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Preliminary Study on Titanium Dioxide (TiO_2) Nanomaterials Catalyst for Palm Oil Diesel Production

By:

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16929

Dissertation submitted in partial fulfilment

of the requirements for the

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(Chemical)

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CERTIFICATION OF APPROVAL

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TRONOH, PERAK DARUL RIDZUAN

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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MHD MUIZZ BIN MHD SUBRI

ACKNOWLEDGEMENT

A great thankful to Allah, The great Almighty, for the strength, guidance and blessing until I accomplish my Final Year Project I (FYP I). Alhamdulillah.

In preparing this progress report, I was in contact with many people, researchers, academicians, and practitioners. They have contributed towards my understanding and thoughts. In particular, I wish to express my sincere appreciation to my Final Year Project supervisor Dr Sujan Chowdhury, for encouragement, guidance, critics and friendship. Without his continued support and interest, this project would not have been the same as presented here.

Last but not least, to those who have directly or indirectly contributed throughout the preparation of this Final Year Project (FYP).

ABSTRACT

The purpose of this study is to develop the production of biodiesel from palm oil with titanium dioxide (TiO_2) as catalyst in order to introduce alternative, renewable source of fossil fuel. This is due to the environmental concern that makes all researchers try to find other way in producing biodiesel that promising environmentally friendly. The characterization of the catalyst is done using several analytical equipment's such as Fourier Transform Infrared Spectroscopy (FTIR), Pyridine-adsorption Infrared Spectroscopy, Scanning Electron Microscopy (SEM), and Raman Spectra. Biodiesel production is generally carried out through the process of transesterification reaction. Titanium oxide, a heterogeneous catalyst with a chemical formula TiO_2 is synthesized and tested in the transesterification of palm oil with methanol. Different morphology of the titanium dioxide catalyst is used to compare the yield of biodiesel produced and the effectiveness of each morphology catalyst is analysed. In addition, the by-product (crude glycerol) from this process will be converted to value-added product.

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CHAPTER 1: INTRODUCTION

1.0 Background

It is generally known that fossil fuel resources are non-renewable and limited. These sources are in the approach of getting extinct[1]. The inadequacy of identified petroleum reserves will make renewable energy resources more attractive. Besides, it has become a problem to the world by the limitation of resources of fossil fuels for the future. The most feasible way to meet this growing demand is by utilizing alternative fuels. Biodiesel, defined as the monoalkyl esters of vegetable oils or animal fats, is an attractive alternative fuel because it is environmentally friendly and can be synthesized from edible and non-edible oils[2]. Biodiesel commonly produce using transesterification of triglycerides with alcohols, principally methanol. In this reaction, triglycerides react with an alcohol to produce fatty acid mono-alkyl esters (FAME) and glycerol[3]. Biodiesel is biodegradable, renewable, and non-toxic. It has a relatively high flash point and can be blended with fossil diesel fuel or used in pure form[4].

Although, various works and research have focused on heterogeneous catalyst development to produce biodiesel more simply, economically and efficiently, homogenous catalyst such as sodium hydroxide and sulphuric acid are still the primary catalyst in industrial scale biodiesel. Biodiesel is another element in the energy matric. The typical biodiesel production process involves a phase of transesterification that produce glycerol as the by-product.

Heterogeneous catalysts can provide clean and recyclable catalyst systems[4]. Titanium oxide is the most widely used photocatalyst since it assist the photocatalysis process for the treatment of organic pollutants. For a long time, it has been successfully degrading the dyes due to its impressive photocatalytic activity which are high stability against photocorrosion, non-toxity, low cost and high chemical stability[5]. Nevertheless, titanium oxide has its own weaknesses. Titanium oxide photocatalyst has wide band gap of 3.2eV which lead to the inefficient use of solar energy. In order to provide enough energy for electron excitation, a wavelength below 400nm is needed. However, only 2-3% fraction of solar light can be used, therefore limiting the use of abundant natural solar energy for the photocatalysis process.

In this final year project, the properties of titanium oxide are highly dependent on its nanosize and shape. By synthesizing titanium oxide through sol-gel method, the properties can be altered which later can enhance the characteristic of the catalyst.

1.1. Problem Statement

Fuel consumption is a major concern in the world as a source of environmental pollution and the issue has become a global issue. Alternative renewable energy has been explored through research and development over the years. Production biodiesel has been increased in recent years to replace fossil fuel. 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. Due to reaction mixture occur, homogenous catalysts quite expensive. In this project, the substitution of common homogenous catalysts with heterogeneous catalysts solves numerous problems related to economic and environmental aspects. Furthermore, the type of catalyst is ecological friendly and reasonable. 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.

1.2. Objective

The objectives of the project are as the following:

i. To synthesis the Titanium Dioxide (TiO_2) nanomaterials.
ii. To characterize the synthesized Titanium Dioxide (TiO_2) nanomaterials.
iii. To enhance the catalytic properties of Titanium Dioxide (TiO_2) nanomaterials.
iv. To perform simulation using ASPEN HYSYS for biodiesel production
v. To produce value-added product by optimizing glycerol which is obtain from biodiesel production

1.3. Scope of Study

i. Synthesizing of Titanium Dioxide (TiO_2) nanomaterials using ionic liquid.
ii. Characterization of Titanium Dioxide (TiO_2) nanomaterials by various analytical tools to identify the structural properties.

iii. Analysing the effect of Titanium Dioxide (TiO_2) nanomaterials as catalyst in biodiesel production.

iv. Performing parametric optimization using response surface methodology.

v. Comparison between experimental and simulation biodiesel production.

CHAPTER 2: LITERATURE REVIEW

1.4. Biodiesel

Biodiesel is chemically constituted of fatty acid alkyl esters that can be obtained through the transesterification of triglycerides, or from the esterification of fatty acids, both in the presence of a short chain alcohol such as ethanol or methanol and, an acid or base catalyst. [6, 7]. It has a relatively high flash point and can be blended with fossil diesel fuel or used in pure form[4]. Biodiesel are monoalkyl esters of long chain fatty acids derived from renewable feed stock like vegetable oils and animal fats [7]. The production of biodiesel is through transesterification process which the oil reacts with monohydric alcohol with a catalyst[8]. Biodiesel can be used in pure form or may be blended with petroleum diesel at any concentration in most injection pump diesel engines. Edible vegetable oils such as palm oil in Malaysia, have been used for biodiesel production and found to be good diesel substitutes[9]. Table 1 shows the biodiesel physical properties.

Table 1 Physical Properties 0f Biodiesel [9]

Common name	**Biodiesel (bio-Diesel)**
Common Chemical name	Fatty Acid Methyl Ester (FAME)
Chemical Formula Range	C14–C24 methyl esters
Kinematic viscosity range (mm^2/s, at 313 K)	3.3–5.2
Density Range (kg/m^3, at 288 K)	860–894
Boiling point range (K)	>475
Flash point range (K)	420–450
Distillation range (K)	470–600
Vapour pressure (mm Hg, at 295 K)	<5
Solubility in water	Insoluble in water
Physical Appearance	Light to dark yellow, clear liquid
Odour	Light musty/soapy odour
Biodegradability	More biodegradable than petroleum Diesel
Reactivity	Stable, but avoid strong oxidizing agents

1.5. Vegetable Oil

Vegetable oil is already tested as fuel for engine by Rudolf Diesel over one hundred years ago[10, 11]. Even today, vegetable oil are becoming an alternative to normal petroleum-derived

diesel because they are renewable, and having a green and environmental friendly effect. Compared to the normal diesel, vegetable oil biodiesel have no sulphur content, have excellent lubrication properties and plants producing vegetable oils absorb more carbon dioxide than the amount they use to burn as biodiesel[12]. In this project, palm oil is used as the feedstock to produce biodiesel. Palm oil which has a balanced fatty acid composition in the level of saturated fatty acids is almost equal to that of the unsaturated fatty acids. Palmitic acid (44%-45%) and oleic acid (39%-40%) are the major component acids, with linoleic acid (10%-11%) and only a trace amount of linolenic acid. The low level of linoleic acid and virtual absence of linolenic acid make the oil relatively stable to oxidative deterioration. Several surveys conducted by Malaysian Palm Oil Board (MPOB) have showed that the Malaysian palm oil has a narrow compositional range. The specifications for the palm oil are given in Malaysian Standard MS814:2007 (Table 2).

