BIODIESEL PRODUCTION FROM PALM OIL OVER CERIUM OXIDE DOPED TITANIUM DIOXIDE ($\mathbf{CeO_2 - TiO_2}$) NANOMATERIALS

BY:

GUNAVICKNESWARY LOGANATHAN

14993

Dissertation submitted in partial fulfillment of the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

Universiti Teknologi Petronas,
32610 Bandar Seri Iskandar,
Perak Darul Ridzuan,
Malaysia.

CERTIFICATION OF APPROVAL

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Approved by,

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(DR. SUJAN CHOWDHURY)

UNIVERSITI TEKNOLOGI PETRONAS
BANDAR SERI ISKANDAR, PERAK

January 2015

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.

(GUNAVICKNESWARY A/P LOGANATHAN)

ACKNOWLEDGEMENT

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ABSTRACT

A brief study was carried out on heterogeneous base catalyst for the transesterification process of oil targeted at effective production of biodiesel. So in order to investigate the catalytic activity and efficiency in improving the production of biodiesel, the characterization and synthesis of Titanium Oxide nanoparticles with ionic liquid to enhance its catalytic effects was carried out. Furthermore, the characterization of Titanium Dioxide was done by using various analytical equipments such as Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM), Raman Spectra Analysis and so on. So by this, the relation of structure and catalytic activity of the prepared substances can be examined. The catalyst dosage, reaction time and temperature, and the catalyst reusability are the main variables that need to be evaluated. Besides that, the biodiesel is fabricated by using selected feedstock which is palm oil, and then it will be characterized to study the reaction of biodiesel with the catalyst prepared in order to improve the production. The Free Fatty Acid of palm oil is 0.11% and it is below 2%. So this allows for one-step transesterification process. Under the optimized condition the reusability of the catalyst is also tested and it can recycle for about 5 times with some decrease in yield. Generally this shows that heterogeneous catalyst can be recycled and dosage and reaction time can also be manipulated to get better yield. The obtained result proves that with increase of dosage and reaction time we can increase the yield of biodiesel. So overall, there is a very high chance to support biodiesel production by using this method.

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CHAPTER 1

INTRODUCTION

1.1 Background Study

Biodiesel is a biodegradable and renewable clean – burning fuel which replaces diesel. Basically it refers to vegetable oils, waste cooking oils and animal fats which are mainly the alkyl esters. Malaysia is one of the countries which produces large amount of biodiesel. It is definitely can be used as a renewable energy source.

It is typically produced by transesterification process where chemical reacting lipids react with alcohol producing fatty acid esters, which requires a catalyst to obtain reasonable conversion rates. There are a lot of advantages in using biodiesel such as, less air pollutants, less greenhouse gas emissions, non-toxic, safer to handle and so on. On the other hand, there are some major obstacles for biodiesel production in current economic market such as lower fuel economy and power and expensive. All these are caused by higher cost of raw materials for biodiesel production [3-5].

Transesterification which is also known as alcoholysis, is the main process in biodiesel production. Basically transesterification is the reactions occur between alcohol and lipid which will form esters and by-product which is glycerol (reaction of fats/oil with alcohol to form esters and glycerol [13]. The stoichiometry for alcohol to lipid are 3:1 but usually in industries the ratio will be increased to 6:1 to get higher production yield [14]. The alcohols that can be used are methanol, ethanol, butanol and amyl alcohol. In large industries, methanol and ethanol are the most frequently used, specifically methanol due to its lower cost and also its physical and chemical properties (polar and shortest chain-alcohol) [13]. Generally, transesterification involves a sequence of three reversible reactions where it will yield one ester molecule from each glycerides at each reaction, as follows:

1. Conversion of triglycerides to diglycerides.
2. Conversion of diglycerides to monoglycerides.

3. Conversion of monoglycerides into glycerol

However, the reaction will not proceed to next extend in lack of catalyst or supercritical condition. So, various kind of catalyst from homogenous and heterogeneous have been used in biodiesel fabrication [12]. Following is the general transesterification process:

$$\begin{array}{lllll} CH_2-OCOR^1 & & & CH_2OH & R^1COOCH_3 \\ CH-OCOR^2 & +3CH_3O & \underline{\quad\text{Catalyst}\quad} & CHOH+ & R^2COOCH_3 \\ CH_2-OCOR^3 & & & CH_2OH & R^3COOCH_3 \end{array}$$

Triglycerides **Methanol** **Glycerol** **Methyl Esters** (1)

Fuel Properties are basically a research on the properties of the oil on different categories such as kinematic viscosity, oxidative stability cloud point, acid value, sulphur content and many more. The studies of the fuel properties are very important as it helps to produce more improvised biodiesel. And also it is essential to know the properties, so that can figure out the effect of catalyst on it and so on as shown in Table 1 and 2 [1]. There are some properties are varies as follows;

- Chemical Structure

Basically the transesterification process where the conversion of glycerides to glycerol (Methyl esters of C_{12} to C_{22} fatty acids)

- Fuel Material

This discusses about the feedstock. Feedstock are, any material the is converted to another form of fuel or energy product. Where, in this case, palm oil is used to produce biodiesel.

- Gasoline Gallon Equivalent

It is the amount of fuel it takes to equal the energy content of one liquid gallon of gasoline. So generally, according to the statistical data, B100 has 103% of the energy in one gallon of gasoline or 93% of the energy of one gallon of diesel. At the same time, B20 has 109% of the energy of one gallon of gasoline or 99% of the energy of one gallon diesel.

- Energy Content

There two categories under energy content which are lower heating value and higher heating value. The lower and higher heating value is the amount of heat released during the combustion of a specific substance, usually fuel. The lower heating value is determined by subtracting the heat of vaporisation of water from higher heating value for a particular substance, treating water a vapour. Usually, the lower heating value is 119,550 Btu/gal for B100.

The higher heating value is determined by bringing all the products of combustion back to the original pre-combustion temperature, condensing any water vapour generated. This value assumes the entire water component is liquid in the products of combustion and that heat can be used. Usually, the lower heating value is 127,960 Btu/gal for B100.

- Physical State

  The physical state of biodiesel is liquid.

- Cetane number

  Cetane number is the fuel susceptibility to self-ignite. The higher the cetane number, the greater the fuel's tendency to self-ignites.

- Flash Point

  The flash point is the minimum temperature at which a liquid gives off vapour within a test vessel in sufficient concentration to form an ignitable mixture with air near the surface of the liquid.

Table 1 : Standard Specifications for biodiesel based on ASTM [1]

