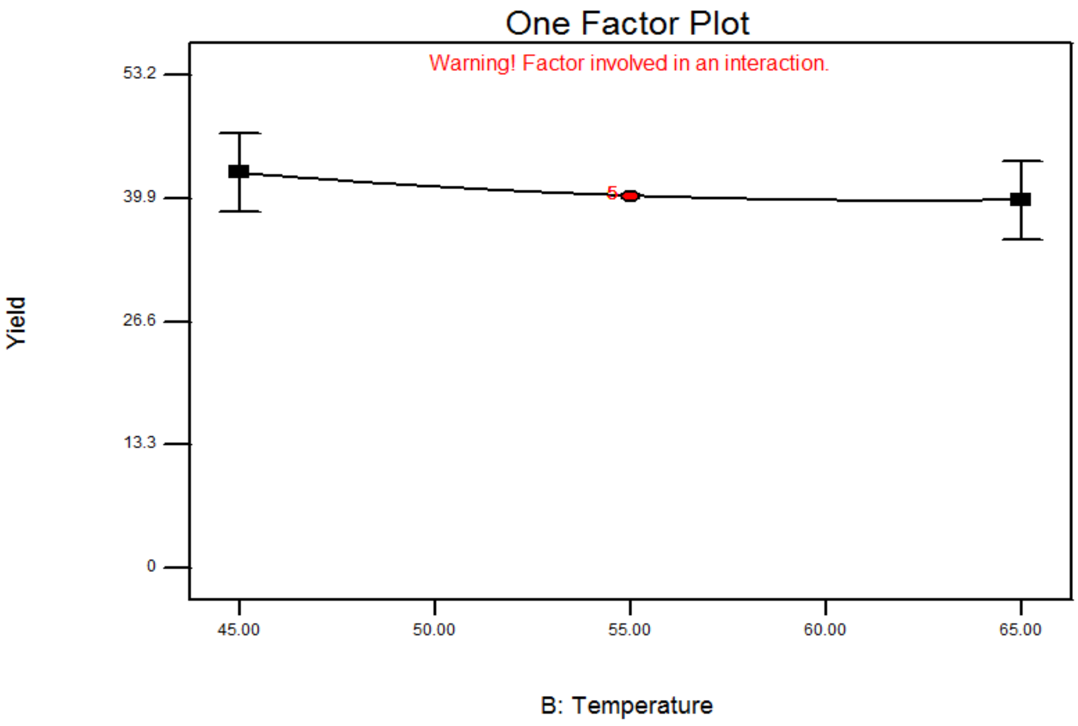


Figure 11 The individual effect of reaction temperature on the biodiesel yield

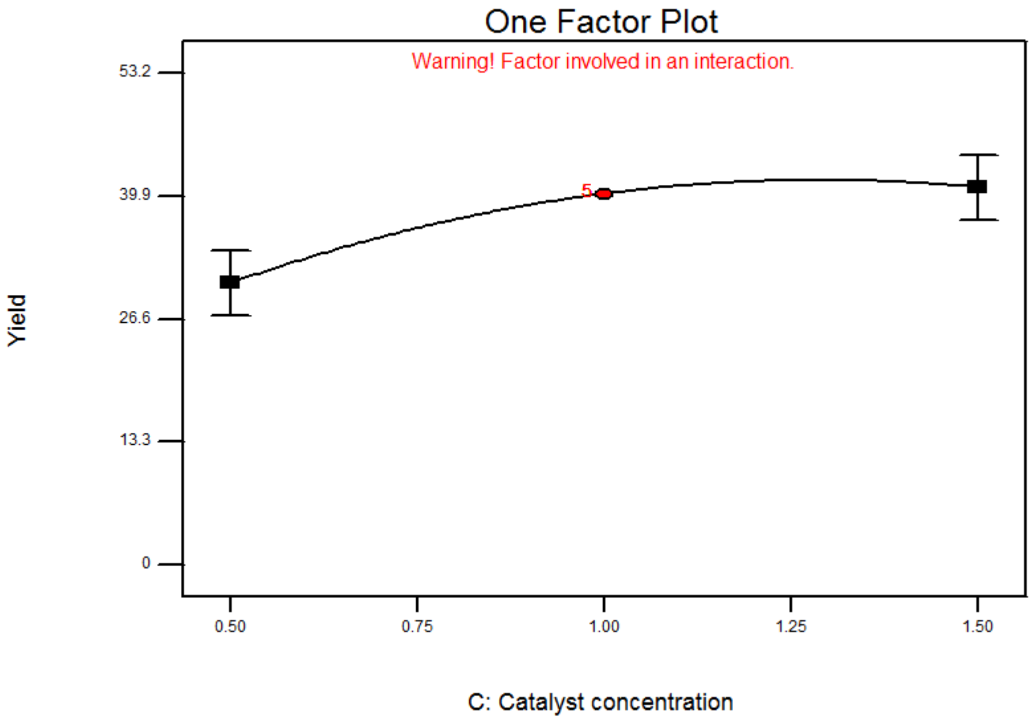


Figure 12 The individual effect of catalyst concentration on the biodiesel yield

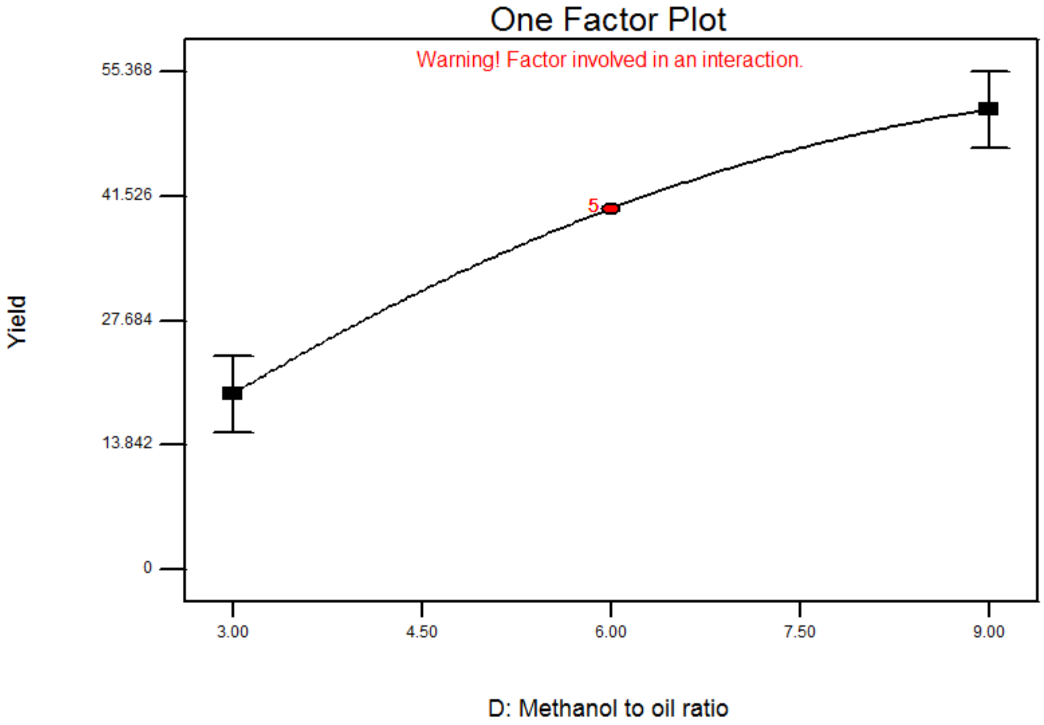


Figure 13 The individual effect of oil to methanol ratio on the biodiesel yield

4.5.2 Interactions between the parameters

Based on the yield equation stated in Equation 4, parameter D with the largest coefficient is found to be the main influence in determining the yield of biodiesel. The model equation also showed that parameter D has a significant interactions with other parameters. Figure 14 show that as the methanol to oil ratio and reaction time increases, the yield also increases. This indicates that the yield of biodiesel can be increased if the reaction has sufficient time to fully react and the amount of methanol is in excess to assist the reaction.

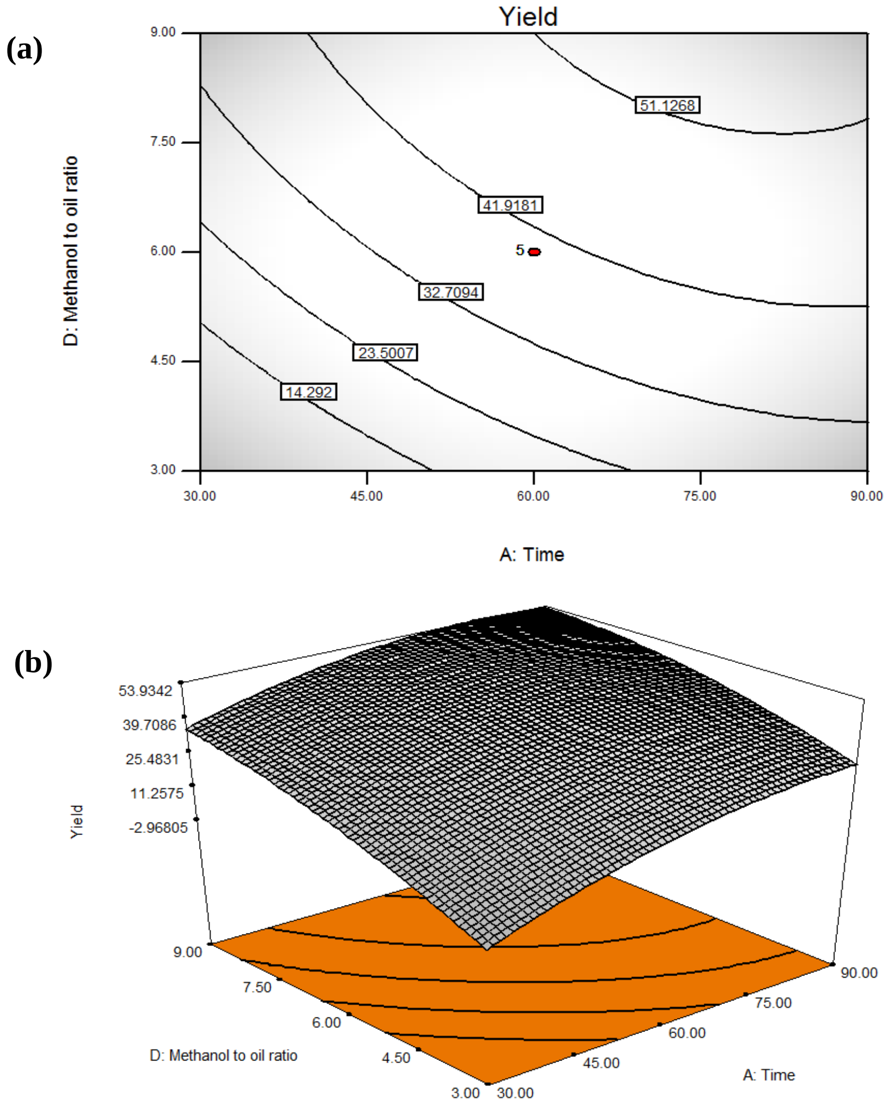


Figure 14 Combined effect of methanol to oil ratio (D) and time (A) in (a) contour plot (b) three dimensional plot

Figure 15 plot the interaction between methanol to oil ratio (D) and temperature (B). Based on the plots, the yield increases when the methanol to oil ratio value is ascending and the temperature is descending. Although the reaction has excess amount of methanol, the high temperature will cause the methanol to evaporates, affecting the overall reaction. The boiling point of methanol is 64. 7^{o}C, therefore, the optimum temperature should be less than the mentioned temperature.