Table 2 Characteristics for Crude Palm Oil[13]

Item No.	Identity Characteristics	Observed min. to max.
(i)	Apparent density, g ml^{-1} at 50°C	0.8889 to 0.8896
(ii)	Refractive index n_D 50°C	1.4521 to 1.4541
(iii)	Saponification value, mg KOH g^{-1} oil	194 to 205
(iv)	Unsaponifiable matter, % by weight	0.19 to 0.44
(v)	Fatty acid composition, (wt% as methyl esters)	
	C12:0	0.0 to 0.5
	C14:0	0.9 to 1.5
	C16:0	39.2 to 45.8
	C16:1	0.0 to 0.4
	C18:0	3.7 to 5.4
	C18:1	37.4 to 44.1
	C18:2	8.7 to 12.5
	C18:3	0.0 to 0.6
	C20:0	0.0 to 0.5
(vi)	Iodine value (Wijs)	50.4 to 53.7
(vii)	Slip melting point (°C)	33.8 to 39.2
(viii)	Total carotenoids as (β-carotene), mg kg^{-1}	474 to 689

1.6. Catalyst

Homogeneous catalysts possess advantages including high activity and mild reaction. However, the use of homogeneous catalysts leads to soap production. Besides, in the homogeneous process the catalyst is consumed thus reducing the catalytic efficiency, causing the increase in viscosity and gels are formed. Thus, the cost of the biodiesel production using

homogeneous catalysis still not competitive compared to cost of diesel produced from petroleum. Heterogeneous catalysts remains in different phase (i.e. solid, immiscible liquid or gaseous) to that of the reactants the process[14]. Therefore, 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[15].

Recently, catalyst separation and pollution problems has been an important subject for many laboratories worldwide. Solid acids offer the advantages of easy catalyst separation and low pollution effects[16]. Alternatively, sulfated titania has shown to be a good acid solid catalyst for a large number of reactions: isomerization, acylation of aromatics, alkylation, esterification, pho-tocatalytic oxidation, decomposition of *iso*-propanol and transesterification of vegetable oils [16].It seems that sulfated titania develops important acidity and because of this property, it has become a promising acid solid catalyst to carry out the esterification of fatty acids[16]. TiO_2 was prepared by sol-gel method [3, 17], and then the synthesized TiO_2 was added into H_2SO_4

1.7. Transesterification Reaction

Transesterification is the displacement of alcohol from an ester by another in a process similar to hydrolysis, except than alcohol is used instead of water[8]. The transesterification reaction is represented by the general equation as in Figure 1.

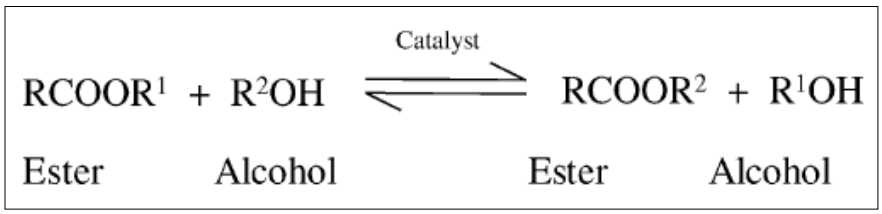


Figure 1 General equation of transesterification

In the transesterification reaction, long chain and branched chain fatty acid molecules are converted to monoester. There are three consecutive reversible steps involved;

i. Conversion of triglycerides to diglycerides,
ii. Diglycerides to mono-glycerides
iii. Glycerides are converted into glycerol and one ester molecule in each step

The ester produced in this reaction has similar properties to diesel. The reaction is as shown in Figure 2.

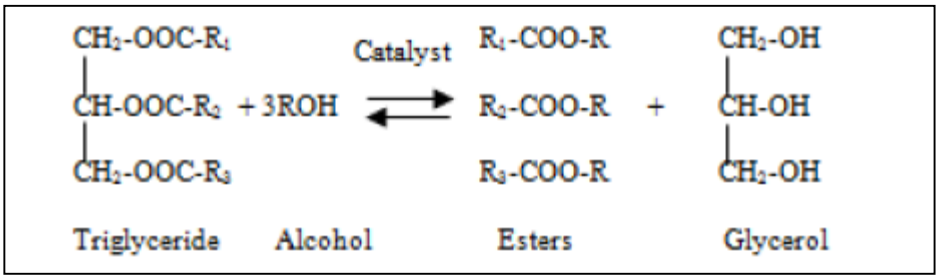


Figure 2 Transesterification of triglycerides with alcohol

The most common alcohol used in transesterification are short chain alcohol such as methanol, ethanol and propanol. Methanol is mostly used because it is the cheapest.

CHAPTER 3 METHODOLOGY/PROJECT WORK

3.1 Chemicals needed

In order to perform the acid esterification and base transesterification to produce biodiesel from castor 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. Toluene
7. Isopropanol
8. Phenolphthalein

3.2 Catalyst Synthesis

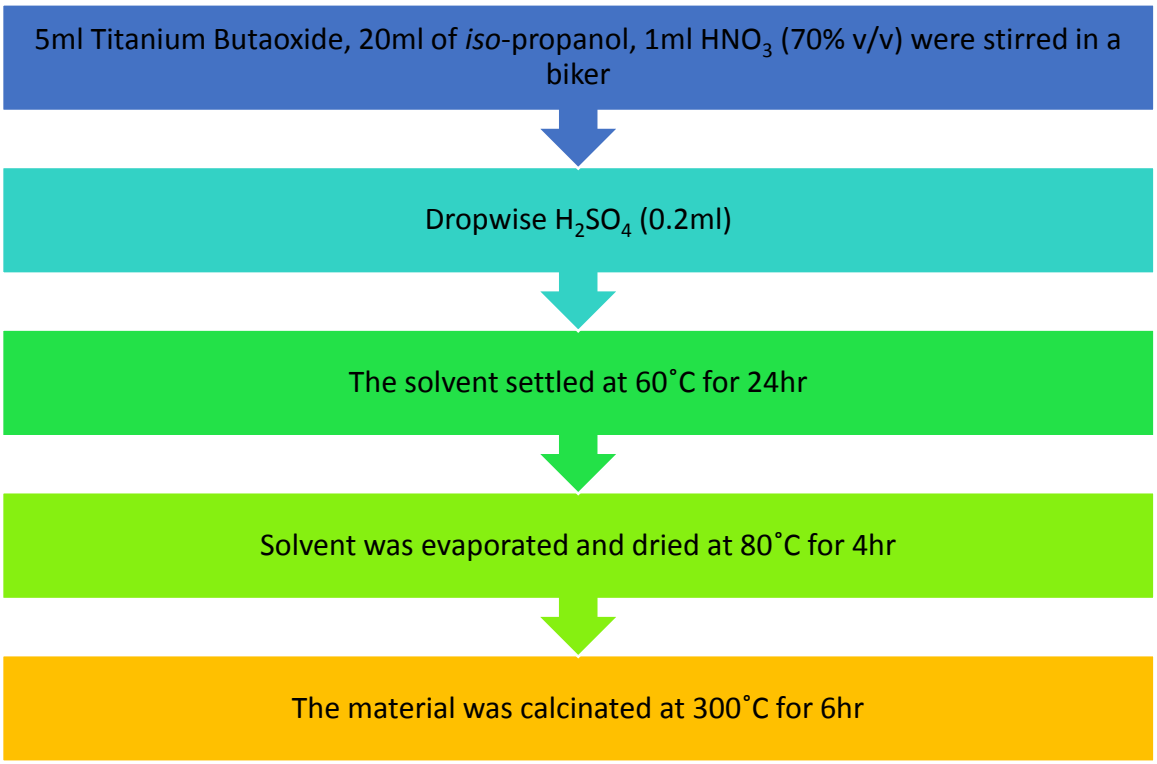


Figure 3 Synthesizing of the catalyst

3.2.1 Analytical Equipment

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

Table 3 Analytical equipment and functions

No	Analytical Equipment	Model	Functions
1	Fourier Transform Infrared Spectroscopy (FTIR)	Perkin Elmer Spectrum One	Organic functional group
2	Scanning Electron Microscopy (SEM)	Zeiss Supra 55 VP	Surface topography
3	Surface Area and Pore Size Analyzer (SAP)	Micromeritics ASAP 2020	Surface are and pore size of the catalyst
4	Raman Spectrometers	Horiba HR 800	Active side of catalyst