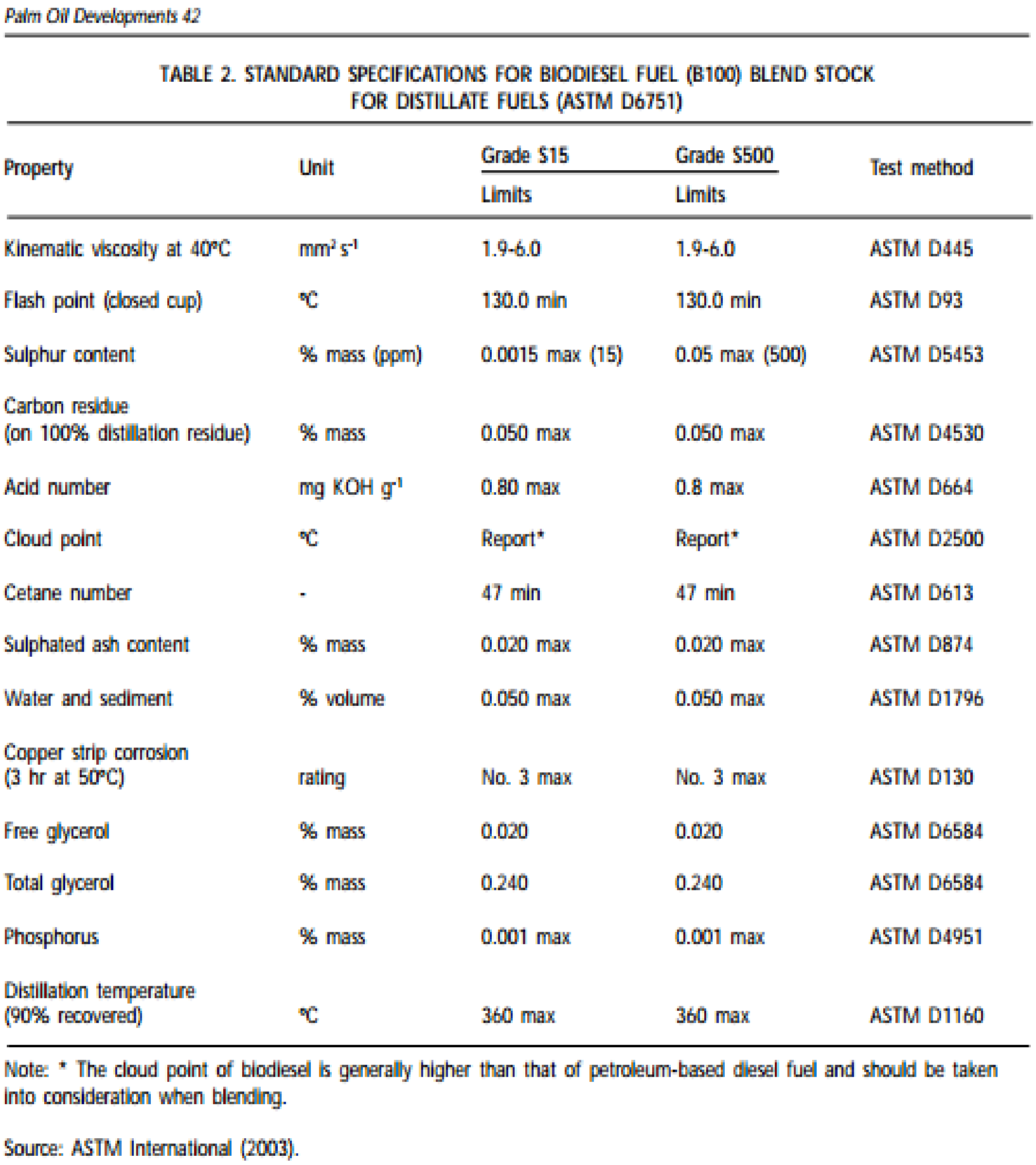

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TABLE 2. STANDARD SPECIFICATIONS FOR BIODIESEL FUEL (B100) BLEND STOCK FOR DISTILLATE FUELS (ASTM D6751)

Property	Unit	Grade S15	Grade S500	Test method
		Limits	Limits	
Kinematic viscosity at 40°C	$mm^2 s^{-1}$	1.9-6.0	1.9-6.0	ASTM D445
Flash point (closed cup)	°C	130.0 min	130.0 min	ASTM D93
Sulphur content	% mass (ppm)	0.0015 max (15)	0.05 max (500)	ASTM D5453
Carbon residue (on 100% distillation residue)	% mass	0.050 max	0.050 max	ASTM D4530
Acid number	mg KOH g^{-1}	0.80 max	0.8 max	ASTM D664
Cloud point	°C	Report*	Report*	ASTM D2500
Cetane number	-	47 min	47 min	ASTM D613
Sulphated ash content	% mass	0.020 max	0.020 max	ASTM D874
Water and sediment	% volume	0.050 max	0.050 max	ASTM D1796
Copper strip corrosion (3 hr at 50°C)	rating	No. 3 max	No. 3 max	ASTM D130
Free glycerol	% mass	0.020	0.020	ASTM D6584
Total glycerol	% mass	0.240	0.240	ASTM D6584
Phosphorus	% mass	0.001 max	0.001 max	ASTM D4951
Distillation temperature (90% recovered)	°C	360 max	360 max	ASTM D1160

Note: * The cloud point of biodiesel is generally higher than that of petroleum-based diesel fuel and should be taken into consideration when blending.

Source: ASTM International (2003).

Table 2 : European Committee Standards of biodiesel [2]

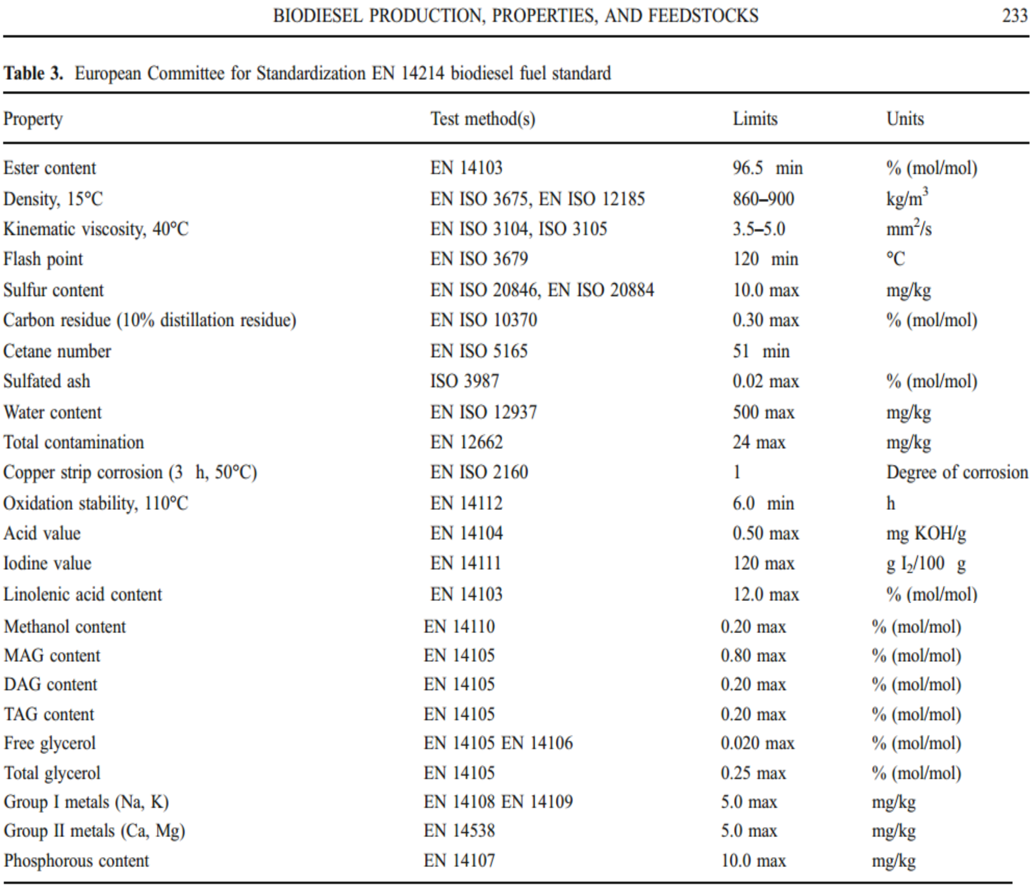

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Table 3. European Committee for Standardization EN 14214 biodiesel fuel standard