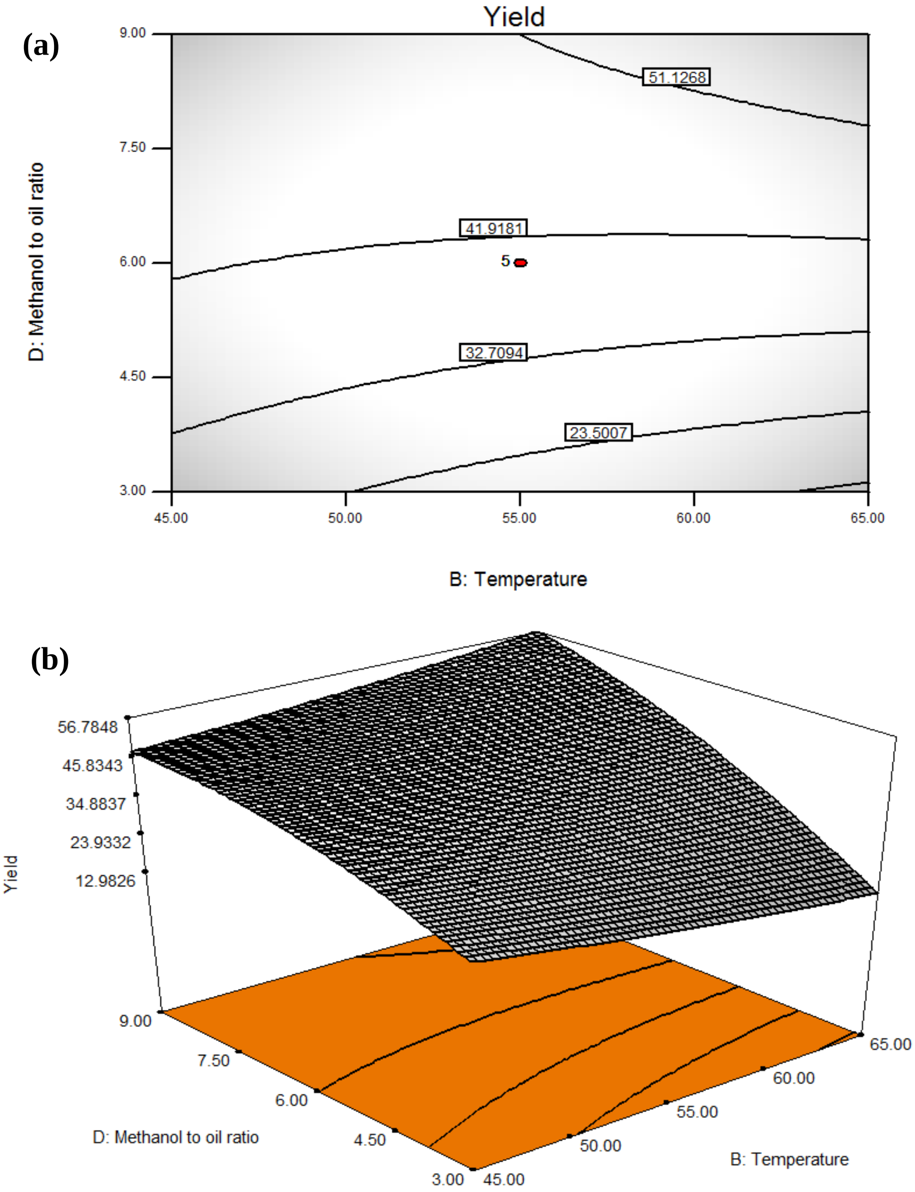


Figure 15 Combined effect of methanol to oil ratio (D) and temperature (B) in (a) contour plot (b) three dimensional plot

The reaction between the ratio of methanol and oil with catalyst concentration also gives a significant effect to biodiesel yield. These plots in Figure 16 show that the yield of biodiesel increases along with the increase of both parameters value. However, too much catalyst will affect the reaction.

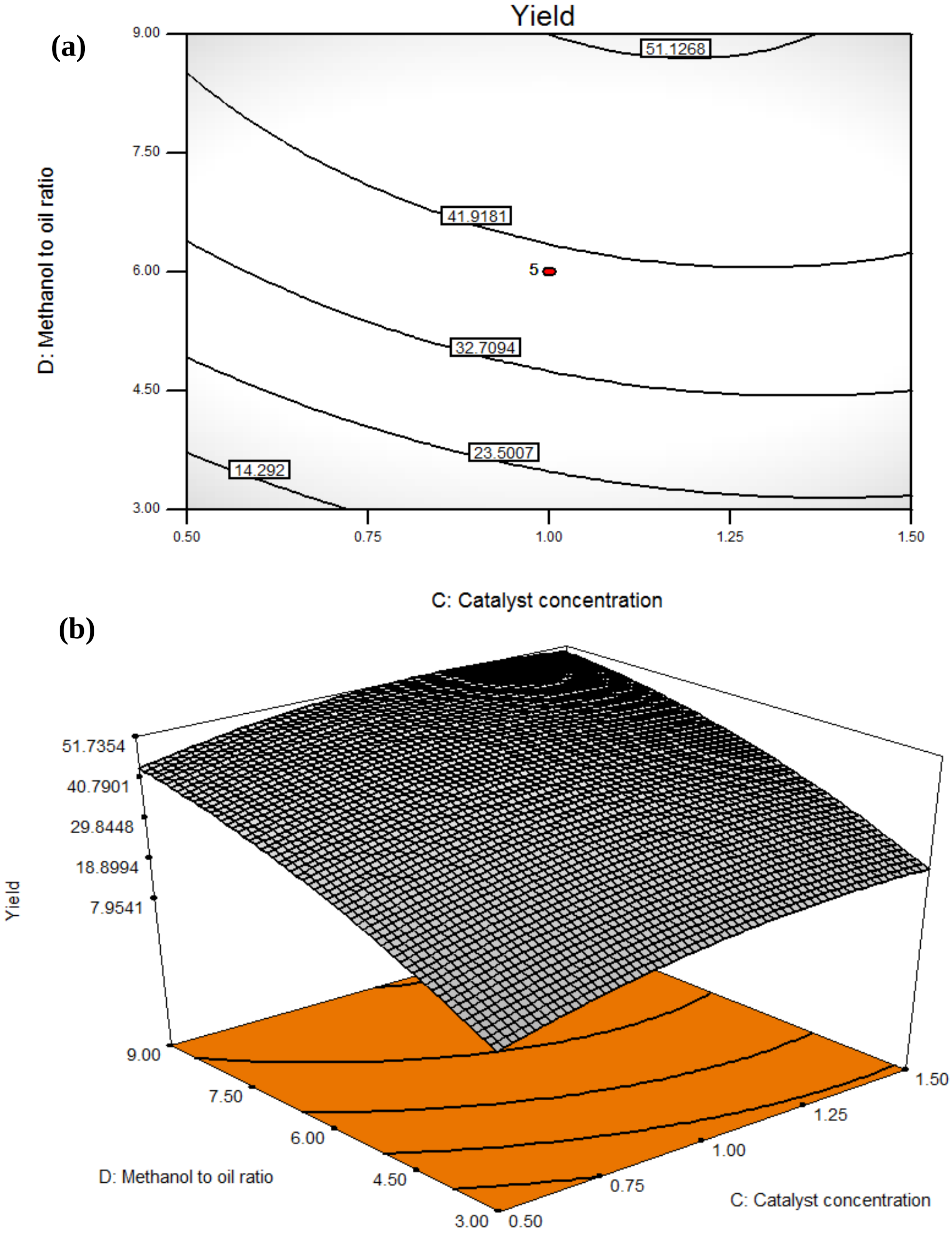


Figure 16 Combined effect of methanol to oil ratio (D) and catalyst concentration (C) in (a) contour plot (b) three dimensional plot

Based on the model equation, the second influential parameter is parameter A which is reaction time. From the Equation 4, the coefficient shows that there is a significant reaction between reaction time and temperature (B). Figure 17 justify that the yield increases when the reaction increases and temperature decreases. The temperature should be maintained around 55^{o}C which is the optimum temperature and increase the reaction time to enhance the reaction.