3.3 Biodiesel Production

The methodology of the experiment basically follows 4 steps shown in Figure 3:

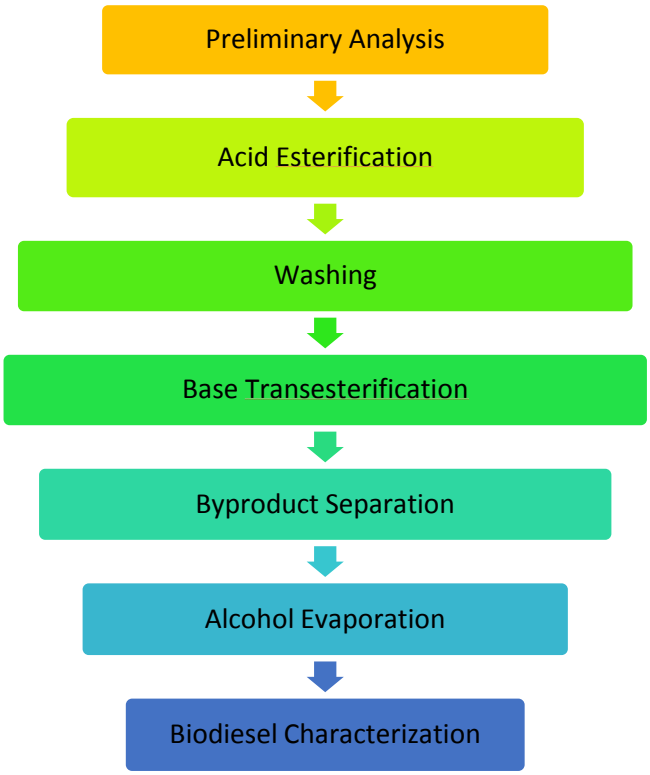


Figure 4 General procedures for biodiesel production

3.3.1 Preliminary Analysis

The basic oil analysis is to be performed on the palm oil and treated palm oil following the American Oil Chemists' Society (AOCS) method[18]. The analysis is to determine the acid value and the free fatty acid (FFA) content in the oil. It is important to know the FFA content because high FFA can lead to saponification of the oil instead of producing biodiesel. Therefore, 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 *iso*-propylene and 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.

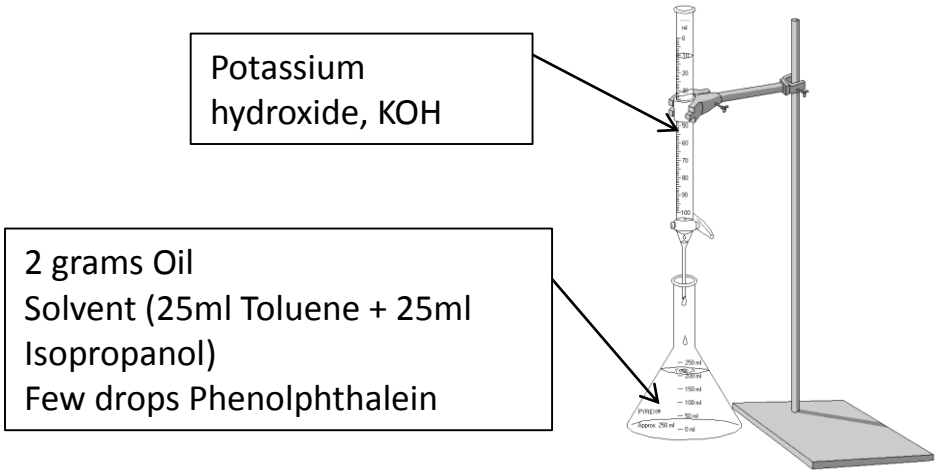


Figure 5 Titration to determine FFA content

The acid value is then calculated by using the equation

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

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

The FFA value is calculated from the acid value

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

3.3.2 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 retreated 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 ˚C

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

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

Sulphuric Acid amount =5% of oil amount

3.3.3 Base Transesterification

The oil or triglycerides undergoes esterification with the presence of base catalyst. The base catalyst to be used is the heterogeneous catalyst, titanium oxide. The process parameters are shown in Table 4 below.

Parameters	***-1***	***0***	***+1***
A: Oil to methanol ratio	6	9	12
B: Catalyst concentration	0.1	0.25	0.4
C: Temperature	50	65	80
D: Time	30	105	180

Table 4 Process Parameters

50 grams of pre-treated oil is mixed together with methanol and the catalyst, titanium oxide and then is stirred for a specific time. 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.

3.3.4 Optimization of parameter values

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 4. The low values are denoted as -1 while the high values are denoted as +1. These parameters are randomized to minimize the unexpected variability on the response.

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 TiO_2-H_2SO_4. 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:

$$Y=\beta 0+\beta 1X1-\beta 2X2+\beta 3X3+\beta 4X4-\beta 11X12+\beta 22X22-\beta 33X32-\beta 44X42$$
$$+\beta 12X1X2+\beta 13X1X3-\beta 14X1X4+\beta 23X2X3+\beta 24X2X4-\beta 34X3X4$$

where Y is the methyl ester yield percentage, β0 is the intercept term, β1,β2,β3 and β4 are linear coefficients, β11,β22,β33,β44 are quadratic equations, β12,β13,β14,β23,β24,β34 are interactive coefficients and X1, X2, X3, X4 are the independent variables. The optimized conditions are then determined and used for further study with synthesized catalyst for biodiesel production.

3.3.5 Optimization on the use of crude glycerol

Value added product will be produce from crude glycerol. Glycerol as the structural component of many lipids is abundant in nature. It is produced by yeasts during osmoregulation to decrease extracellular water activity due to its compatible solubility [19]. The glycerol will be transform to poly-3-hydoroxybutyrate (PHB) through fermentation process by using *Cupreavidus necatoras* the bacteria. The process can be simplify as Figure below

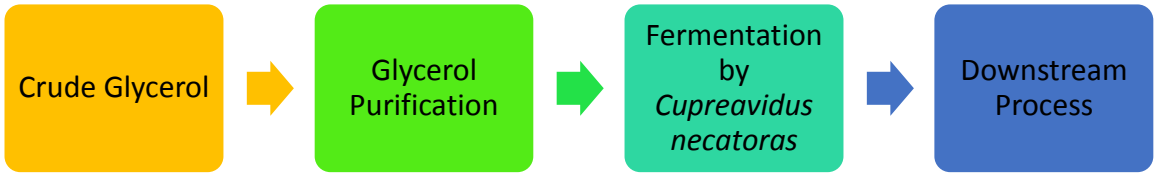


Figure 6 Schematic representation of the PHB production from crude glycerol by C. necator

CHAPTER 4 RESULTS AND DISCUSSION

All results, data and observations are obtained and explained in this chapter. This includes catalyst characteristic and yield values for 21 runs of base transesterification. The yield values are then used to optimize the parameters which are oil to methanol ratio, catalyst concentration, temperature and time using the Response Surface Methodology. The relationship between each parameter is also studied.

4.1 Characterization of Catalyst

4.1.1 Raman Spectra

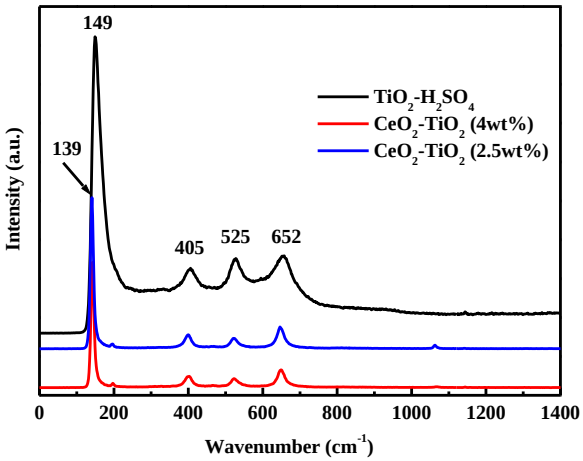


Figure 7 Raman data for TiO_2-H_2SO_4 and different weight percent of CeO-TiO_2 nanomaterials.