Property	Test method(s)	Limits	Units
Ester content	EN 14103	96.5 min	% (mol/mol)
Density, 15°C	EN ISO 3675, EN ISO 12185	860–900	kg/m^3
Kinematic viscosity, 40°C	EN ISO 3104, ISO 3105	3.5–5.0	mm^2/s
Flash point	EN ISO 3679	120 min	°C
Sulfur content	EN ISO 20846, EN ISO 20884	10.0 max	mg/kg
Carbon residue (10% distillation residue)	EN ISO 10370	0.30 max	% (mol/mol)
Cetane number	EN ISO 5165	51 min	
Sulfated ash	ISO 3987	0.02 max	% (mol/mol)
Water content	EN ISO 12937	500 max	mg/kg
Total contamination	EN 12662	24 max	mg/kg
Copper strip corrosion (3 h, 50°C)	EN ISO 2160	1	Degree of corrosion
Oxidation stability, 110°C	EN 14112	6.0 min	h
Acid value	EN 14104	0.50 max	mg KOH/g
Iodine value	EN 14111	120 max	g I_2/100 g
Linolenic acid content	EN 14103	12.0 max	% (mol/mol)
Methanol content	EN 14110	0.20 max	% (mol/mol)
MAG content	EN 14105	0.80 max	% (mol/mol)
DAG content	EN 14105	0.20 max	% (mol/mol)
TAG content	EN 14105	0.20 max	% (mol/mol)
Free glycerol	EN 14105 EN 14106	0.020 max	% (mol/mol)
Total glycerol	EN 14105	0.25 max	% (mol/mol)
Group I metals (Na, K)	EN 14108 EN 14109	5.0 max	mg/kg
Group II metals (Ca, Mg)	EN 14538	5.0 max	mg/kg
Phosphorous content	EN 14107	10.0 max	mg/kg

In current biodiesel production industry, use of catalyst is essential as it produce optimum conversion rates. Generally there are various types of catalyst has been used, such as basic, acidic, lipases or supercritical fluids. Furthermore, conventional industrial processes currently favour the usage of homogenous basic catalysts for example alkaline methoxides and alkaline hydroxides. Besides that, usage of heterogeneous base catalyst has also implemented in industries, as they give higher catalytic activity than solid acid catalysts [6, 7]. As a solid base catalyst, metal oxides, mixed metal oxides, alkali-doped metal oxides, alkali metal oxide catalyst and magnetic composites were utilized. Although these heterogeneous catalyst has certain advantages, such as simple catalyst separation and pollution lessen, but mainly they have restrictions such as they demanded excessive response temperature (>170°C), extended reaction time (>24H) and low catalytic strength. Binary metal oxides have been utilized as solid acid catalyst for quite long time and very familiar for having surface acidity. Basically, divalent metal oxide catalyst having significant quantity of covalent characters will assist the transesterification process of vegetable oils. Nevertheless, they are quite responsive to water, which reduce their industrial applications. Hence, it is needed to find further useful and cost-effective catalyst for transesterification of triglycerides for commercial usages. Therefore, the usage of nanocatalyst gives higher catalytic activity, easier to split and recycle, eco-friendly and easy operational procedures [8].

Titanium dioxide (TiO_2) is a white solid inorganic material that consists of several characteristics such as, non-flammable, thermally stable, poorly soluble and so on. It is the ninth large universal component in the earth's crust as it happens purely in some kinds of rock and mineral sands. TiO_2 nanomaterials has the smaller size of primary atoms and higher exterior area and this allows the manufacturers to invent various catalyst of increased activity. Basically TiO_2 is been classified as transition metal oxides which has some universally known polymorphs which exist purely in earth. Those are brookite (orthorhombic), TiO_2 (B) (monoclinic), rutile (tetragonal) and anatase (tetragonal) [9, 10]. Figure 1, shows the crystal structure of a) rutile, b) anatase and c) brookite of titanium dioxide.

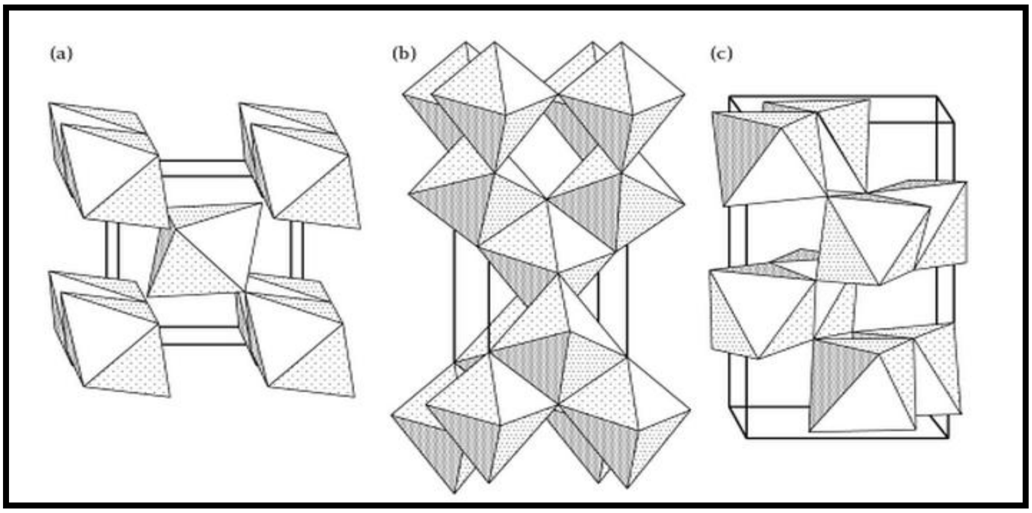


Figure 1: The crystal structure of a) rutile, b) anatase and c) brookite of titanium dioxide.

So in this study, titanium dioxide nanoparticles are experimented as a catalyst in biodiesel production. In order to improve the tranesterification process in biodiesel production these catalyst are blend by metal oxides to improve its catalytic effects. In order to get a better result, both biodiesel and nanomaterial are categorized using different analytical equipment to obtain the optimum operating conditions which are crucial in improving the outcome of biodiesel. Moreover, parametric optimization is carried out by using response surface methodology [9, 10].

1.2 Problem Statement

Recently the increase of fuel price has gathered the nations concern. The world has start concerning and worrying about the petroleum and natural gas which is depleting from year to year. Researches show that we only have enough petroleum supply for next 50 years. So now our concern is to find for the alternative resources to overcome this problem. One of the best solutions is biodiesel. It is not only renewable source of energy but also eco-friendly which will reduce the greenhouse effects. Generally biodiesel is synthesised by tranesterification process which are from waste cooking oils, animal fats and also vegetable oils with the help of catalyst. Again there's conflict in using either homogenous catalyst or heterogeneous catalyst. Research shows that, usage of homogenous catalyst is expensive because of the separation process involved and also homogenous catalyst cannot be recycled. Another disadvantage of homogenous catalyst is, the catalyst is consumed during the process in which it reduces the catalytic efficiency and causes the increase in viscosity and gels formation. It also leads to soap production. Therefore, usage of heterogeneous catalyst will solve various conflicts involved in the biodiesel production process as this is more eco-friendly. And also this type of catalyst is also easy to be prepared with high selectivity and activity. So for instance, Titanium Oxide can develop in biodiesel production as a new active substance in transesterification process because of its high catalytic movement.

1.3 Objectives and Scope of Study

The objectives of this project are as the following:

- ✓ Synthesis Titanium Dioxide (TiO_2) nanoparticles with Cerium Oxide as a catalyst.
- ✓ To investigate the characteristics and the activity level of Titanium Dioxide (TiO_2) nanoparticles.
- ✓ To enhance the transesterification process of biodiesel production by using Titanium Dioxide (TiO_2) nanoparticles as catalyst.
- ✓ To test the reusability, dosage effect and reaction time effect on biodiesel yield.

The scopes of the study of this project are:

- ✓ Usage of various analytical instruments to determine the structural properties and characterization of Titanium Dioxide (TiO_2)
- ✓ Carry out parametric optimization via response surface method.
- ✓ Study the result of Titanium Dioxide (TiO_2) nanoparticles as a catalyst in biodiesel fabrication.

CHAPTER 2

LITERATURE REVIEW AND THEORY

The constant increases of global prices of crude oil together with the decreasing reserved conventional energy resources and their allied environmental troubles have risen the alertness of other alternative sustainable and renewable supply for fuel industry. Therefore as a solution to this problem, internationally biodiesel is becoming the choice which is the favourable biofuel. Generally biodiesel are produced from vegetable oils and animal fats which consist of mono-alkyl esters of long chain fatty acids (triglycerides). It has many advantages such as very good lubricant, low emission, cost effective, biodegradable, eco-friendly, renewable and have high flash point [11, 12].