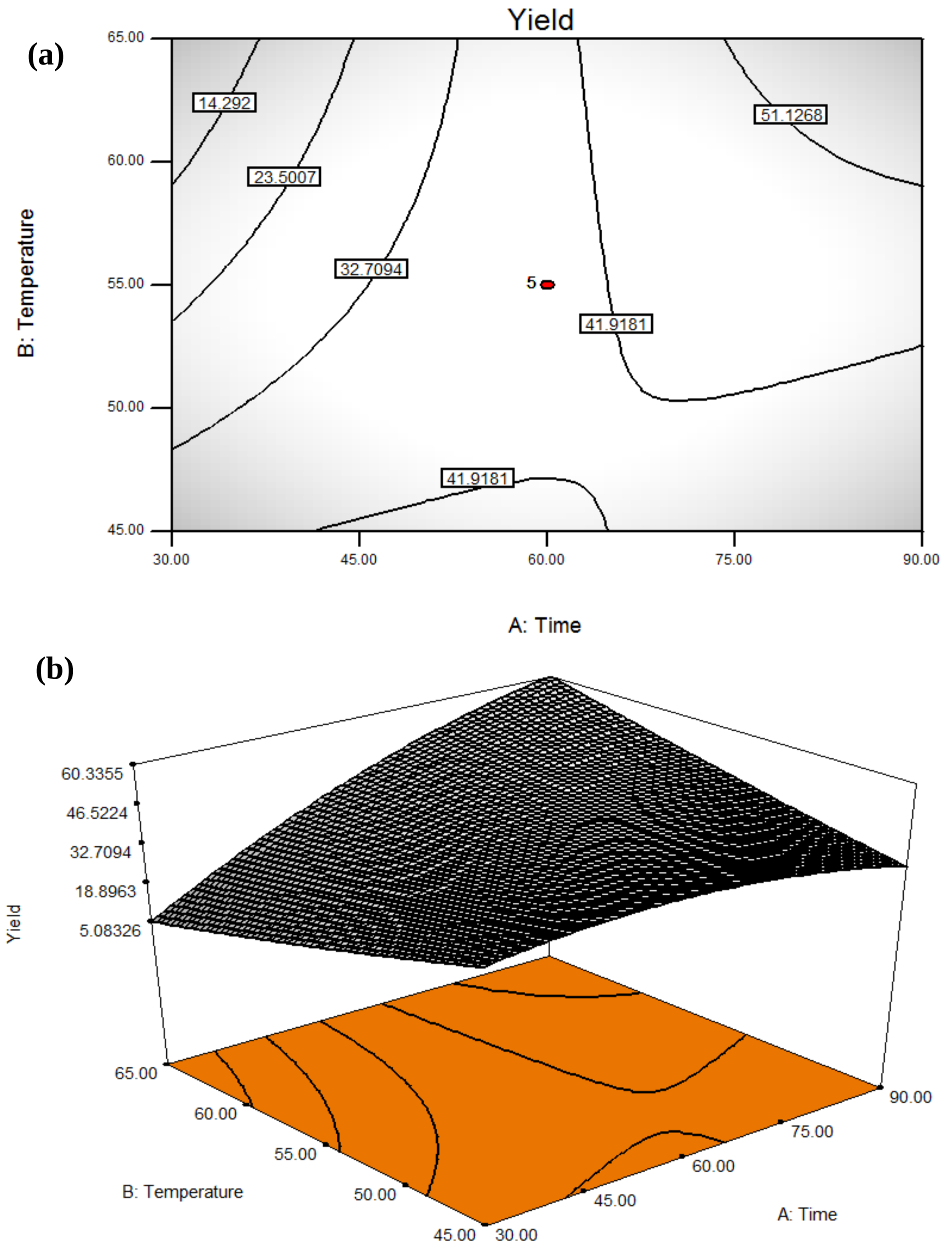


Figure 17 Combined effect of time (A) and temperature (B) in (a) contour plot (b) three dimensional plot

4.6 Characterization of Catalyst

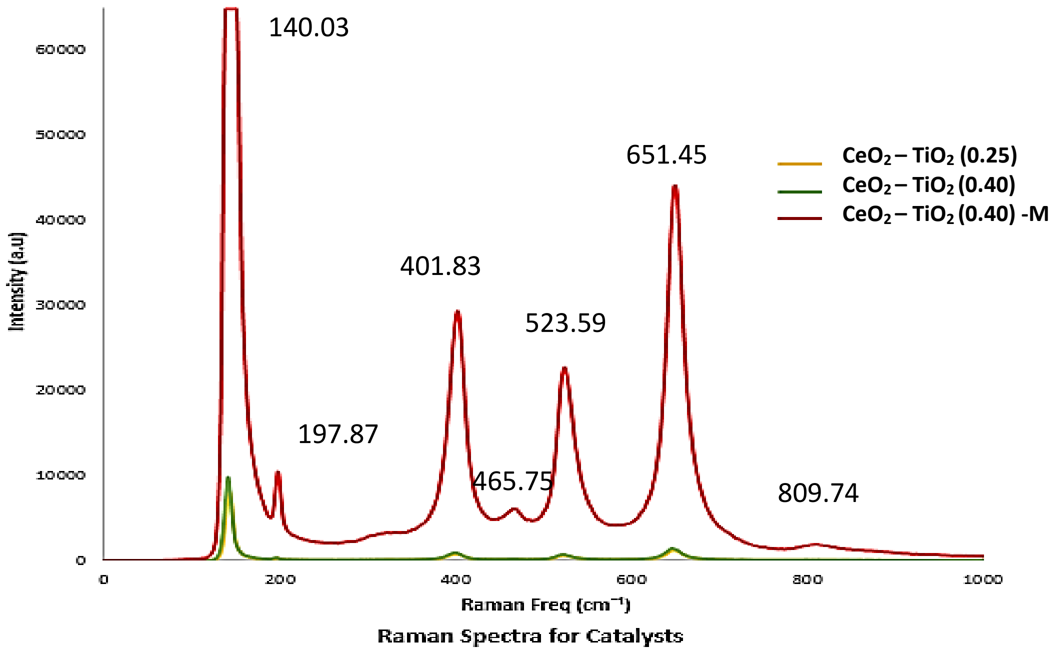


Figure 18 Raman Spectra for CeO_2-TiO_2

The result is obtained from Raman Spectrometer (Model: Horiba JobinYvonHR800). The Raman spectra for the catalysts are shown in Figure 18 above. The catalyst is synthesized with several loading using two different method. The yellow and green lines indicate the result for catalysts synthesized by method A which did not use alcohol during the preparation. This method also applies low dry temperature which is 80-90^{o}C. The result shows the higher the loading, the band resolves at higher value. The red line shows the catalyst prepared based on method explained in Figure 4, using propanol. The same loading which is 0.4 wt% synthesized by different method shows a large comparison. For the catalyst used in this project, which is the one labeled as CeO_2-TiO_2 (0.4)-M, some bands were resolved at 140.03 cm^{-}1, 197.87 cm^{-}1, 401.83 cm^{-}1, 465.75 cm^{-}1, 523.59 cm^{-}1, 651.45 cm^{-}1 and 809.74 cm^{-}1. This characterizing the anatase crystalline form of the TiO_2 and CeO_2. Based on literature, it was already studied and identified that the titanium with anatase crystalline form exhibits better catalytic activity in several reactions. This is due to the availability of a enormous number of vacant active sites on the surface of the catalyst compared to the rutile crystalline form [21].

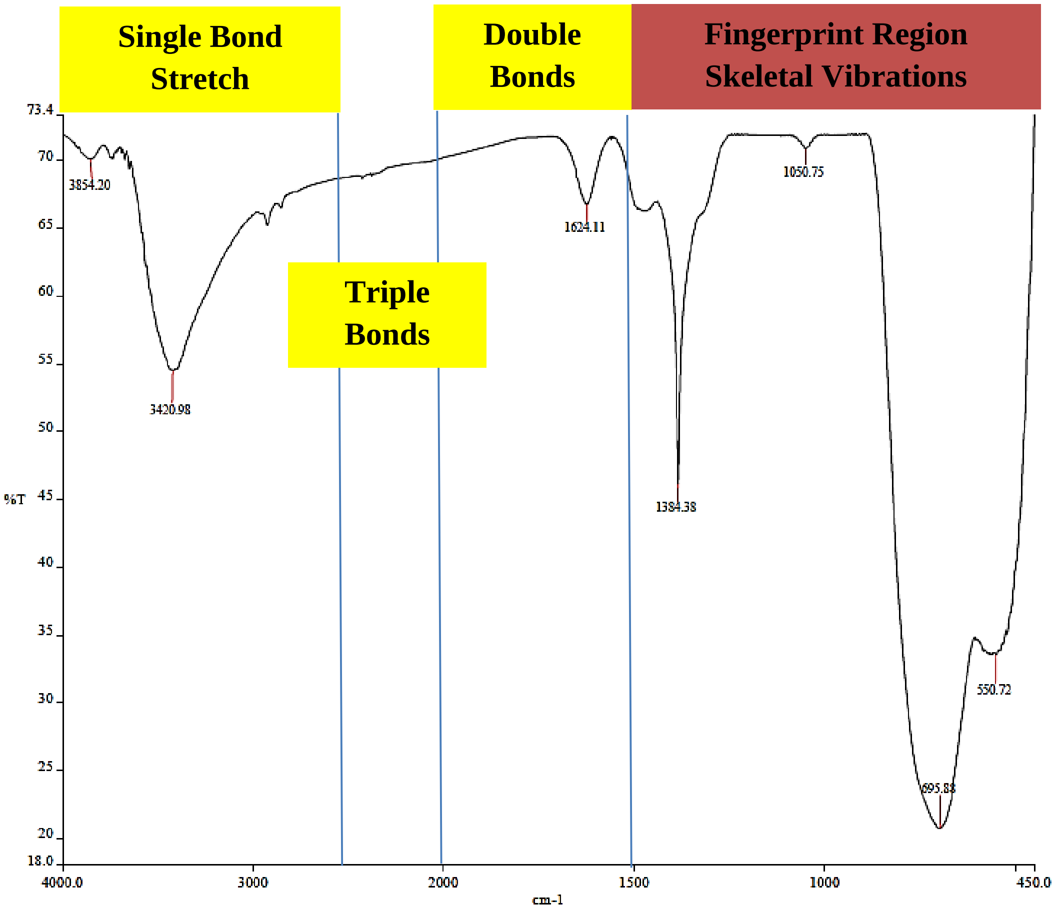


Figure 19 FTIR spectra of CeO_2-TiO_2

The first part of the spectra indicates the bands for single bond, hydroxyl group, in this case H-O-H bond. There is no band resolved for the second part of spectra which is for triple bond molecule. The double bond part shows the band resolved for carboxylic group. As for the last part of spectra, the region from 1500 cm^{-}1 to 450 cm^{-}1 is called fingerprint region, which normally contains complicated series of molecule absorptions. These happens due to the bending vibrations occurs within the molecule. The bands resolve at wavelength of 1384.38 cm^{-}1, 1050.75 cm^{-}1, 695.88 cm^{-}1 and 550.72 cm^{-}1 for the CeO_2-TiO_2 catalyst. The bands shown indicate the functional group within the catalyst synthesized. Higher calcination temperature can lower the content of hydroxyl group which will improve the catalytic property and activity of the catalyst.