The result is obtained from Raman Spectrometer (Model: Horiba HR800). The Raman spectra for the catalysts are shown in Figure 7 above. The catalyst is synthesized with different method. The black lines indicate result of the TiO_2-H_2SO_4 catalyst. The blue and red lines indicate result of the catalysts synthesized of the CeO_2-TiO_2 with 4wt % and 2.5wt % respectively. The result shows the TiO_2-H_2SO_4 catalyst give band resolves higher than the CeO_2-TiO_2 catalyst. It is also shown that the higher loading of the CeO_2, the band resolves at higher value. For the catalyst used in this project, which is the one labeled as TiO_2-H_2SO_4 (S1), some bands were resolved at 149 cm^{-1}, 405 cm^{-1}, 525 cm^{-1}, 652 cm^{-1}. This characterizing the anatase crystalline form of the TiO_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 an enormous number of vacant active sites on the surface of the catalyst compared to the rutile crystalline form [21].

4.1.2 Infrared Spectroscopy

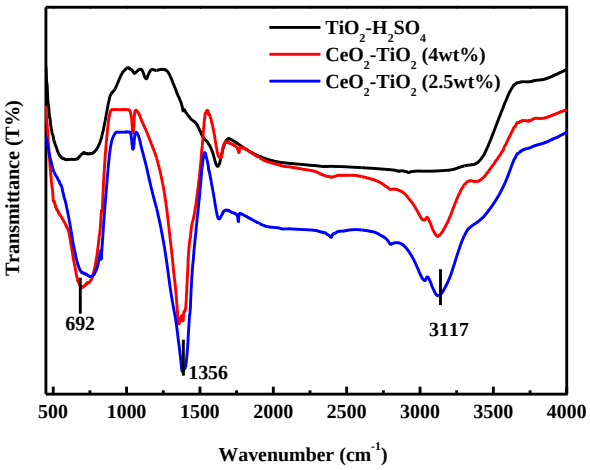


Figure 8 FTIR spectra for TiO_2-H_2SO_4 and different weight percent of CeO-TiO_2 nanomaterials

The first part of the spectra indicates the bands for single bond, hydroxyl group, in this case H-O-H bond. The infrared spectra of the catalyst shown in the Figure 8. It is observed that all catalyst present bands of absorption between 650 cm^{-1} and 1600 cm^{-1}. These happens due to the bending sulfate and cerium vibration mod. For the TiO_2-H_2SO_4 catalyst (black line), the bands pattern less fluctuate. This catalyst bands resolve at wavelength of 652 cm^{-1}, 1665 cm^{-1}, 3117 cm^{-1} However, the bands resolve at wavelength of 692 cm^{-1}, 1356 cm^{-1}, 3117 cm^{-1} for the both 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.

4.1.3 SEM

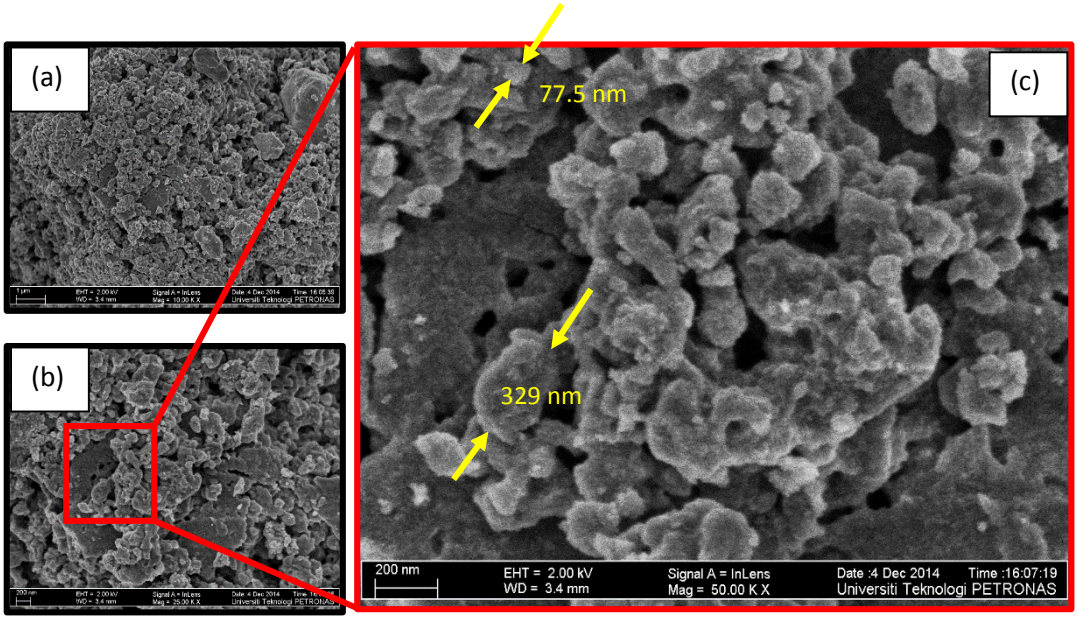


Figure 9 SEM images for as synthesized TiO_2-H_2SO_4 sample

These images were taken from Variable Pressure Field Emission Scanning Electron Microscope (VPFESEM, Zeiss Supra55 VP). Based on Figure 9 (c), the particle size of this catalyst is shown to be in the range of between 77 nm to 329 nm. The smaller the particle size, more reaction can take place.

4.2 Preliminary Analysis

The experimental work is currently undergoing using different types of oil to familiarize with the methodology of the experiment. The experiment has been completed from the characterization of oil feed and the acid esterification and is planning to continue with base transesterification. For the characterization of oil feed, various types of oil were used, namely soybean oil, waste castor oil and palm oil. The characterization of feed is done to determine the free fatty acid amount within the oil. The results of the experiment are as in Table 5.

Table 5 Free fatty acid (FFA) amount for untreated oils

Oil	**Acid value (mg KOH/g)**	**Free fatty acid (FFA) amount**
Palm Oil	0.22	0.11 %
Soybean oil	2.98	1.29%
Castor oil	3.61	1.81%

Palm oil has taken as the feedstock for this project.

4.3 Acid esterification

The experiment is continued with acid esterification whereby palm oil is taken for is reacted with methanol with the presence of an acid catalyst, sulphuric acid in order to reduce the FFA content. After the esterification process, the oil is extracted and characterized again to determine the new free fatty acid amount.

Table 6 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

To continue the process of base transesterification, the FFA should be lower than 2%. Based on Table 6, the results showed that the FFA increased after acid esterification greater than FFA untreated palm oil as shown in Table 5. This shows that the oil has been changed acid content increased less, this is occurs because the acid catalyst not fully separated in the mixture. To get the correct result without being affected by acid catalyst, water pH should be cleaned the same before and after washing biodiesel. A large amount of water needed and this is no better than economically. However, for this project FFA amount is already below 2%.

4.4 Base transesterification

The base transesterification is performed by following the design in Table 7 for TiO_2-H_2SO_4 catalyst. The response factor is the yield percentage based on the mass of biodiesel product.