According to ASTM International, biodiesel is a fuel composed of monoalkyl esters of long chain fatty acids derieved from vegetable oils or animal fats (by meeting the requirements of ASTM D6751). The main advantage of biodiesel is, it is miscible with petrodiesel in any proportion and have several advantages over ultra-low sulphur diesel fuel (ULSD, <15 ppm S); such as, inherent lubricity, low toxicity, higher flash point and biodegradability, negligible sulphur content and lower overall exhaust emission [2]. The particular advantages of using vegetable oils are liquid nature portability, heat content (80% diesel fuel), ready availability and renewability[13].

Besides that, initially on bigger scale homogeneous base catalyst has been widely used. However there are some disadvantages in using homogeneous catalyst such as corrosion and waste management from neutralization of acids. The acid catalysed process will also utilize much time with resulting utilization of energy [11]. Acidic-catalyst reaction not only removes saponification but also have advantages of capability to recover and reuse the catalyst and also easier downstream product purification processes [15]. So we can know that, heterogeneous catalyst can give green and recyclable catalytic activities compared to homogenous catalyst. In that case, heterogeneous catalyst process is expected to be an operative biodiesel production with cost effective and least environmental effect due to the possibility of simplifying the production and purification process under mild condition [6, 15].

Furthermore, another main variable that influencing the yield of ester is the molar ratio of alcohol to triglycerides. The stoichiometric ratio for transesterification is 3 mole of alcohol and 1 mole of triglyceride to produce 1 mole of glycerol and 3 moles of fatty acid alkyl esters. Nevertheless, to direct the reaction to the right, a huge excess of alcohol is vital since transesterification is an equilibrium reaction. A molar ratio of 6:1 should be used, for maximum conversion to the ester. The molar ratio has no effect on acid, peroxide, saponification and iodine value of methyl esters [16]. Then again, due to increase in solubility the high molar ratio of alcohol to vegetable oil obstructs the separation of glycerine. Once glycerine stays in solution, it drives the equilibrium to back to the left, lowering the yield of esters. For example the transesterification of Cynara oil with ethanol was investigated at molar ratios between 3:1 and 15:1. The ester yield, rise as the molar ratio rise, up to a value of 12:1. The finest products were for molar ratios between 9:1 and 12:1. The reaction was incomplete, for molar ratios less than 6:1. On the other hand, for a molar ratio of 15:1, a part of the glycerol remains in the biodiesel phase and it causes the separation of glycerine become hard and the visible yield of esters decreased. As a result, molar ratios 9:1 appear to be the most suitable [13, 16, 17].

On the other hand, Ionic Liquids are the organic salts made up of anions and cations that are liquid at room temperature. Their characteristics are colourless, have potential recyclability, low viscosity and non-flammable [18]. Moreover ionic liquids have drag the attention of manufacturers because of its very good catalytic activity but it requires high cost and also must carried out under high temperature. It has been defined as fluid form of organic salts consists of anions and cations at temperatures around -96°C because of their packed ions arrangement [18]. These compounds have almost void vapour pressure which causes the reason of no emission of volatile organic components due adequate ion attraction. There are few characteristics of ionic liquid such as low viscosity, non-flammable, colourless, high catalytic activity, easy to handle and manipulate and also recyclable [19].

Besides that, one of the biggest plus point of ionic liquid is its ability to design a molecule with specific properties such as viscosity, density, melting point, selectivity and solubility. Due to their variable structure, they also can dissolve various substances such as organic, inorganic and polymeric particles. Basically the syntheses of ionic liquids are easy and simple and it is also has the potential to manipulate the purity of substances produced by controlling the synthesis [19]. Furthermore, formation of biphasic system at the end of reaction occurs when ionic liquids are used in transesterification process. It is due to physical characteristics of ionic liquid which is insoluble in organic phases and it remains in the aqueous phase together with alcohol, while the catalyst and glycerol are produced through the reaction. The major part of organic phase is biodiesel. So this proofs that the solubility of glycerol in mixture of ionic liquid and alcohol gives a great yield [20, 21].

Besides that, another interesting fact about ionic liquids is, they have high acidic value in them. Generally ionic liquids are definite as liquid state salts at low temperature. As explain above, the anions and cations are relatively used as solvents in the reactions and it is also used as a good alternatives to traditional solvents due to its thermal stability and non-volatile components[22]. Certain ionic liquids are classified as Lewis and Franklin acids. Acidic ionic liquids are still new in market as it has high density active sites as liquid acids but non-volatile in solid state. Since the ions in ionic liquids can be manipulated into desired properties, it has been used for regulating the acidity. The acidic ionic liquids are mainly used to replace the traditional liquid acids such as sulphuric acid and hydrochloric acid especially for biomass conversion [18, 22].

CHAPTER 3

METHODOLOGY AND PROJECT WORK

3.1 Material and Equipment

There are few analytical equipment used biodiesel and Titanium Dioxide characterization. Those are as following:

Table 3: Analytical Equipments

Equipment	**Function**
X-Ray Diffraction (XRD)	Crystal structure analysis
Transmission Electron Microscopy (TEM)	Particle size analysis
Scanning Electron Microscopy (SEM)	Surface topography
Fourier Transform Infrared Spectroscopy (FTIR)	Organic Functional Group
Gas Chromatography (GC)	Separating the different components of a mixture (to determine the relative amounts of components)
Thermogravimetric analysis (TGA)	Thermal Stability

3.2 Methodology

The procedures are divided into two parts which are the synthesising and characterisation of Cerium Oxide doped Titanium Dioxide (TiO2) nanoparticles and also biodiesel production. So the basic steps for the synthesis of Cerium Oxide doped Titanium Oxide are as follows:

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

3.2.1 Catalyst Preparation Procedure

1. Prepare 100ml of distilled water and maintain the pH around 2.5 using nitric acid, HNO_3
2. Add calculated amount of Titanium Oxide powder in 25 ml propanol (A)
3. Prepare the calculated amount of cerium nitrate hexahydrate solution (B)
4. Add solution (A) and (B) into prepared distilled water drop by drop in 20 minutes and stirred for 3 hours (500 rpm)
5. Dried at 100^oC for 3 hours and calcinated at 300^oC for 4 hours

3.2.2 Biodiesel Production

For the biodiesel production generally transesterification process will be used. Following are the general methods of biodiesel process as shown in Figure 2:

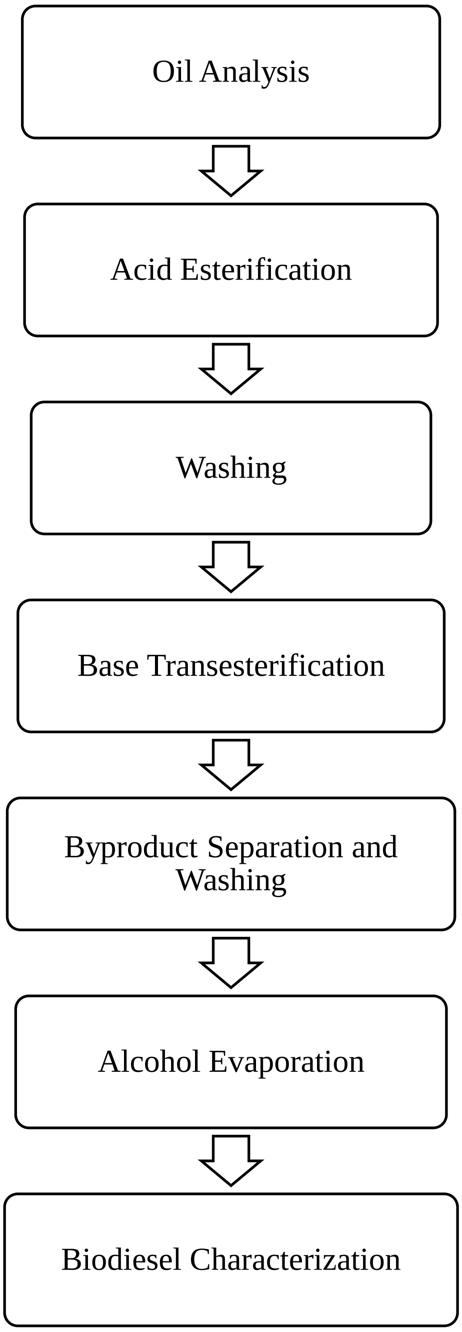
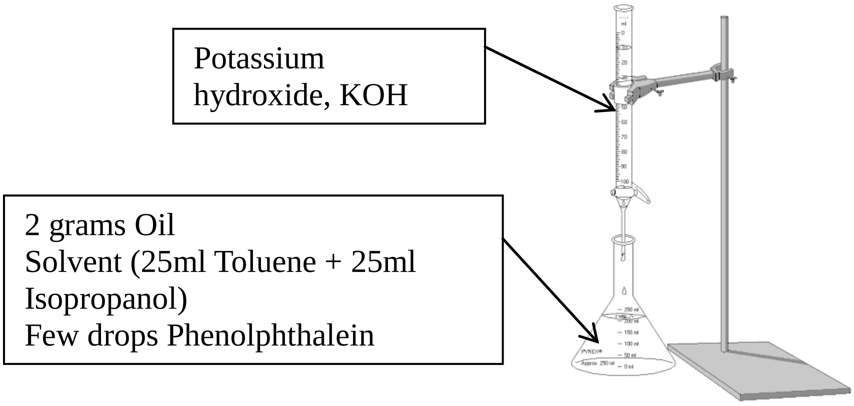


Figure 2: General biodiesel process

3.2.2.1 Oil analysis


Potassium hydroxide, KOH

2 grams Oil
Solvent (25ml Toluene + 25ml Isopropanol)
Few drops Phenolphthalein

Figure 3: Titration for Oil Analysis

The basic oil analysis method is done in order to determine the acid value and the free fatty acid (FFA) content as in Figure 3. It is because, high FFA can lead to saponification (the soap production) of oil instead of biodiesel production. So in order to obtain high yield of biodiesel, it is important to have as low FFA content as possible. 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, in order to determine the FFA content of the oil. A blank sample is first titrated and proceeds to the second titration with 2 grams of oil added to the conical flask.

The acid value is the calculated as follows;

$$Acid\ Value = \frac{(V_a - V_b) \times N \times \rho}{W} \tag{2}$$

Where;

$Va = Volume\ of\ potassium\ hydroxide\ used\ against\ the\ sample$

$Vb = Volume\ of\ potassium\ used\ against\ blank$

$N = Normality\ of\ oil$

$\rho = Density\ of\ oil$

$W = Weight\ of\ sample\ used$

In order to determine the FFA content, potassium hydroxide is used for the titration as the titrate and it was titrated to a mixture of isopropylene and toluene with phenolphthalein indicator to indicate the changes. The FFA value is calculated from the acid value;

$$\boldsymbol{FFA = \frac{Acid\,Value}{2}} \tag{3}$$

3.2.2.2 Acid Esterification

In order to lesser the acid and free fatty acid concentrations, the oil get through acid esterification. This is where it responds with lower alcohol such as methanol with the presence of acid catalyst. H_2SO_4, sulphuric acid is used as the acid catalyst. The acid significance is the number of milligrams of potassium hydroxide required to neutralize the free acid in 1 gram of sample. The experiment is conducted by using a triple neck round bottom flask together with a reflux condenser; to avoid any methanol loss. Each experimental run needs 50 grams of oil to be heated up 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 undergo separation of the pre-treated oil and excess methanol and catalyst. The treated oil is separated and collected for base transesterification process. The free fatty acid amount should be less than 2% before proceeding to the base transesterification else the acid esterification process should be repeated with different parameter values.

Conditions used in this project:

Oil amount = 50 gram

Time = 2 hours

Temperature = 60 ^{o}C

$$\text{Methanol amount} = \boldsymbol{\frac{50\,g\,oil}{MW\,of\,oil}\,X\,MW\,of\,methanol\,X\,ratio = x\,gram} \tag{4}$$

$$\boldsymbol{V = \frac{x\,gram\,of\,methanol}{density\,of\,methanol} = y\,ml\,of\,methanol} \tag{5}$$

Sulphuric Acid amount = 5% of oil amount

3.2.2.3 Transesterification

Corresponding to acid esterification, the oil or triglycerides undergoes base esterification but with the existence of base catalyst. Sodium hydroxide (homogenous catalyst) is used as the base catalyst. For this experiment, 50 grams of pre-treated oil is mixed together with methanol and the catalyst then is heated and stirred for a specific time as shown in Figure 4. Water bath is used to endorse even heating. Then the oil undergoes separation in the separating funnel and will be left for overnight (24 hours). Two layers will be formed in the separating funnel; the upper layer is methyl ester (biodiesel) while the lower layer is glycerol, methanol and other impurities. The conditions 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.

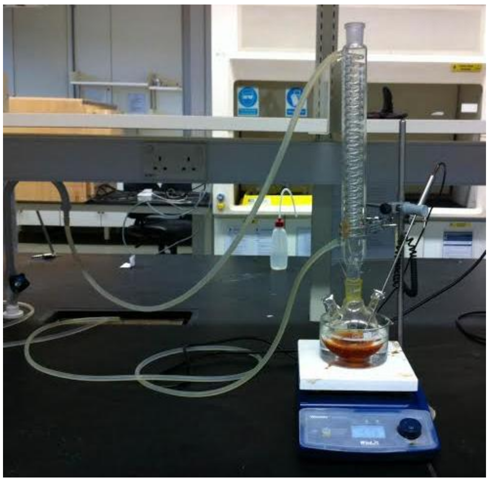


Figure 4: Experiment set up of Base Transesterification

3.2.2.4 Parameters Optimization

The optimization of base transesterification process is carried out and optimized using the Response Surface Methodology (RSM) from the Design Expert 6.0.8 software. In order to investigate the effects of four parameters on the yield, the total number of experiments required is 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 reduce the sudden variability on the response.

Table 4: Value range for parameters

Parameters	**-1**	**0**	**+1**
A : Time (min)	30	60	90
B : Temperature (^{o}C)	45	57.5	70
C : Oil to methanol ratio	3	6	9
D : Catalyst concentration (wt%)	0.1	0.25	0.4

The optimized conditions are then determined from the 21 runs, and this is used as the parameters for the experiment with heterogeneous catalyst for biodiesel production. Taking these values, the experiment is repeated by using cerium oxide doped TiO_2 catalyst. The yield is the compared to determine the effect of catalyst towards the yield of biodiesel.

The project timeline and achieved key milestone are represented in Table 5 and Table 6 respectively.

3.3 Project Timeline

Table 5 : Project Timeline

No	**Details/ Week**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
1	FYP II - 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 Milestone

Table 6: Key Milestone

Task	Date	Weeks	Remarks
Project Work	12/01/15 – 20/03/15	1-10	DONE
Submission of Progress Report	06/03/15	8	DONE
Pre-SEDEX	25/03/15	11	DONE
Submission of Final Report Draft	03/04/15	12	DONE
Submission of Dissertation (Soft Bound)	10/04/15	13	DONE
Submission of Technical Paper			DONE
Viva	15/04/15 – 16/04/15	14	DONE
Submission of Dissertation (Hard Bound)			

CHAPTER 4
RESULTS & DISCUSSION

4.1 Oil Analysis

In this experiment, 3 types of oil are used for comparison. Three types of oil which are Palm oil, Castor Oil and Kapok Seed Oil have tested. Based on the analysis, the FFA value for the respective oils are as follows in Table 7:

Table 7: Free Fatty Acid (FFA) amount of untreated oils

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

4.2 Acid Esterification

Acid esterification is done for the raw palm oil to identify the change of the free fatty acid (FFA) content. Low FFA is vital in order to prevent saponification during the base transesterification process Table 8.