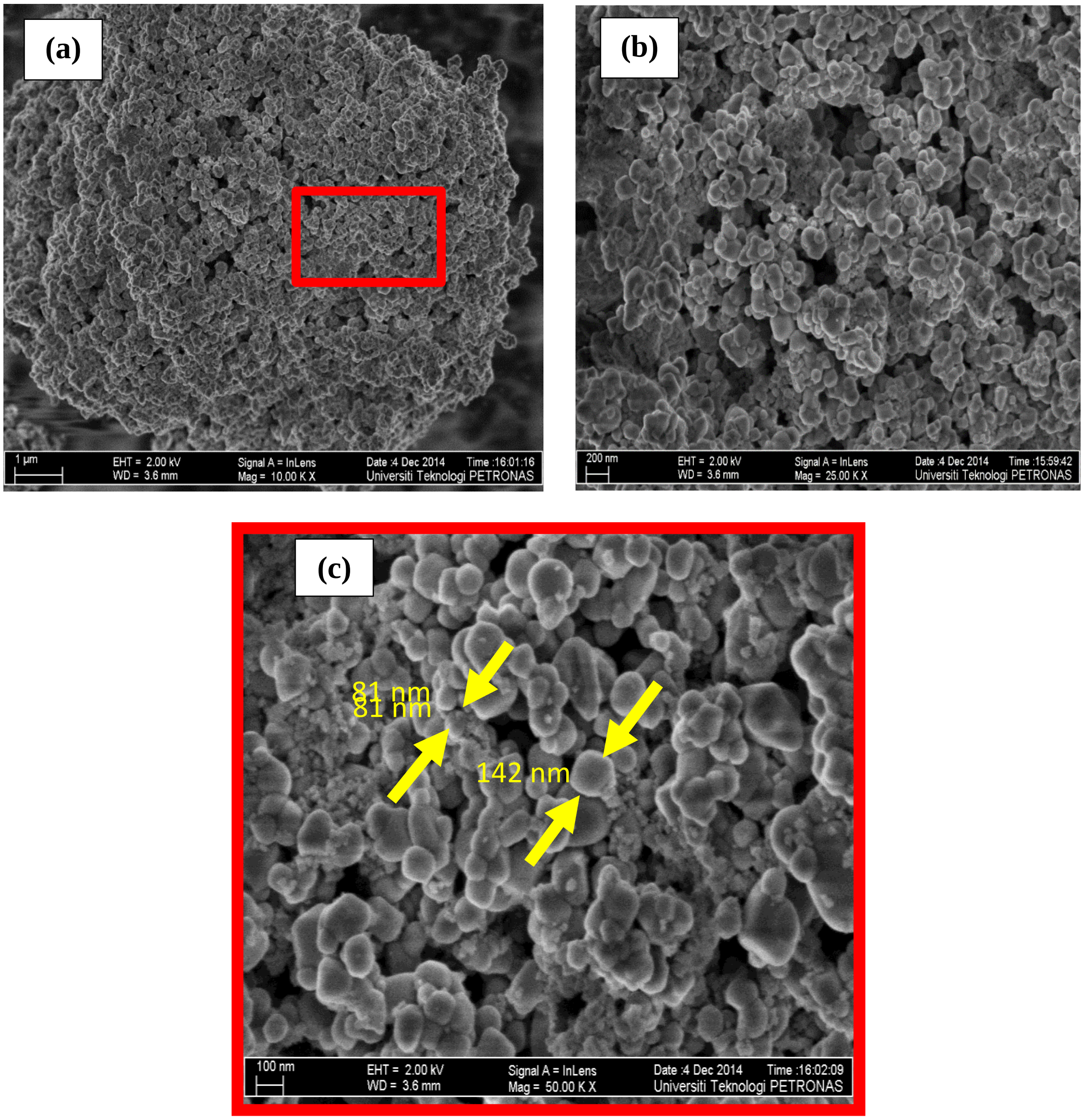


Figure 20 SEM images for CeO_2-TiO_2 at (a) 1µm (b) 200 nm (c) 100 nm

These images were taken from Variable Pressure Field Emission Scanning Electron Microscope (VPFESEM, Zeiss Supra55 VP). Based on Figure 20 (c), the particle size of this catalyst is shown to be in the range of between 81 nm to 142 nm. The smaller the particle size, more reaction can take place. To decrease the particle size of the catalyst, the calcination temperature should be increased. However, the calcination temperature should not exceed 600 ^{o}C as it can ruin the catalytic structure of the catalyst.

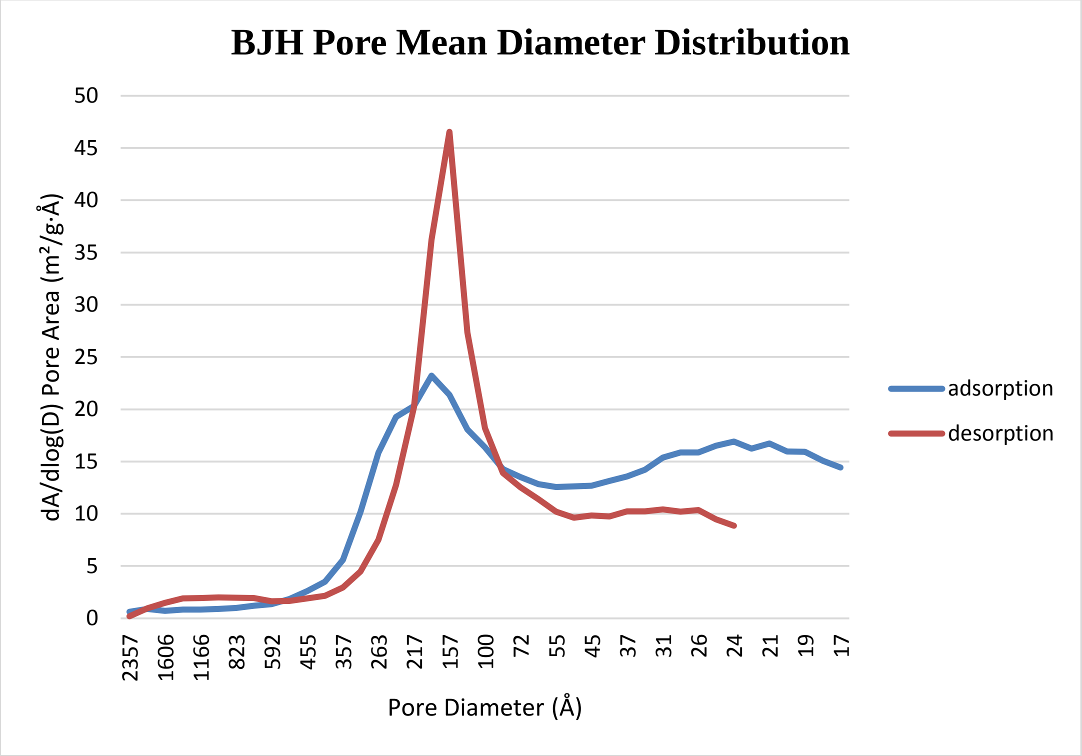


Figure 21 Pores mean diameter distribution based on the BJH method for CeO_2-TiO_2

Table 11 Specific surface area (BET), pores mean diameter (BJH) and pores volume

Catalyst	**Specific Surface Area**	**Average Pores Diameter**	**Pores Volume**
CeO_2-TiO_2	20.6875 m^2/g	15.043 nm	0.083701 cm^3/g

These data is obtained from Surface Area and Pore Size Analyzer (Model: Micrometrics ASAP 2020). Analysis of the pore diameter distribution is done via BHJ method indicates that the catalyst synthesized contains mesoporous sizes (2-50 nm) as shown in Figure 21. The results obtained are resulted from the addition of cerium which compromise the crystalline structure of the catalyst. It also enhance the specific surface area and pores average diameter of the catalyst. The smaller the surface area, more catalytic activity can occur during the reaction. Specific surface area can be decreased by increasing the temperature for calcination. This is because the higher the calcination temperature, more nitrates from the cerium precursor can be removed which will automatically enhance the catalytic properties of the catalyst.

Using the same optimized conditions, the transesterification reaction of palm oil is repeated using the synthesized catalyst, CeO_2-TiO_2. The yield of biodiesel is 59.7 % which is higher than using NaOH.

4.7 Reusability of Catalyst

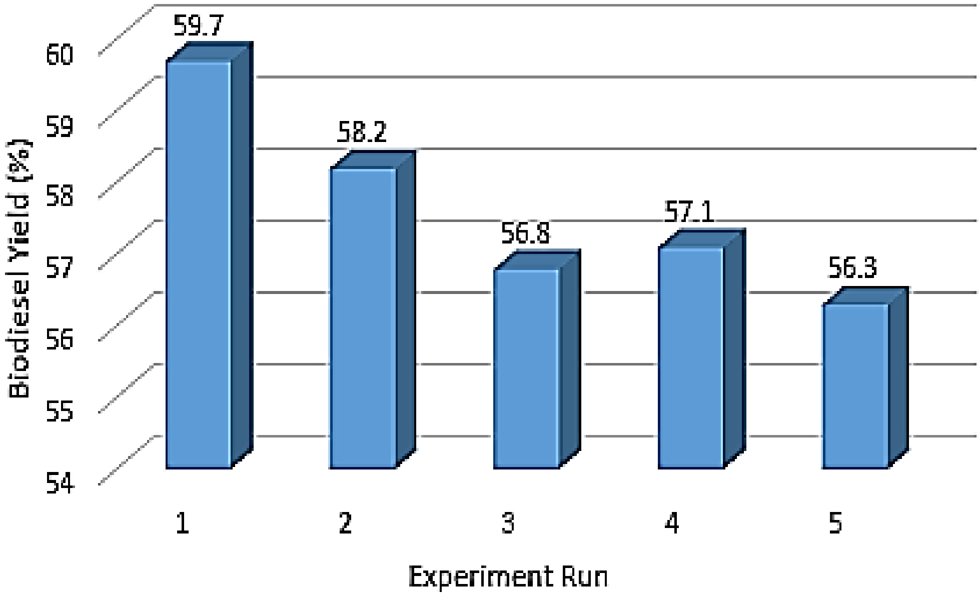


Figure 22 Graph of Reusability of CeO_2-TiO_2 catalyst

The experiments were done using the same optimum conditions to test the reusability of the synthesized catalyst. The results were summarized in Figure 22. From the graph, it is shown that the yield of biodiesel is slightly lower than the fresh catalyst in Run 1. The yield decreases in between 2.5% to 5.7% from the first run. For this purpose, the catalyst is recovered from each reaction run by using phosphoric acid. Phosphoric acid will lead to formation of three layers which are remaining FFA (upper layer), glycerol and methanol in the middle and catalyst at the bottom. The bottom layer was then washed with alcohol, dried at temperature of 100^oC and calcinated at 300^oC to be used in next run. It can be concluded that CeO_2-TiO_2 catalyst has the ability to be reused by maintaining the biodiesel yield in range of less than 3% reduction after each run. In terms of economic for large production, heterogenus catalyst ability to be used repeatedly may contributes to production cost reduction.

4.8 Catalyst Dosage and Reaction Time Effects

Under the same optimized conditions, catalyst dosage and reaction time is manipulated to increase the yield of biodiesel.

4.8.1 Catalyst Dosage

Table 12 tabulated the biodiesel yield using different dosage of catalyst. The results show that more dosage of catalyst will increase the yield for both catalyst. By increasing the catalyst dosage under suitable temperature, reaction time and methanol/oil ratio, biodiesel yield can be increased.