Table 7 The yield percentage of biodiesel for each experimental run

Run	**Time (min)**	**Temp. (˚C)**	**Catalyst Concentration (wt %)**	**Methanol to Oil ratio**	**Yield (%)**
1.00	110.45	55.00	1.00	6.00	41.90
2.00	90.00	65.00	1.50	3.00	41.50
3.00	90.00	65.00	0.50	3.00	24.20
4.00	30.00	65.00	0.50	9.00	21.10

5.00	60.00	55.00	1.00	11.05	54.30
6.00	90.00	45.00	1.50	9.00	32.30
7.00	30.00	45.00	0.50	3.00	15.30
8.00	60.00	71.82	1.00	6.00	40.70
9.00	60.00	55.00	1.00	6.00	40.10
10.00	60.00	55.00	1.84	6.00	44.00
11.00	9.55	55.00	1.00	6.00	0.00
12.00	60.00	55.00	1.00	6.00	40.10
13.00	60.00	38.18	1.00	6.00	47.60
14.00	60.00	55.00	1.00	6.00	40.10
15.00	60.00	55.00	1.00	0.95	0.00
16.00	60.00	55.00	1.00	6.00	40.10
17.00	60.00	55.00	1.00	6.00	40.10
18.00	30.00	45.00	1.50	3.00	17.70
19.00	90.00	45.00	0.50	9.00	28.40
20.00	30.00	65.00	1.50	9.00	21.70
21.00	60.00	55.00	0.16	6.00	13.20

4.5 Optimization of parameter values

The optimization of parameter values are conducted by using the Design Expert 6.0.8. All data and graphs are obtained from the software. Perturbation plot compares all factors that can influence the process. Figure 10 shows the perturbation plot 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 the yield percentage, which is parameter C, catalyst concentration. The second most influencing factor is parameter D, oil to methanol ratio.

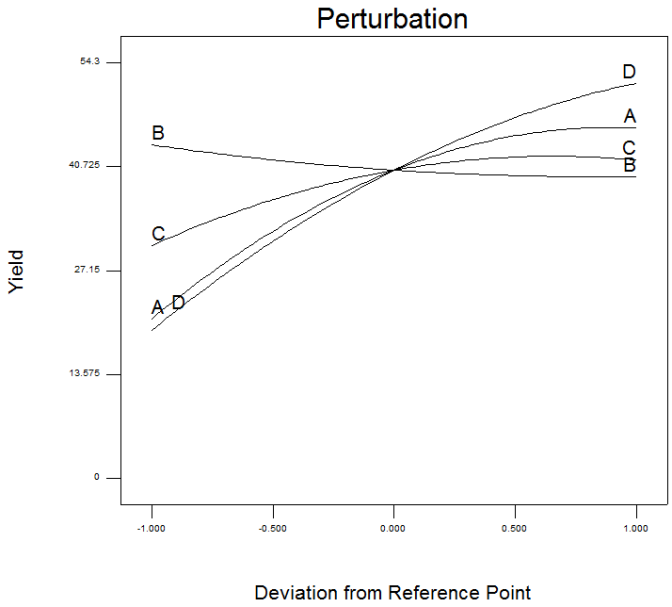


Figure 10 Perturbation plot for base transesterification

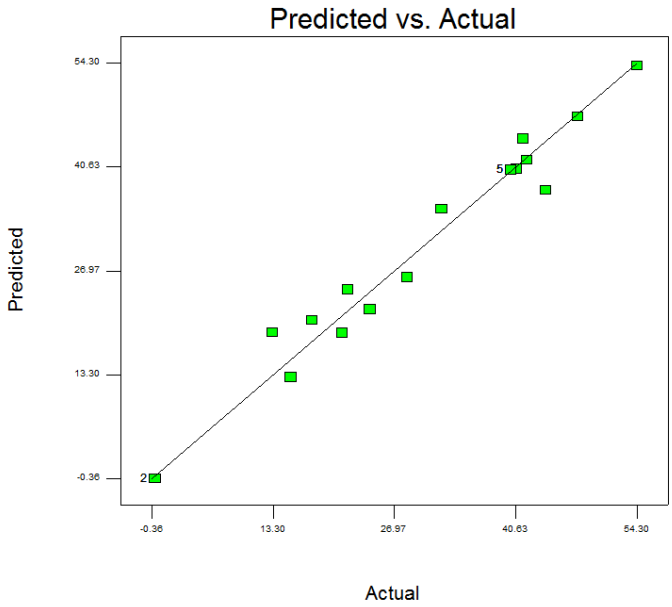
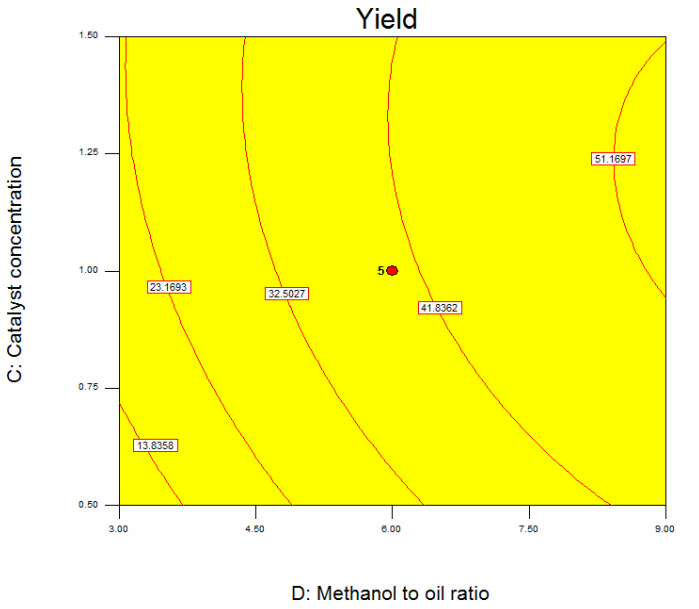


Figure 11 Predicted versus experimental values for base transesterification

Figure 11 shows the comparison between actual values of FFA% with the predicted values for acid esterification and Yield with predicted values for base transesterification respectively. From the plot we can see whether the points are linear, which indicates that the predicted values are close to the experimental values. It can be observed that the actual values lies near the predicted line thus these results are reliable. To further compare the factors, a three dimensional plot and contour plot can be done. Figure 12 to 17 show the effect of the different parameters on the biodiesel transesterification process. Figure 12 shows that by increasing the oil to methanol ratio and catalyst concentration, the yield will decrease.



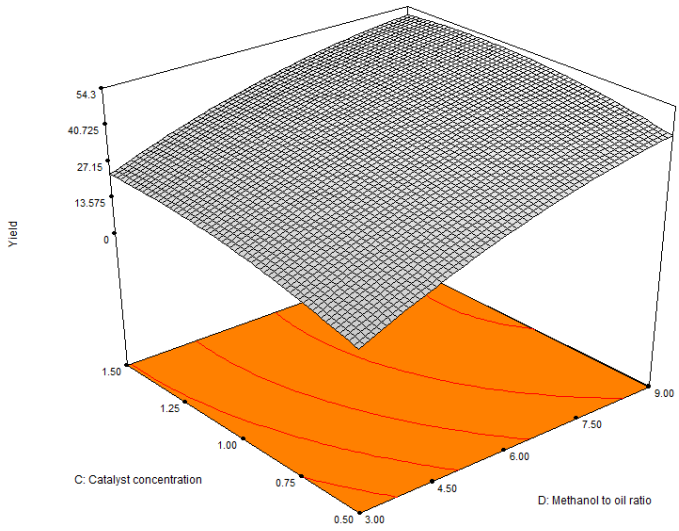


Figure 12 Combined effect of oil to methanol ratio and catalyst concentration (a) contour plot and (b) three dimensional plot

Figure 13 shows that by increasing the oil to methanol ratio and temperature, the yield will decrease.