Table 8: Result of acid esterification of palm oil

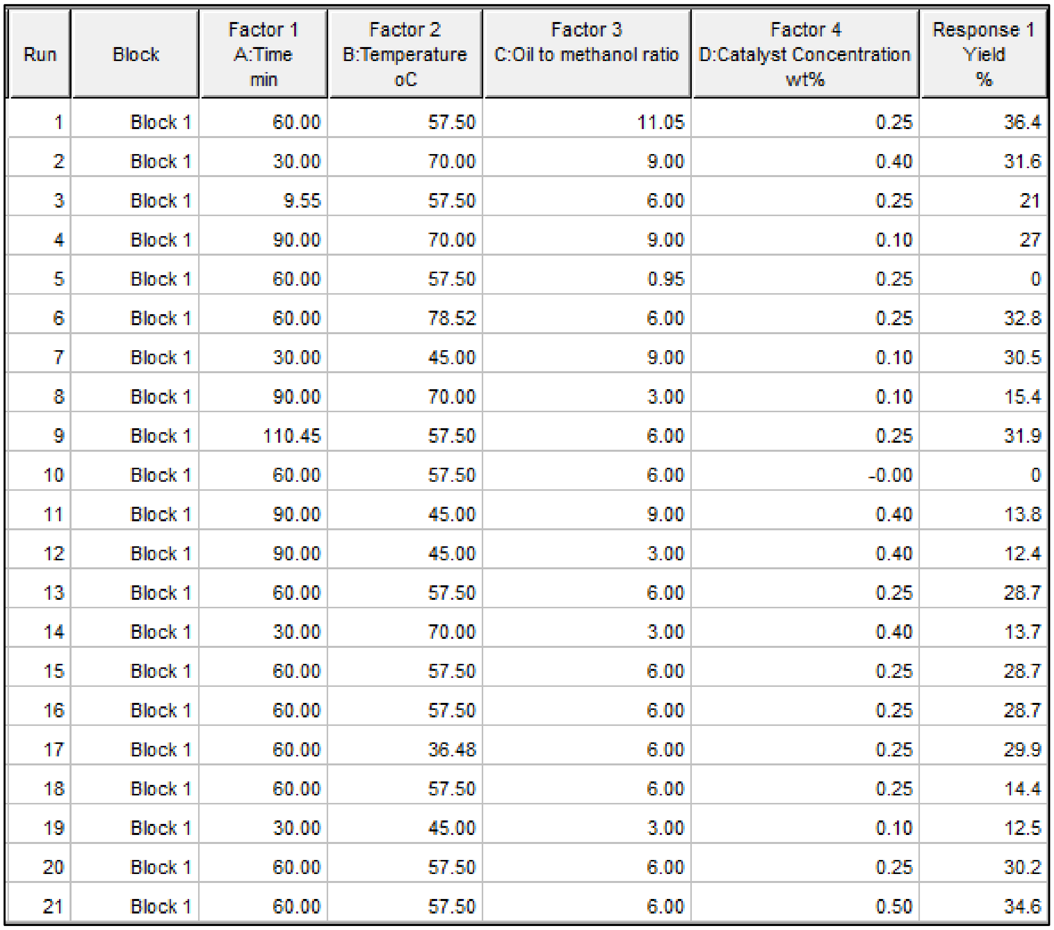
Run	**Time (min)**	**Temperature (°C)**	**Oil to methanol ratio**	**Catalyst concentration (wt %)**	**Acid value**	**Free Fatty Acid (%)**
1	120	60	9	5	4.47	2.24

For this project, the FFA value should be lower than 2% to proceed with base transesterification process. However, the result obtained shows that the FFA is increased after the acid esterification. Besides, the FFA after acid esterification is greater than 2%. This shows that the acid content of the oil has not decreased, instead it increases. This happened due to the un-separated acid catalyst within the mixture. So, 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 raw palm oil is used for the base transesterification as the FFA amount is already below 2%.

4.3 Transesterification

The experiment is conducted based on the conditions tabulated in Design Expert software as follows in Table 9:

Table 9 : Yield percentage for every experimental run



Run	Block	Factor 1 A:Time min	Factor 2 B:Temperature oC	Factor 3 C:Oil to methanol ratio	Factor 4 D:Catalyst Concentration wt%	Response 1 Yield %
1	Block 1	60.00	57.50	11.05	0.25	36.4
2	Block 1	30.00	70.00	9.00	0.40	31.6
3	Block 1	9.55	57.50	6.00	0.25	21
4	Block 1	90.00	70.00	9.00	0.10	27
5	Block 1	60.00	57.50	0.95	0.25	0
6	Block 1	60.00	78.52	6.00	0.25	32.8
7	Block 1	30.00	45.00	9.00	0.10	30.5
8	Block 1	90.00	70.00	3.00	0.10	15.4
9	Block 1	110.45	57.50	6.00	0.25	31.9
10	Block 1	60.00	57.50	6.00	-0.00	0
11	Block 1	90.00	45.00	9.00	0.40	13.8
12	Block 1	90.00	45.00	3.00	0.40	12.4
13	Block 1	60.00	57.50	6.00	0.25	28.7
14	Block 1	30.00	70.00	3.00	0.40	13.7
15	Block 1	60.00	57.50	6.00	0.25	28.7
16	Block 1	60.00	57.50	6.00	0.25	28.7
17	Block 1	60.00	36.48	6.00	0.25	29.9
18	Block 1	60.00	57.50	6.00	0.25	14.4
19	Block 1	30.00	45.00	3.00	0.10	12.5
20	Block 1	60.00	57.50	6.00	0.25	30.2
21	Block 1	60.00	57.50	6.00	0.50	34.6

The yield percentage is calculated using the formula:

$$\textbf{Biodiesel yield} = \frac{\textbf{Weight of oil after base transesterification}}{\textbf{Weight of oil before base transesterification}}\ \mathbf{x\ 100\%} \qquad (3)$$

Based on the tabulated data, it is found that Run 1 has the highest biodiesel yield at 36.4%, and thus it has the optimum process conditions for base transesterification. This condition has been used as the main reference to set the optimum conditions.

4.4 Optimization of Parameter Values

The optimization of parameter values are conducted by using the Design Expert 6.0.8 software. Pertubation plot compares all factors influencing the yield of biodiesel. Figure 5 shows the pertubation plot base transesterification for palm oil biodiesel based on studies conducted. The steepest plot shows the most significant and influential factor towards the response (yield), which is parameter D, oil to methanol ratio. The second most influencing factor is parameter C, reaction time.