Table 12 The Effect of catalyst dosage on biodiesel yield

Catalyst Dosage (wt%)	**Biodiesel Yield (%)**
	CeO_2-TiO_2
0.5	45.3
1.0	59.7
1.5	62.5
2	64.4

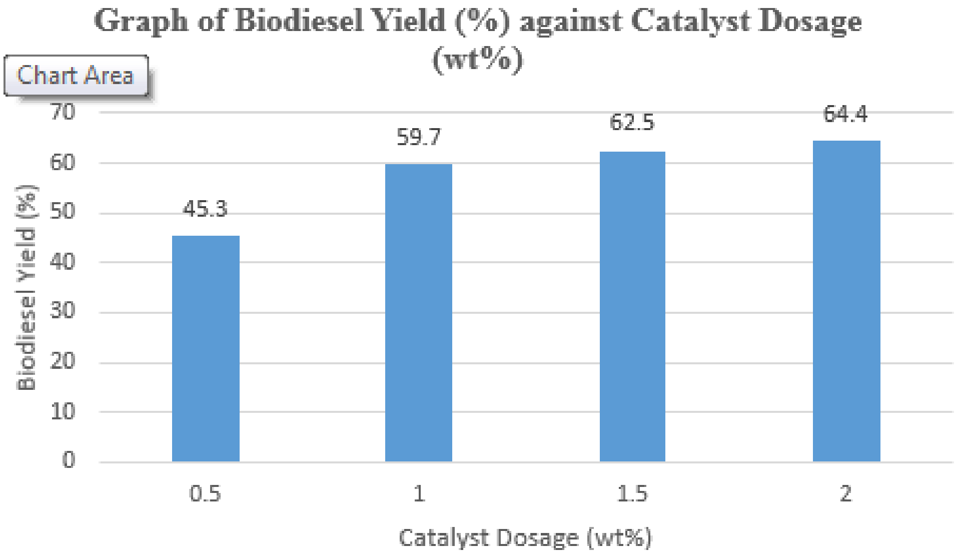


Figure 23 Graph of Biodiesel Yield against Catalyst Dosage (wt%) of CeO_2-TiO_2 catalyst

4.8.2 Reaction Time

Under the same optimum conditions; temperature of 55°C, methanol oil ratio of 11.05:1 and 1.0 wt% of catalyst, the reaction time was varied in range between 30 min to 150 min. The data shows that the higher the reaction time, the higher the yield for both part as the reactants have sufficient time to fully react with each other and catalyst. The yield can be increased up to 70.6% when the reaction time is increased.

Table 13 The effect of reaction time on biodiesel yield

Reaction time (min)	**Biodiesel Yield (%)**
	CeO_2-TiO_2
30	27.8
60	59.7
90	63.4
120	67.5
150	70.6

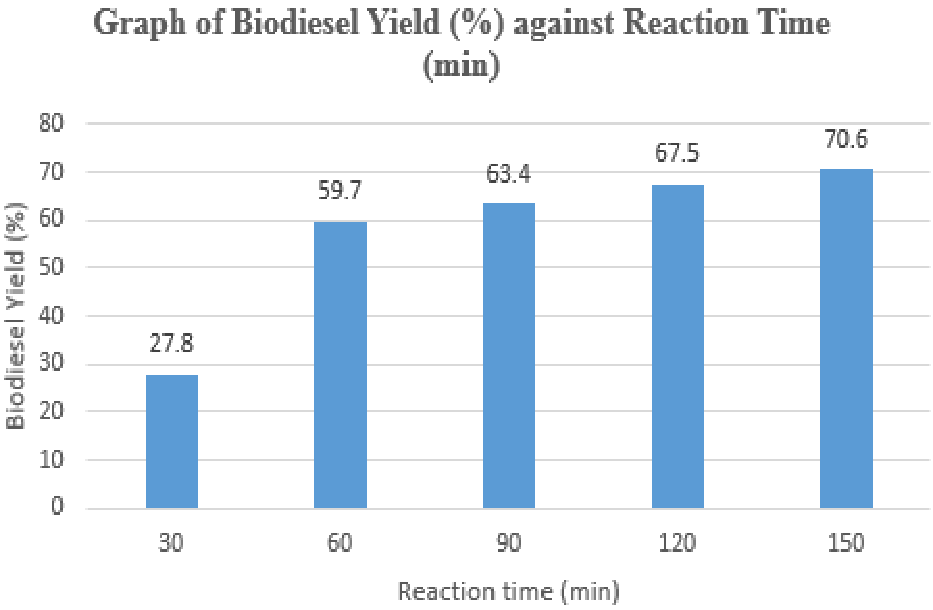
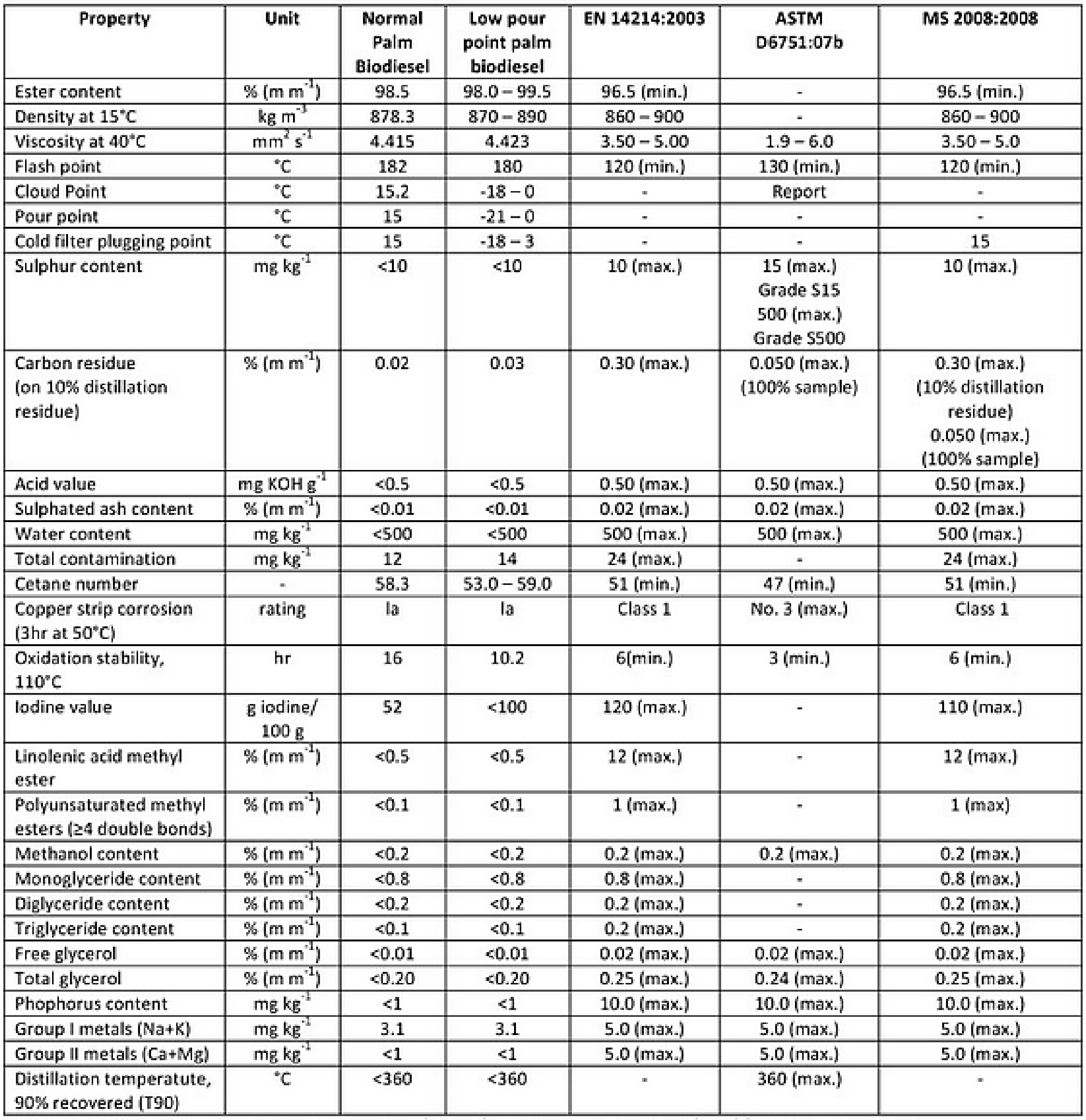


Figure 24 Graph of Biodiesel Yield against Reaction Time (min) of CeO_2-TiO_2 catalyst

4.9 Fuel Properties

According to Malaysian Palm Oil Board (MPOB), Table 14 are the fuel properties for normal and low pour point palm oil biodiesel [22].

Table 14 The fuel properties for normal and low pour point palm oil biodiesel



Property	Unit	Normal Palm Biodiesel	Low pour point palm biodiesel	EN 14214:2003	ASTM D6751:07b	MS 2008:2008
Ester content	% (m m^{-1})	98.5	98.0 – 99.5	96.5 (min.)	-	96.5 (min.)
Density at 15°C	kg m^{-3}	878.3	870 – 890	860 – 900	-	860 – 900
Viscosity at 40°C	mm^2 s^{-1}	4.415	4.423	3.50 – 5.00	1.9 – 6.0	3.50 – 5.0
Flash point	°C	182	180	120 (min.)	130 (min.)	120 (min.)
Cloud Point	°C	15.2	-18 – 0	-	Report	-
Pour point	°C	15	-21 – 0	-	-	-
Cold filter plugging point	°C	15	-18 – 3	-	-	15
Sulphur content	mg kg^{-1}	<10	<10	10 (max.)	15 (max.) Grade S15 500 (max.) Grade S500	10 (max.)
Carbon residue (on 10% distillation residue)	% (m m^{-1})	0.02	0.03	0.30 (max.)	0.050 (max.) (100% sample)	0.30 (max.) (10% distillation residue) 0.050 (max.) (100% sample)
Acid value	mg KOH g^{-1}	<0.5	<0.5	0.50 (max.)	0.50 (max.)	0.50 (max.)
Sulphated ash content	% (m m^{-1})	<0.01	<0.01	0.02 (max.)	0.02 (max.)	0.02 (max.)
Water content	mg kg^{-1}	<500	<500	500 (max.)	500 (max.)	500 (max.)
Total contamination	mg kg^{-1}	12	14	24 (max.)	-	24 (max.)
Cetane number	-	58.3	53.0 – 59.0	51 (min.)	47 (min.)	51 (min.)
Copper strip corrosion (3hr at 50°C)	rating	Ia	Ia	Class 1	No. 3 (max.)	Class 1
Oxidation stability, 110°C	hr	16	10.2	6(min.)	3 (min.)	6 (min.)
Iodine value	g iodine/ 100 g	52	<100	120 (max.)	-	110 (max.)
Linolenic acid methyl ester	% (m m^{-1})	<0.5	<0.5	12 (max.)	-	12 (max.)
Polyunsaturated methyl esters (≥4 double bonds)	% (m m^{-1})	<0.1	<0.1	1 (max.)	-	1 (max)
Methanol content	% (m m^{-1})	<0.2	<0.2	0.2 (max.)	0.2 (max.)	0.2 (max.)
Monoglyceride content	% (m m^{-1})	<0.8	<0.8	0.8 (max.)	-	0.8 (max.)
Diglyceride content	% (m m^{-1})	<0.2	<0.2	0.2 (max.)	-	0.2 (max.)
Triglyceride content	% (m m^{-1})	<0.1	<0.1	0.2 (max.)	-	0.2 (max.)
Free glycerol	% (m m^{-1})	<0.01	<0.01	0.02 (max.)	0.02 (max.)	0.02 (max.)
Total glycerol	% (m m^{-1})	<0.20	<0.20	0.25 (max.)	0.24 (max.)	0.25 (max.)
Phophorus content	mg kg^{-1}	<1	<1	10.0 (max.)	10.0 (max.)	10.0 (max.)
Group I metals (Na+K)	mg kg^{-1}	3.1	3.1	5.0 (max.)	5.0 (max.)	5.0 (max.)
Group II metals (Ca+Mg)	mg kg^{-1}	<1	<1	5.0 (max.)	5.0 (max.)	5.0 (max.)
Distillation temperatute, 90% recovered (T90)	°C	<360	<360	-	360 (max.)	-

The biodiesel properties were analyzed and compared to ASTM D6751 and EN 14214 standard as tabulated Table 15.