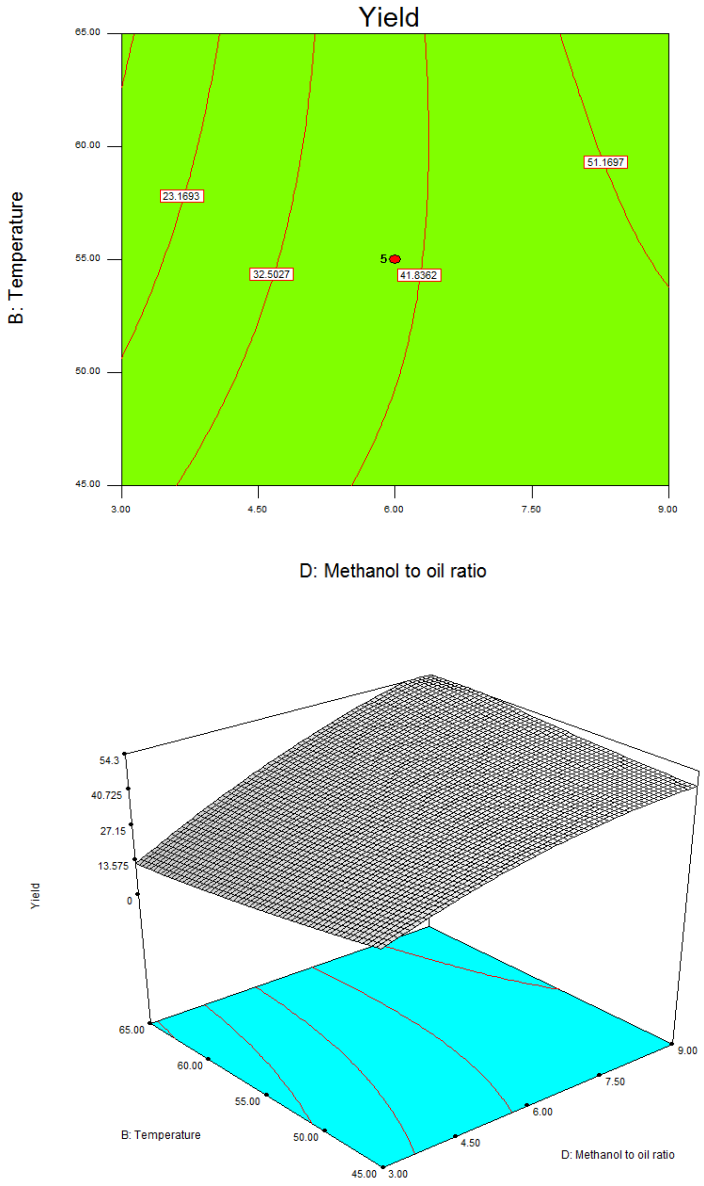


Figure 13 Combined effect of oil to methanol ratio and temperature (a) contour plot and (b) three dimensional plot

Figure 14 shows that by increasing the oil to methanol ratio and time, the yield will increase at first but will decrease for a higher value of oil to methanol ratio and time.

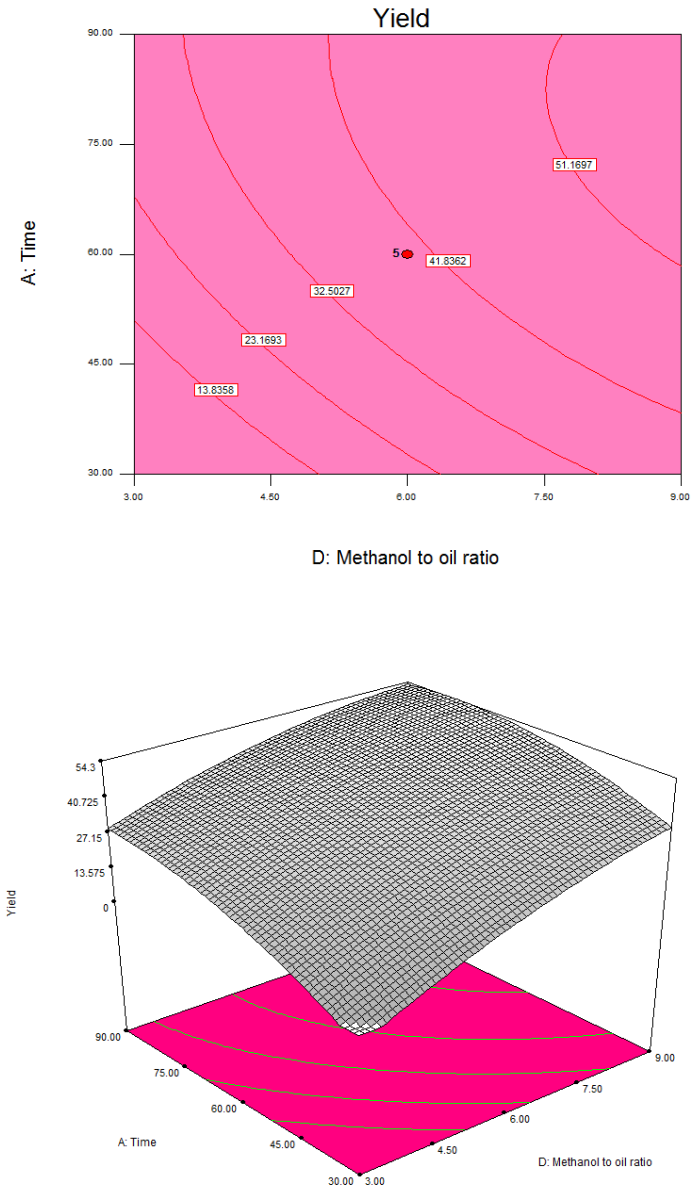


Figure 14 Combined effect of oil to methanol ratio and time (a) contour plot and (b) three dimensional plot

Figure 15 shows that by increasing the oil to catalyst concentration and temperature, the yield will decrease.

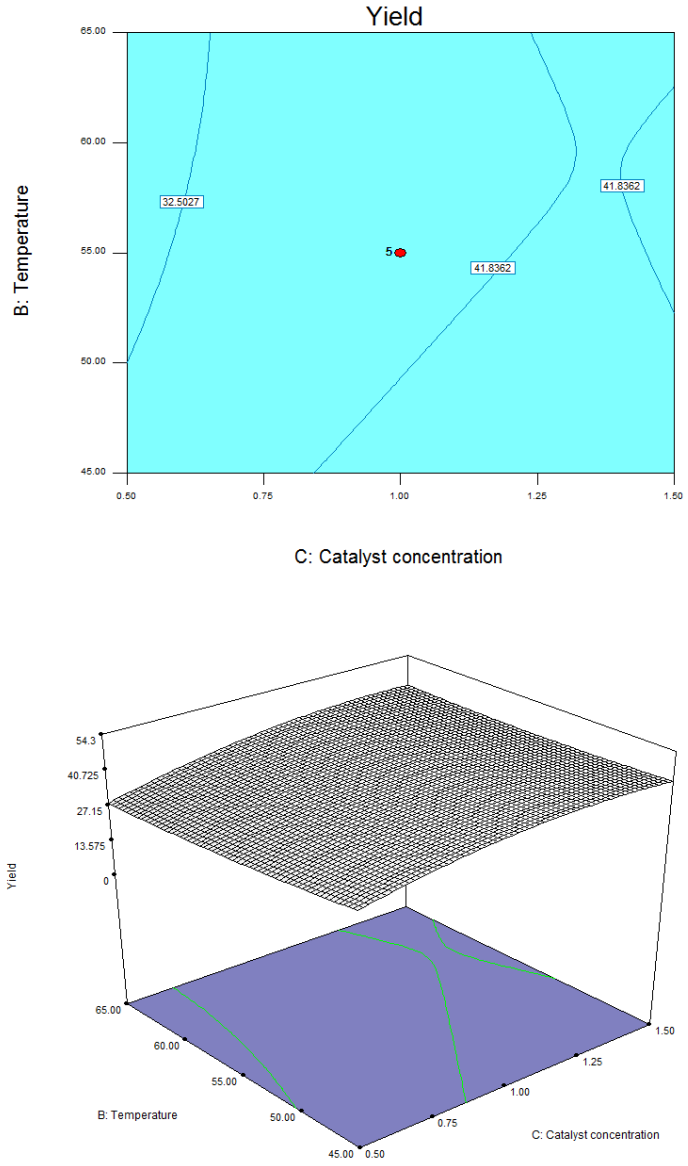


Figure 15 Combined effect of catalyst concentration and temperature (a) contour plot and (b) three dimensional plot

Figure 16 shows that at low value of catalyst concentration and time, by increasing the oil to methanol ratio and temperature, the yield will decrease. At high catalyst concentration and time, the yield will decrease.