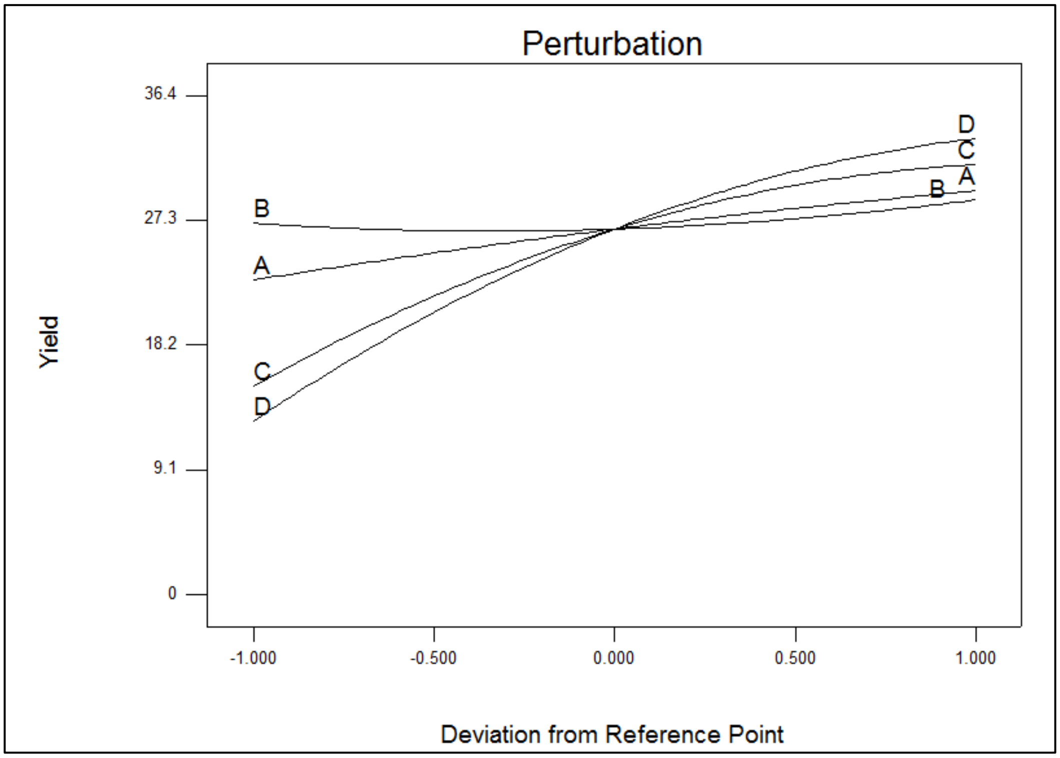


Figure 5: Pertubation graph for Base Transesterification

Figure 6 shows the comparison between actual values of FFA% with the predicted values for acid esterification and the yield with predicted values for 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. Besides that, the graph shows that the actual values indicated by the coloured dots lie near the predicted line thus these results are reliable and closer to the actual data.

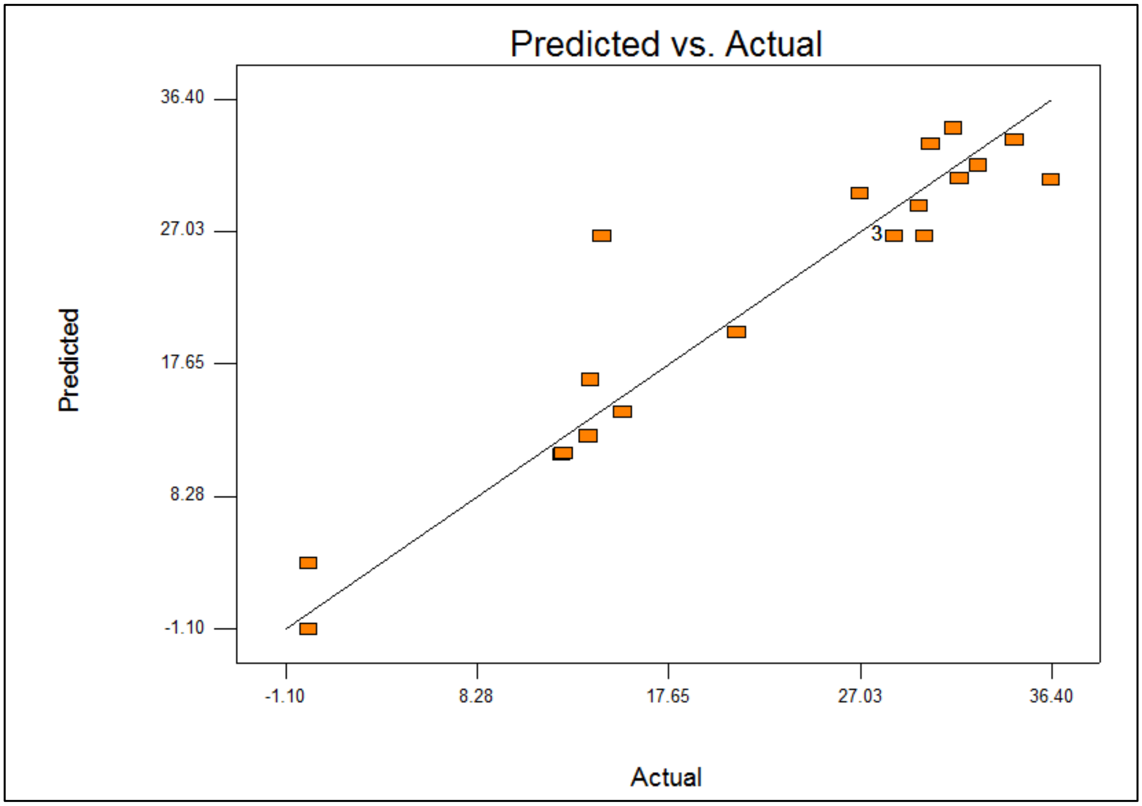


Figure 6: Predicted versus experimental values for base transesterification

4.4.1 The effect of individual parameter

The effect of reaction time on the biodiesel yield is shown in Figure 7. As the reaction time increases, the biodiesel yield also increases. This shows that, sufficient reaction time is essential for the transesterification reaction to completely occur.

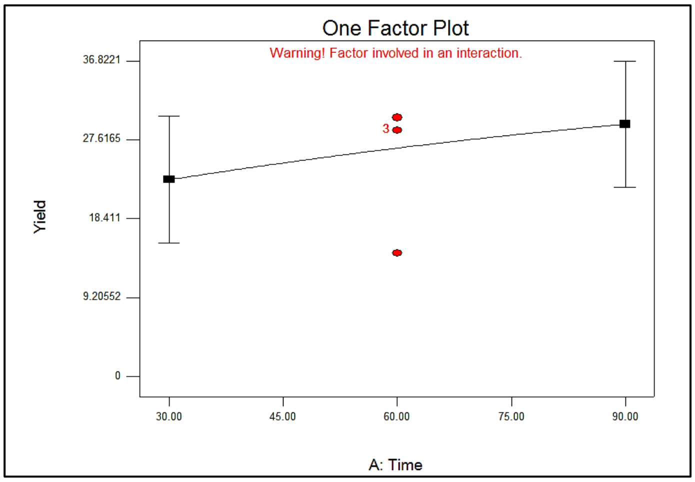


Figure 7 : The effect of reaction time on the biodiesel yield

The plot in Figure 8 proves that although the reaction has excess amount of methanol, the high temperature will cause the methanol to evaporates, affecting the overall reaction.