Table 15 Parameters of biodiesel sample and the value of standards EN14214 and ASTM D6751

No	Parameter	NaOH	CeO_2-TiO_2	ASTM D6751	EN 14214
1	Viscosity	5.7 ns/m^3	12 ns/m^3	1.9 -6.0 ns/m^3	3.5 – 5 ns/m^3
2	Density	879.7 kg/m^3	920.9 kg/m^3	-	860 – 900 kg/m^3
3	Cloud Point	4.8	5.5	-	-
4	Pour Point	2.6	3.4	-	-

Most of the values of properties for the palm oil biodiesel produced with NaOH catalyst is close to the standard. However, the properties for palm oil biodiesel produced with CeO_2-TiO_2 catalyst deviates slightly from the standards. This shows that the quality of biodiesel produced using homogeneous catalyst is better than that of heterogeneous catalyst. The density and the viscosity for the biodiesel produced with homogeneous catalyst is close to the standards range, however, it is observed that the density and the viscosity for the biodiesel produced with heterogeneous catalyst is not within the required limit.

4.10 Experimental-Simulation Comparison

4.10.1 Reaction Modelling

Equation 2 described the reversible reaction of converting crude palm oil to biodiesel. The chemical equation below shows that excess methanol is needed to force the equilibrium to the next side of the reaction [23].

$$\mathrm{Triglycerides\ [TG] + 3\ Methanol\ [ML] \rightarrow 3\ Methylesters + Glycerol}$$

$$\mathrm{r} = -\frac{\mathrm{d[TG]}}{\mathrm{dt}} = \mathrm{k[TG][ML]}$$

Equation 6 Transesterification Second Order Equation

4.10.2 ASPEN HYSYS Modelling

In ASPEN HYSYS, there are several component for this project which are not available in the library. Therefore, these components for instance palmitic acid and CeO_2-TiO_2 catalyst were generated using Hypothetical Manager. All the information on physical properties, molecular weight, density and others are manually added in the software library. The properties of the feed stream which includes methanol dissolved with CeO_2-TiO_2 and palm oil and also product stream which contains methyl ester, water, methanol balance, glycerol and catalyst were obtained from NRTL fluid package of this software. This transesterification reaction was defined as kinetics. The kinetics constant is obtained through Equation 3, which is integrated from Equation 2 [24].

$$t = \frac{1}{k[TG]_o(\frac{[ML]_o}{[TG]_o} - 3)} \ln\left(\frac{\frac{[ML]_o}{[TG]_o} - 3x_{TG}}{\frac{[ML]_o}{[TG]_o} - 1x_{TG}}\right)$$

Where; t = reaction time, $[TG]_o$= initial oil concentration, $[ML]_o$= initial methanol concentration, k = kinetic parameter, x_{TG}=triglycerides yield.

Equation 7 Integrated Form of Second Order Equation

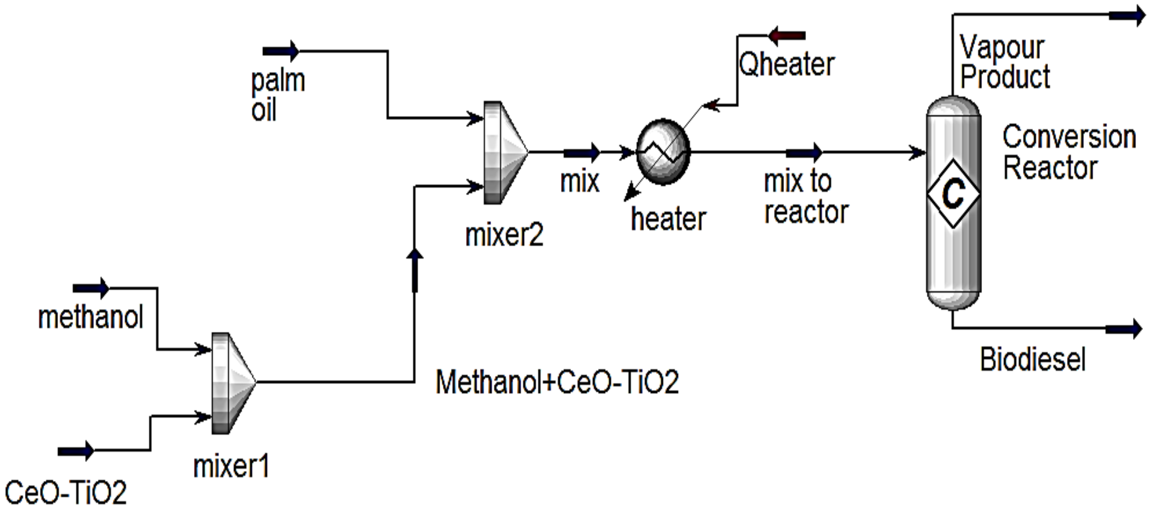


Figure 25 ASPEN HYSYS Flow sheet of conversion reactor for transesterification reaction of palm oil under optimized conditions

Table 16 Experimental-Simulation Comparison Yield at Optimum Conditions

t (min)	**x_{TG} (%)**	
	Experimental	**ASPEN HYSYS**
30	27.8	27.5
60	59.7	58.3
90	63.4	62.9
120	67.5	65.3
150	70.6	69.4

The tabulated data shown in Table 16 states that there is only a slight different between experimental and simulation data of biodiesel yield. This shows that the result obtained in reliable and acceptable. Figure 26 plotted the temporal profile of transesterification reaction of palm oil under optimized conditions obtained from experimental and simulation values.

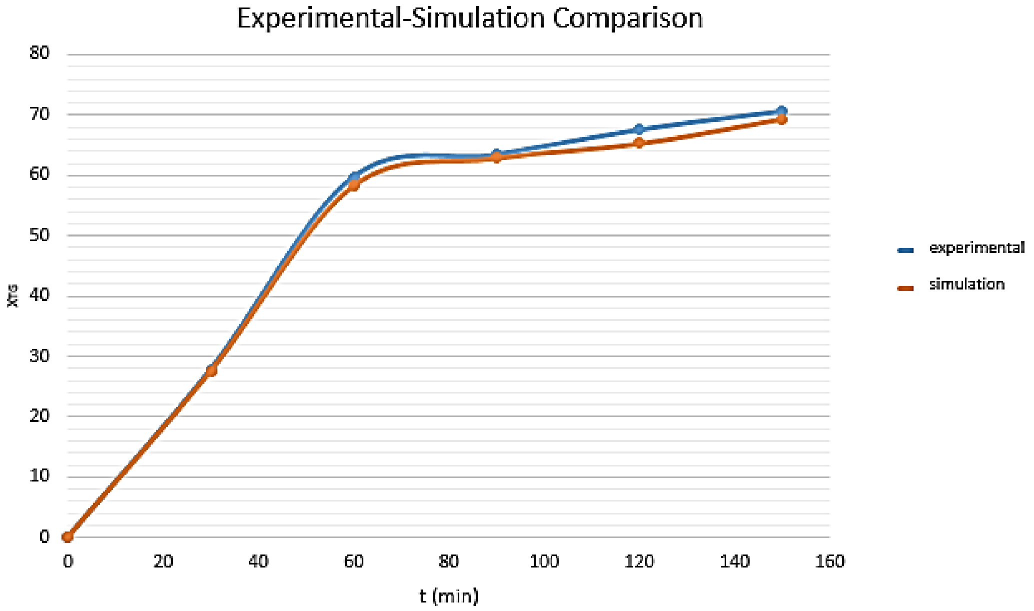


Figure 26 Temporal profile of transesterification reaction of palm oil under optimized conditions

4.11 Comparison of optimum operating parameters with previous studies

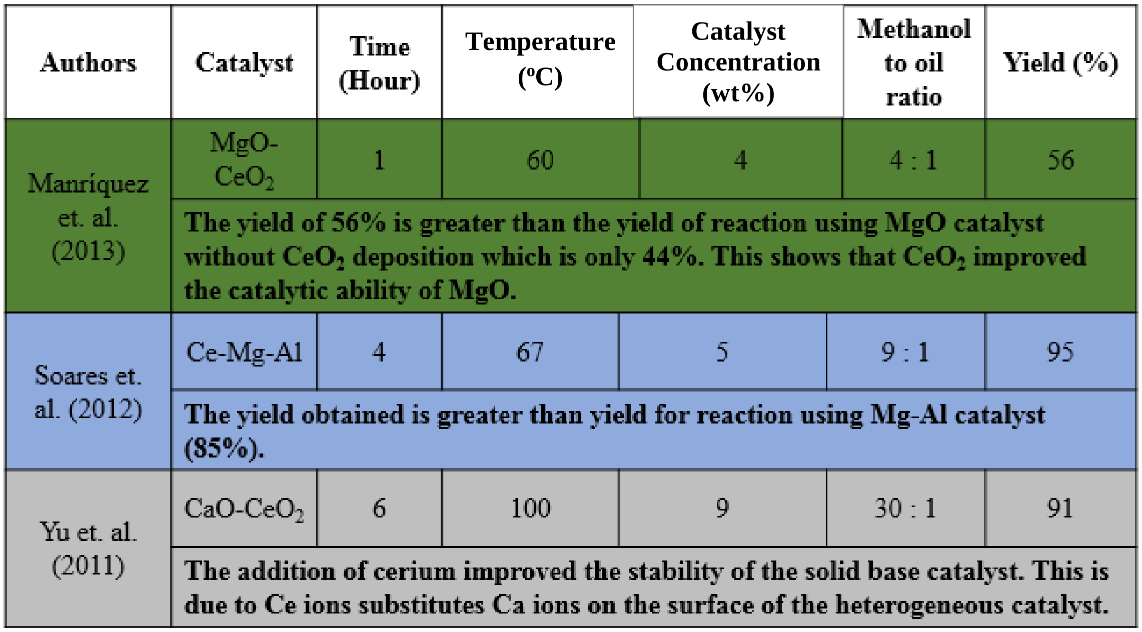
There are several researches are done to identify the effect of optimized parameters with the presence of mixed metal oxide catalyst for palm oil transesterification. The optimum operating parameters of present work are compared to previous findings which using different catalyst as shown in Table 17.