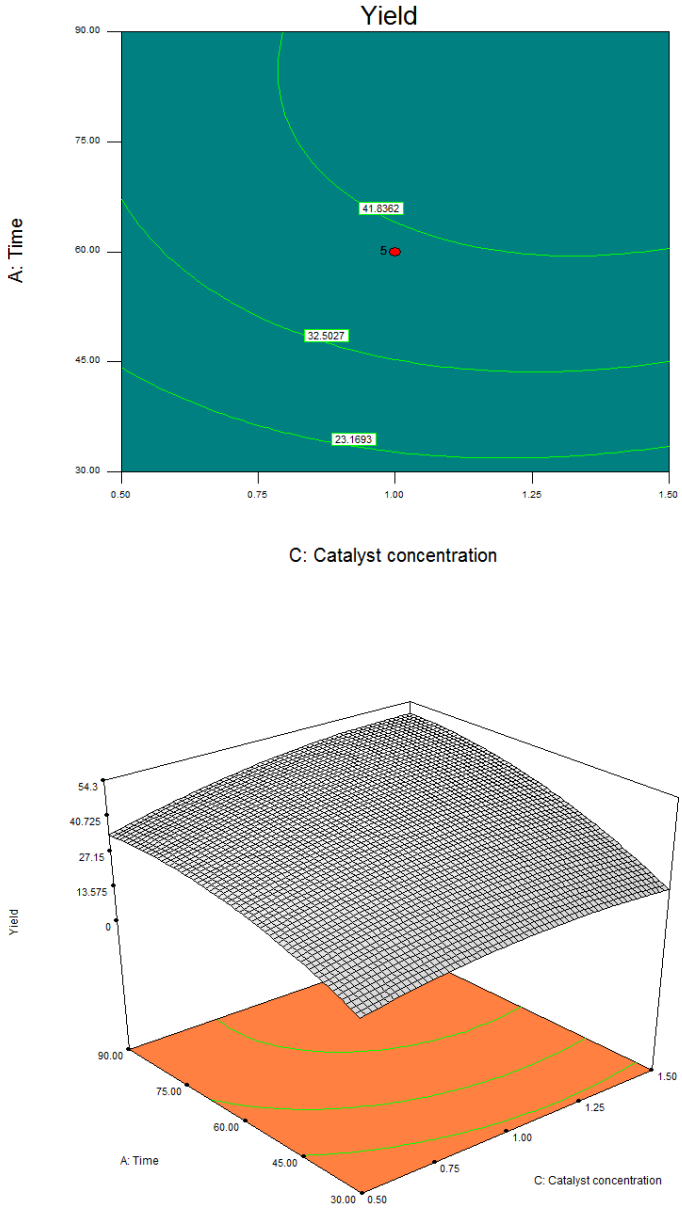


Figure 16 Combined effect of catalyst concentration and time (a) contour plot and (b) three dimensional plot

Figure 17 shows that by increasing the time and temperature, the yield will decrease.

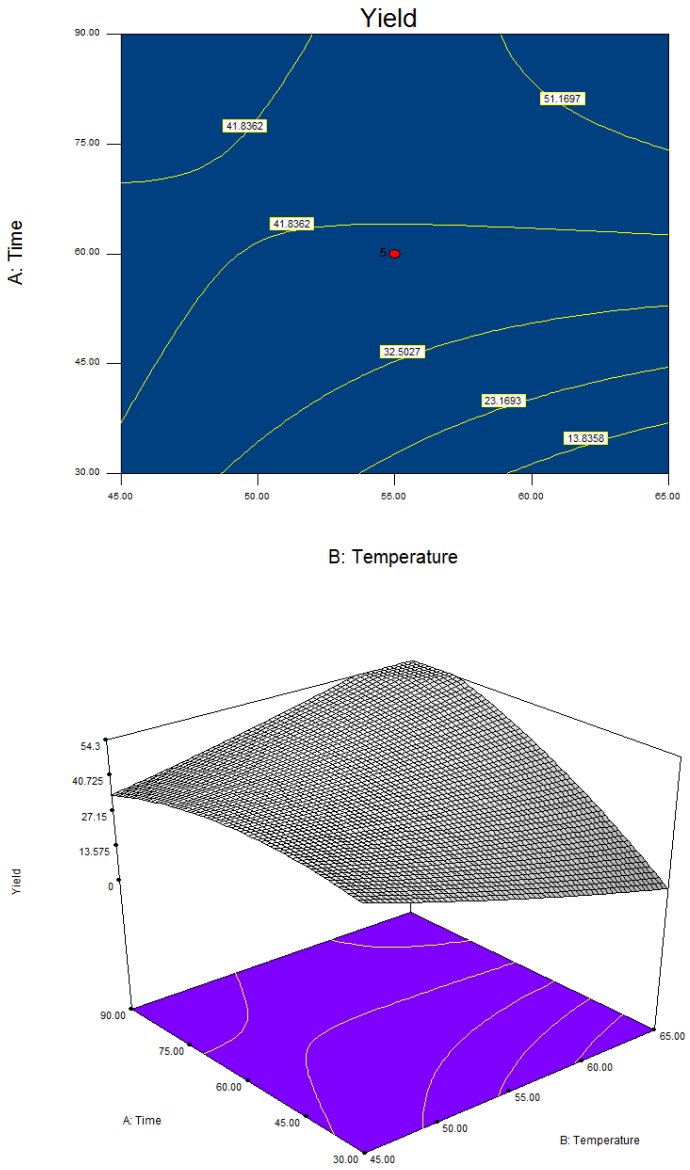


Figure 17 Combined effect of temperature and time (a) contour plot and (b) three dimensional plot

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 0-54.3%. The second order model equation in terms of coded factors are as follow:

Yield = 40.27 + 12.46A - 2.05B + 5.56C + 16.14D – 6.96A2 + 1.24B2 - 4.24C2 – 4.77D2 + 15.54AB + 2.27AC - 3.90AD + 1.45BC + 6.13BD - 1.90CD

4.6 Comparison of optimum operating parameters with previous studies

Table 8 summarizes the optimal parameter values obtained for the biodiesel production process. The values are compared to previous studies' findings.

Table 8 Comparison of process parameter values with previous studies

Parameters	M.L. Testa et al.[20]	J.L. Ropero-Vega et al.[16]	This project
A: Oil to methanol ratio	1:4	1:10	1:11.05
B: Catalyst concentration (%)	5	2	1
C: Temperature (^{o}C)	60	80	55
D: Time (min)	60	60	60

4.7 Biodiesel Properties

The biodiesel properties were analyzed and compared with ASTM D6751 and EN 14214 standard methods as shown in Table 9.

Table 9 The paramaeter of biodiesel sample and the value of standards EN14214 and ASTM D6751

No	**Parameter**	**Heterogeneous**	**EN 14214**	**ASTM D6751**
1	Viscosity	25.73 ns/m^3	3.5 -5 ns/m3	1.9 – 6.0 ns/m3
2	Density	987.241 kg/m^3	860 – 900 kg/m3	-
3	Flash point	129 min	120 min	93 min
4	Cloud point	3.7 ^{o}C	-	-
5	Pour point	2.9 ^{o}C	-	-

The density and the viscosity data obtained unable to get within the required limit for the biodiesel produced.

4.7 Experimental-Simulation Comparison

4.7.1 Reaction Modelling

This Equation 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[21] .

Triglycerides [TG]+3 Methanol [ML]→3 Methylesters+Glycerol

r=−d[TG]dt=k[TG][ML]

4.7.2 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 TiO_2-H_2SO_4 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 TiO_2-H_2SO_4 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 [22].