Table 17 Optimum Condition Comparison for Palm Oil biodiesel using various catalyst

Authors	**Catalyst**	**Time (hour)**	**Temperature (^oC)**	**Catalyst Concentration (wt%)**	**Methanol to oil ratio**
This Project	**CeO_2-TiO_2**	**1**	**55**	**1**	**11.05 : 1**
Hameed B.H., Lai L.F & Chin L.H	KF/ZnO	9.72	65	5.52	11.43 : 1
Noiroj et. al.	KOH/Al_2O_3 KOH/Na	3	70	10	15 : 1
Yee K.F. & Teong, L. K.	Sulphatedzirconia alumina	3	127	6	8 : 1
Yap, Y. H. T., Abdullah, N. F., & Basri, M.	$NaOH/AL_2O_3$	3	60	3	15 : 1
Bo et. al.	KF/Al_2O_3	3	65	4	12 : 1
Kansedo J., Lee K.T. & Bhatia S.	Montmorillonite KSF	3	190	3	8 : 1

Table 18 show the condition used in previous research. All these research utilized cerium as doping material to improve the existing catalyst.

Table 18 Previous Research using Ce as doping metal



Authors	Catalyst	Time (Hour)	Temperature (ºC)	Catalyst Concentration (wt%)	Methanol to oil ratio	Yield (%)
Manríquez et. al. (2013)	MgO-CeO_2	1	60	4	4 : 1	56
	The yield of 56% is greater than the yield of reaction using MgO catalyst without CeO_2 deposition which is only 44%. This shows that CeO_2 improved the catalytic ability of MgO.					
Soares et. al. (2012)	Ce-Mg-Al	4	67	5	9 : 1	95
	The yield obtained is greater than yield for reaction using Mg-Al catalyst (85%).					
Yu et. al. (2011)	CaO-CeO_2	6	100	9	30 : 1	91
	The addition of cerium improved the stability of the solid base catalyst. This is due to Ce ions substitutes Ca ions on the surface of the heterogeneous catalyst.					

CHAPTER 5

UTILIZATION OF BIODIESEL BYPRODUCT

In 2012, the global biodiesel production is at 22.5 billion litres where Malaysia is among the major exporters of biofuel alongside with Brazil, Argentina and Indonesia. However, the global production of biofuel has been seen to be increasing at a slower rate. One of the reasons for the scenario is a relatively high production cost of biodiesel due to its high by-product generation of mainly glycerol around 10%[25]. The large amount of by-products however has no commercial value, where it could be easily obtained with a price of RM 0.63[26]. Hence, there lies a need to come up with technologies to process the crude glycerol into value-added products with commercial value. Among the popular value-added products are citric acid, docosahexaenoic acid (DHA), poly (hydroxyalkanoates), 1,3-propanediol, and 1,2-propanediol. For this project, the chosen value-added product is 1,2-propanediol which is produced via the process route of hydrogenolysis. It has a relatively high market value of RM 7520 per tonne [27].

1,2-propanediol offers a unique combination of properties. It has an incomparable reputation for safe used in a wide range of consumer and industrial applications. It has been used safely for more than 50 years. In industrial applications, it is widely used to make unsaturated polyester resins that are used in bath and kitchenware, pipes or windmill blades. Apart from that, it is also used to manufacture plastics, resins, paints and coatings and plays an important role as an ingredient of formulations for heat transfer fluids, liquid detergents or aircraft de-icing. Besides that, referring to the United States and European Pharmacopeia,1,2-propanediol is a high-purify grade of mono propylene glycol that is widely used ingredient in pharmaceutical, food, cosmetic, personal care, flavors and animal feed applications [28] .

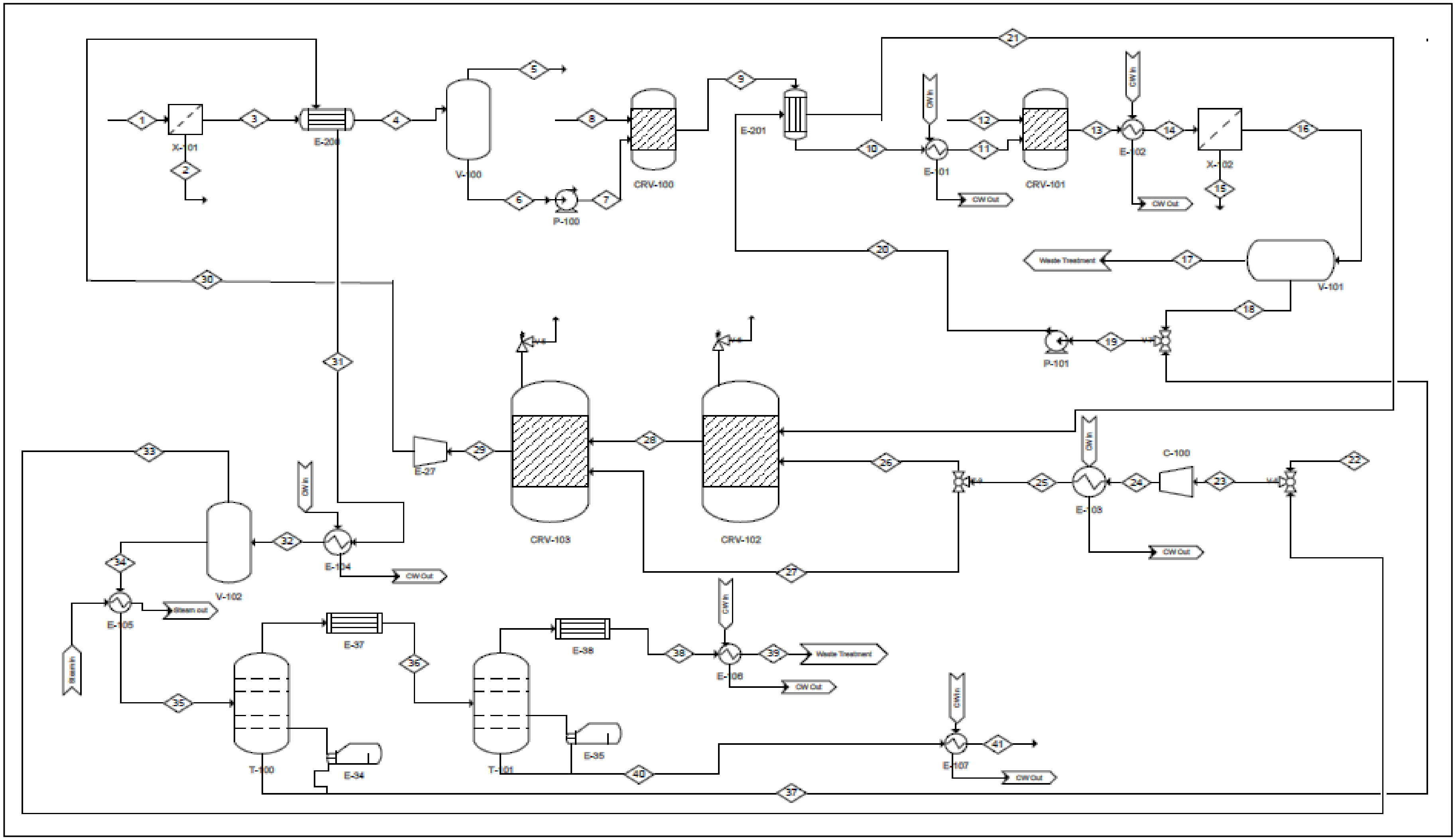


Figure 27 Process Flow Diagram of 1,2-propanediol Production

This production process consist of two parts which are purification of the feed glycerol and hydrogenolysis. Purification is required as the processes to produce 1,2-propanediol require high purity of glycerol. Since typically crude glycerol from biodiesel only contains less than 65wt% glycerol [29], purification is required. Most of the applications of glycerol would be producing value added products through catalytic conversion where most catalyst is vulnerable to contamination if impurities are present. Besides that, in order for the produced 1,2-propanediol to have high market value, a high purity of the product is a must. This is because the applications using this product should be impurity free. Therefore, it can be said that even if the production process of 1,2-propanediol with large amount of impurities could be carried on, the product would still require removal of impurities at the end of the process in order to suit the market demand of quality. Another reason of purification is that the impurities such as ash and solids will cause the vessels and equipment to be vulnerable to damage.

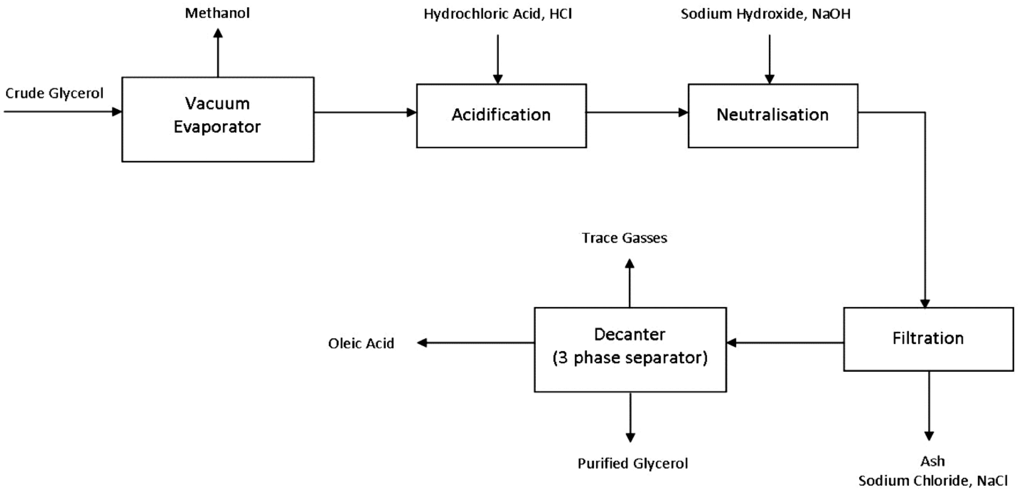


Figure 28 Block Diagram of Crude Glycerol Purification

First, the crude glycerol is fed into vacuum evaporator to remove methanol. Then, the next impurity to remove is soap. It could be done by acidification of the soap using acid, for instance hydrochloric acid, HCL to convert soap into free fatty acid, FFA. The acidification is done with excess HCL as feed to ensure all soap has reacted with acid and converted fully to FFA. Excess HCL will then be neutralized at the next step by addition of sodium hydroxide, NAOH to produce sodium chloride salt and water. Ash and salts produced will go through microfiltration for removal. After this stage, the glycerol is free from methanol, soap, ash and salts. The only impurity left is FFA which could be removed using a decanter, particularly a 3-phase separator by density. The glycerol which is the heaviest component will be at the bottom stream, while the FFA will be in the middle stream while the trace gasses will be removed at the top stream. The purified glycerol through this process would be able to produce glycerol with a purity of 99% [30].

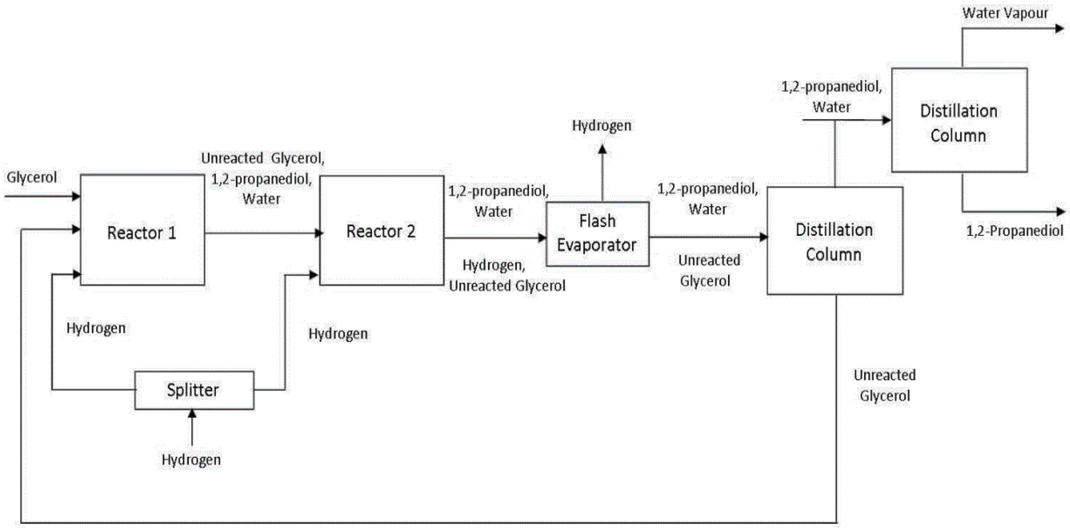


Figure 29 Hydrogenolysis Block Diagram

The process to produce marketable grade1,2-Propanediol from crude glycerol can be divided into two parts; hydrogenolysis of 1,2-Propanediol and product purification.

i. Hydrogenolysis of 1,2-Propanediol

This design utilizes two reactors for better yield of 1,2-propanediol. Purified glycerol diluted to 80wt% in water is fed to the first reactor operating at 200°C and 1378.95kPa. Hydrogen is split into two streams and channelled to both the reactors. The products of the first reactor with 54.8% conversion are unreacted glycerol, excess hydrogen, 1,2-propanediol and water. This stream of reactor 1 outlet is then fed to the second reactor with hydrogen. The second reactor shares similar temperature and pressure conditions as well as conversion rate. The product from the second reactor will then undergo purification process to remove products other than 1,2-propanediol.

ii. Product Purification

The output of the second reactor contains 1,2-propanediol, water, unreacted glycerol and hydrogen. First of all, hydrogen is removed through evaporation. Then, two distillation columns are used. The first distillation column is used to separate glycerol from the 1,2-propanediol and water stream. The separation achieved approximately 99.99% separation of glycerol at the bottom stream to be recycled and fed to the first reactor. The top stream of the first distillation column containing water and 1,2-propanediol is fed to the second distillation column to obtain 99.99% separation of 1,2-propanediol as the bottom product of the distillation column. The top stream contains water.

This production process produced several byproducts which can be treated, reused, sold to be used in other industries or discharged as waste. Among the treatment strategy and waste handling are as follows:

Table 19 Waste Handling and Treatment Strategy

Type of Waste	Treatment Strategy
Ash	• Sell to produce new materials i.e Lafarge
Sodium Chloride	• Disposal to Kualiti Alam Sdn. Bhd
Methanol	• Sell as raw material at RM1.10/Litre
Oleic Acid	• Sell to industry at RM4.50/Litre
Wastewater effluent	• Treatment according to EQA 1974 Standard B Requirement

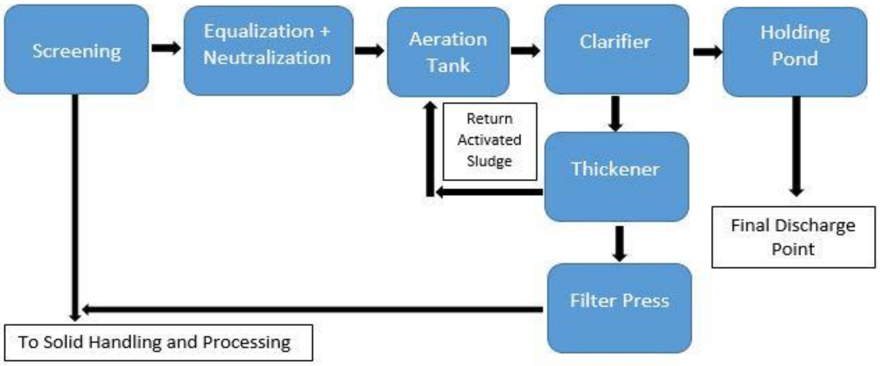


Figure 30 Example of Waste Water Treatment Proces

CHAPTER 6

CONCLUSION AND RECCOMENDATION

The environmental problem and scarcity of fossil fuels supply currently have gathered a great world concerns and commenced the study in exploring new alternatives, preferably environmental and economic friendly. Biodiesel is one of the biodegradable and non-toxic fuel which can be produced by transesterification of natural feed stocks. In this project, biodiesel is produced by one-step transesterification reaction of crude palm oil in the presence of synthesized heterogeneous catalyst, which is the mixed metal oxides catalyst, CeO_2-TiO_2. This loading of catalyst is 0.4 wt% and is calcinated under temperature of 300^{o}C. The catalyst is characterized using several analytical equipment for instance VPFESEM, FTIR, SAP and Raman Spectroscopy. Based on the analytical results, the structure of the catalyst enhance the catalytic properties and can be improved with a few modifications.

The optimized conditions of biodiesel production are determined in the presence of NaOH catalyst by using the response surface methodology (RSM) of Design Expert Software prior the other runs using the synthesized catalyst. The optimized parameters value are; 60 minutes reaction time, temperature of 55^{o}C, 1.0wt% of catalyst concentration and methanol to oil ratio of 11.05:1. Using these conditions, the reusability of CeO_2-TiO_2 is tested. The results shows that the catalyst can be recovered and reused up to 5 runs with only 3% to 6% decrement of yield from the fresh catalyst in the Run 1. Catalyst dosage and reaction time of the reaction are furthered study. The results stated that the yield increases as the dosage and reaction time increase as the reactants have sufficient time to react with each other in the presence of sufficient catalyst.

Experimental-simulation comparison was done using ASPEN HYSYS to compare the values. The data shows that the value obtained is reliable as the value difference is small. The additional study is done on the application of byproduct of biodiesel, glycerol, which can be converted in several value added chemicals. In this project, brief explanation is done on the process of converting glycerol into 1,2-propanediol which is widely used in many industries and of high demand nowadays. Al the objectives of the project are achieved. For future continuation, the synthesized catalyst can be improved by improving its structure to enhance the reaction. More comparison on metal oxides catalyst should be done to identify the most reactive combination for transesterification process.

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APPENDICES

APPENDIX I – GCMS Result for Crude Palm Oil

```
           Library Search Report

  Acq On    : 7 Nov 2014 11:10

  Sample    : Raw Palm Oil
  Data File : A-1.D
  Data Path : C:\msdchem\CAL 2010\DATA\2014\Syaza\
  DataAcq Meth:FAME-01.M
  Misc      :

  Operator  : Hasbullah

Search Libraries:     C:\Database\NIST05a.L          Minimum Quality: 50

Unknown Spectrum:     Apex minus start of peak

Integration Events:   ChemStation Integrator - events3.e

Pk#     RT Area%      Library/ID                      Ref#     CAS# Qual
______________________________________________________________________
  1               1.437 26.72 C:\Database\NIST05a.L
            Methylene Chloride                        1500000075-09-2 72
            Methylene Chloride                        1499000075-09-2 64

            Methylene Chloride                        1498000075-09-2 64

  2               1.463 63.40 C:\Database\NIST05a.L
            Hexane                                    1792000110-54-3 78
            Hexane                                    1790000110-54-3 78

            Hexane                                    1791000110-54-3 72

  3   14.465              4.82 C:\Database\NIST05a.L
            Palmitoyl chloride                      108201000112-67-4 22
            Cyclododecanone, 2-methylene-            52812003045-76-9 9
            Ethyl .alpha.-fluoro-3-nitro-cinna       843121000148-09-2   9

            mate

  4   14.481              1.25 C:\Database\NIST05a.L
            2-(2(3H)-Oxo-4H-1,4-benzoxazin-4-y       61937006243-07-8    9
            l)acetic acid
            2,3-Naphthalenediol, decahydro-, (       36283042177-35-5    7
            2.alpha.,3.beta.,4a.alpha.,8a.alph
            a.)-

            2,3-Naphthalenediol, decahydro-          36140057397-07-6    7

  5   15.851              1.00 C:\Database\NIST05a.L
            Silane, chloromethylphenyl-              27586001631-82-9 12
            Iron, tricarbonyl[(2,3,4,5-.eta.)-       82827012306-93-3 12
            2,4-cyclohexadien-1-ol]-
            benzaldehyde 4-[2-pyridyl]-3-thios       95795066243-84-3 10

            emicarbazone

  6   16.063              1.17 C:\Database\NIST05a.L  679611000212-45-5 25
```

```
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             (3H)-one
             9-Borabicyclo[3.3.1]nonane, 9-meth       356051000154-59-5 16
             ylthio-
             2-Ethoxymethyl-3-methyl-4-nitro-ph       648841000191-44-1 10

             enol

  7   16.100             1.65 C:\Database\NIST05a.L
             p,p-Bis(1-aziridinyl)-N-(2,4-xylyl       92496027824-44-8 10
             )phosphinic amide
             8,8,9-Trimethyl-deca-3,5-diene-2,7       628121000194-25-9   9
             -dione

             1,3-Dithiane, 2-(phenylmethylene)        62535017590-58-8    9
PAHSIM-APRIL-2014.M Mon Nov 10 09:14:50 2014
```

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Instrument  :   gcms1
Sample Name: Raw Palm Oil
Misc Info   :
Vial Number: 1
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