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

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

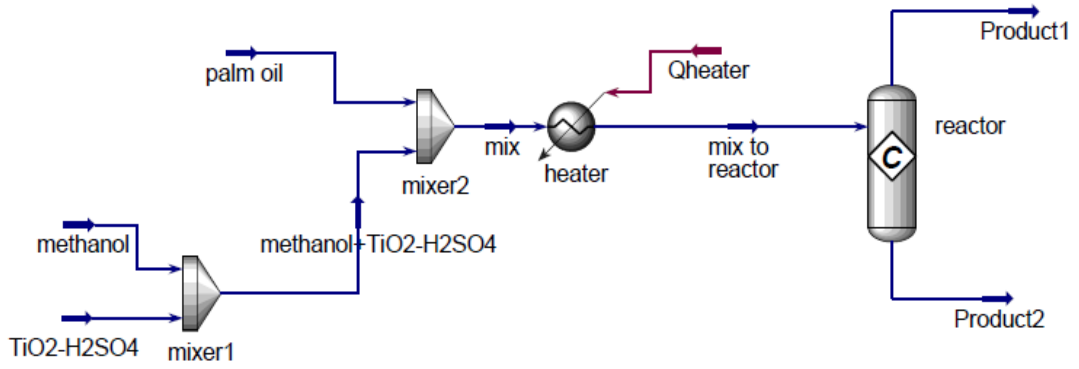


Figure 18 ASPEN HYSYS Flow sheet of conversion reactor for transesterification reaction of palm oil under optimized conditions

Table 10 Experimental-Simulation Comparison Yield at Optimum Conditions

t (min)	x_{TG} (%)	
	Experimental	ASPEN HYSYS
30	25.9	25.2
60	54.3	53.5
90	61.2	59.8
120	66.7	65.9
150	70.2	68.5

The tabulated data shown in Table 10 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 19 plotted the temporal profile of transesterification reaction of palm oil under optimized conditions obtained from experimental and simulation values.

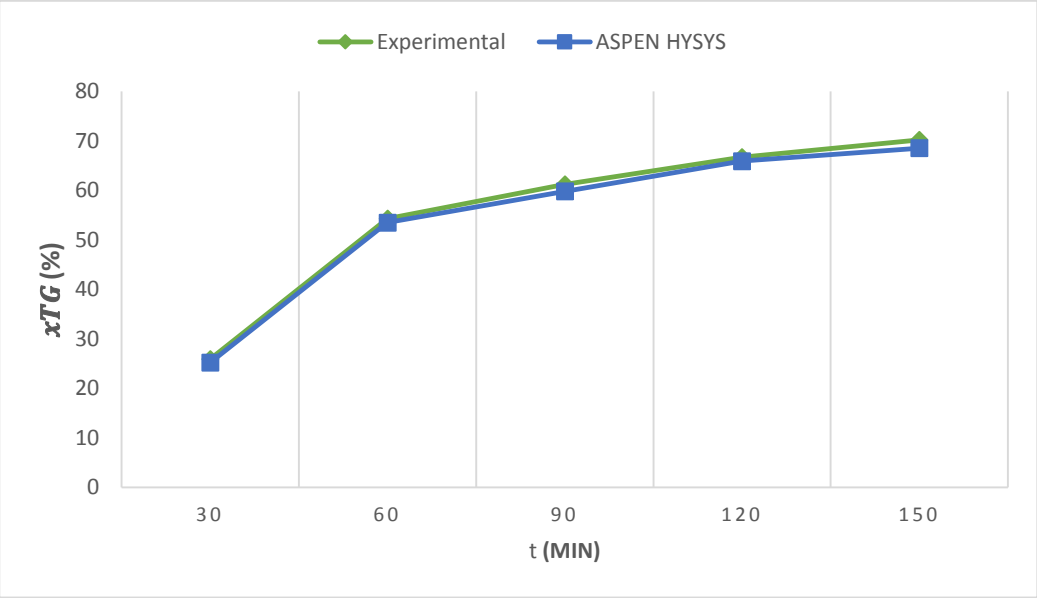


Figure 19 Temporal profile of transesterification reaction of palm oil with using oil to methanol ratio 1:11.05, reaction time of 60˚C, catalyst concentration 1

4.7 Value added product

Since glycerol is an unrefined raw material that must be refined before to be converted into new product, the use of glycerol is limited. As the productions of biodiesel were increased dramatically, the production of its by-product which is glycerol also multiplied over times. So, it's important to utilize this crude glycerol, the main by-product of biodiesel production, in

order to produce more valuable chemicals. For typical crude glycerol it will contains less than 65 wt % of glycerol. Purification of crude glycerol will be the first step to utilize the glycerol into value-added products. There are many process can be done to the glycerol to produce value added product. For example the processes are dehydration, fermentation, oxidation and catalytic conversion. For this project, the glycerol been produced to poly-3-hydoroxybutyrate (PHB) through fermentation process by using *Cupreavidus necatoras* the bacteria. PHB is the most studied among a wide variety of polyhydroxyalkanoates[23], bacterial biodegradable polymers known as potential substitutes for conventional plastics.

Poly-3-hydroxybutyrate (PHB) is a linear polyester od D(-)-3 hydroxybutyric acid which was first discovered in bacteria in 1925. It is collected in intracellular granules by a wide variety of Gram-positive and Gram-negative organisms under conditions of a nutrient limitation besides the carbon source [24]. The polymer which serves as a reserve of carbon and energy is now exposed, although the most abundant of a general class of compounds denoted as poluhydroxyalkancates and possesses a general formula.

Glycerol purification, glycerol fermentation (cell growth and PHB accumulation), mass cell pretreatment, PHB isolation, and PHB purification are the five stages needed for the process of PHB production from raw glycerol. In this project, C.Necator is used as the bacterial strains in order to undergo the fermentation process. Glycerol purified at 98% was considered as a substrate in this project. The downstream process for PHB purification from a fermentation broth can be divided in three parts: pre-treatment, extraction, and purification. The overall process of PHB production and downstream process as in the figure below:

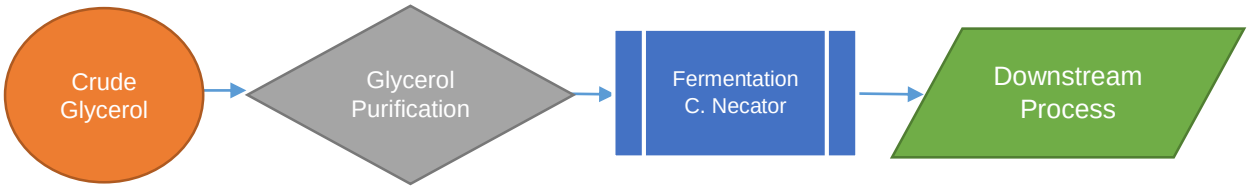


Figure 20 Overall Process of PHB

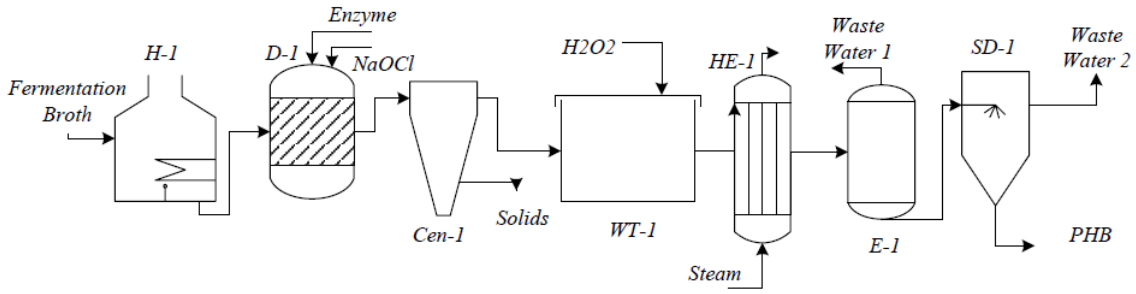


Figure 21 Simplified flowsheet for the first downstream process. H-1: Heater I, D- 1: Digestor I, Cen-1: Centrifuge I, WT-1: Washer Tank I, HE-1: Heat Exchanger I, E-1: Evaporator I, SD-1: Spray Drier I

CHAPTER 5: CONCLUSION AND RECOMMENDATION

In conclusion, all the objectives can be achieved. This project aims to explore the palm oil as feedstock and a heterogeneous catalyst, Titanium Dioxide. The synthesis and characterization of Titanium Dioxide nanomaterials are expected to be one of the potential alternatives in the production of biodiesel. The utilization of sulphuric acid in synthesizing Titanium Dioxide nanomaterials will assist in improving the yield of biodiesel and other production factors. The effect of oil to methanol ratio and the operating conditions to achieve an optimal response with 54.3% of biodiesel yield for the catalyst (S1) and 59.7% yield for catalyst (S2) were found to be 1:11.05 for the methanol to oil ratio, 1% for the catalyst concentration, 55°C for the reaction temperature and 60 minutes for the reaction time. With further and improved research, this material can be used widely in biodiesel industry.

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