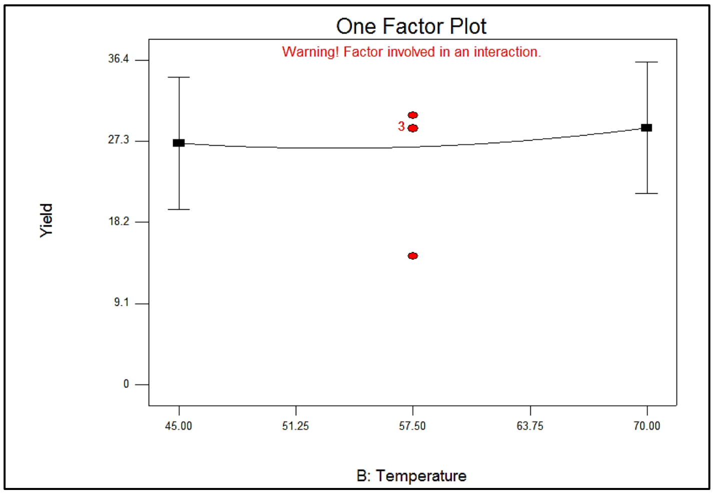


Figure 8: The effect of reaction temperature on the biodiesel yield

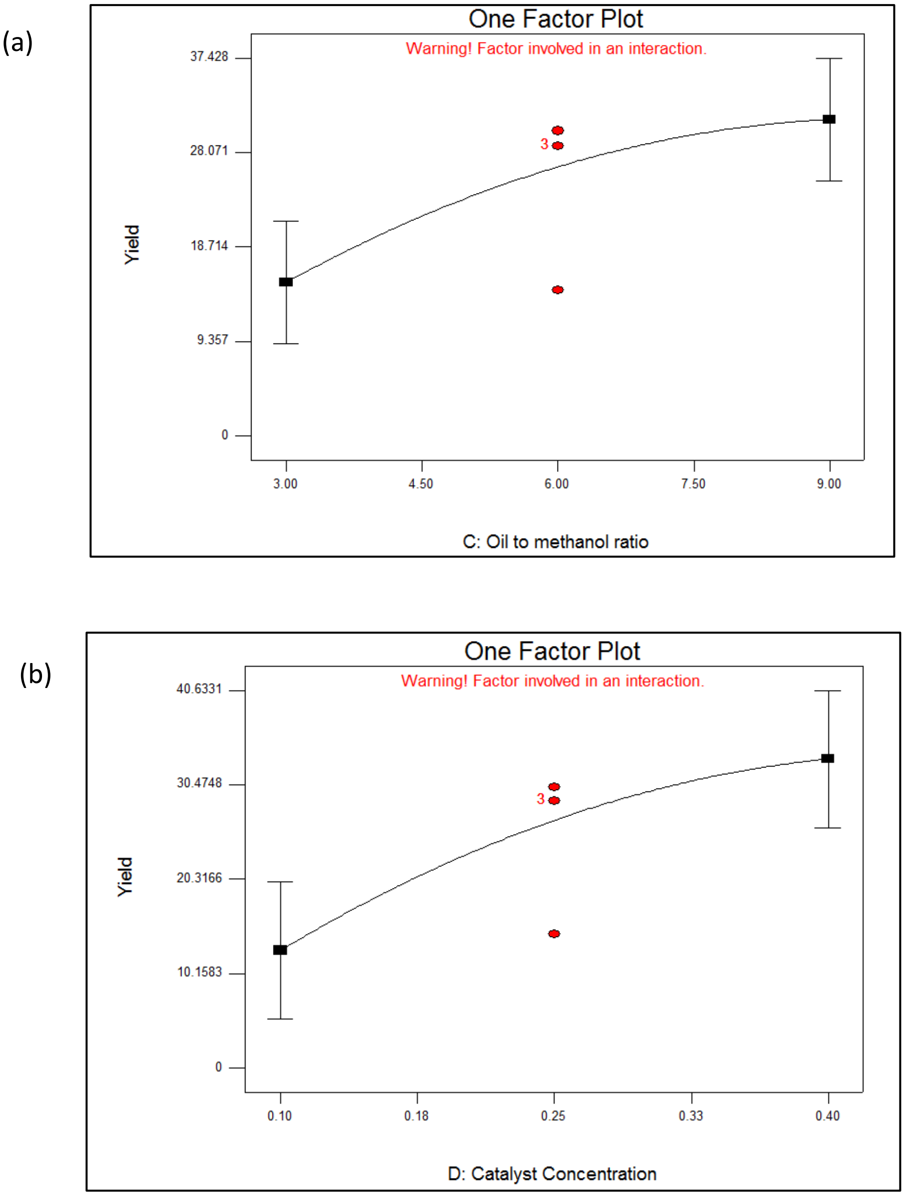


Figure 9: The effect of (a) oil to methanol ratio and (b) catalyst concentration on the biodiesel yield

Figure 9, shows the effect of methanol ratio and catalyst concentration on the biodiesel yield. For both plot, as the oil to methanol ratio and catalyst concentration increases, the biodiesel yield also increases. This shows that, the amount of methanol is in excess to assist the reaction.

4.4.2 Comparison of optimum operating parameters with previous studies

The optimum operating parameters of present work are compared to previous findings as shown in Table 10.

Table 10 : Comparison of Optimum Conditions

Parameters	Current project	Shao, G. N. Sheikh, R. Hilonga, A. Lee, J. E. Park, Y. H. Kim, H. T. [23]	Takase, M. Chen, Y. Liu, H. Zhao, T. Yang, L. Wu, X. [11]	Wen, Z. Yu, X. Tu, S. T. Yan, J. Dahlquist, E. [3]	Fan, Ming Ming Zhou, Jing Jie Han, Qiu Ju Zhang, Ping Bo [19]
A : Time (min)	180	180	30	180	480
B :Temperature (°C)	90	120	60	169.85	120
C : Oil to methanol ratio	11.0	20	16	30	8
D : Catalyst Concentration (wt%)	4	10	5	10	5

4.4.3 Interactions between the parameters

Based on the perturbation plot, 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 interaction with other parameters. Figure 10 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.

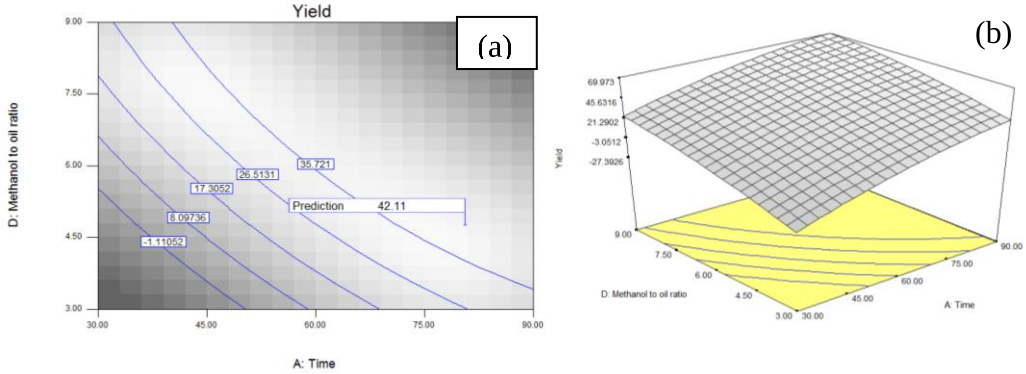


Figure 10: Effect of methanol to oil ratio and time in (a) contour plot (b) 3D surface plot

Based on the perturbation plot, the second influential parameter is parameter A which is reaction time. There is a significant reaction between reaction time and temperature (B). Figure 11 justify that the yield increases when the reaction increases and temperature decreases. The temperature should be maintained around 90°C which is the optimum temperature and increase the reaction time to enhance the reaction.

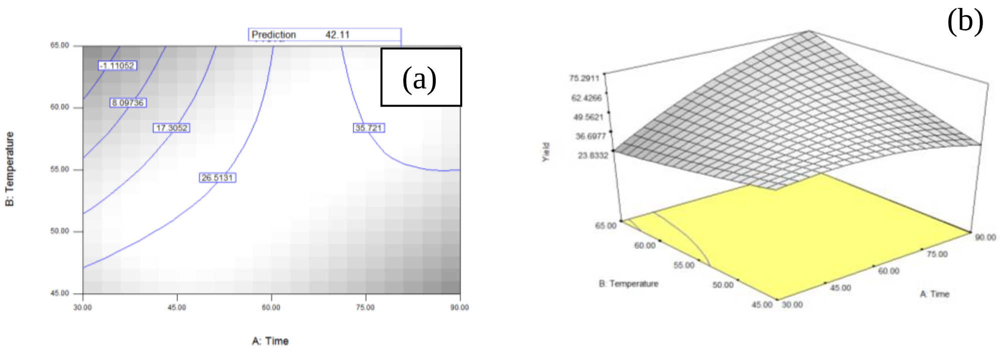


Figure 11: Effect of temperature and time in (a) contour plot (b) 3D surface plot

Figure 12 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 increasing. Although the reaction has excess amount of methanol, the high temperature will cause the methanol to evaporates, affecting the overall reaction. Therefore, the optimum temperature should be maintained at 90°C.

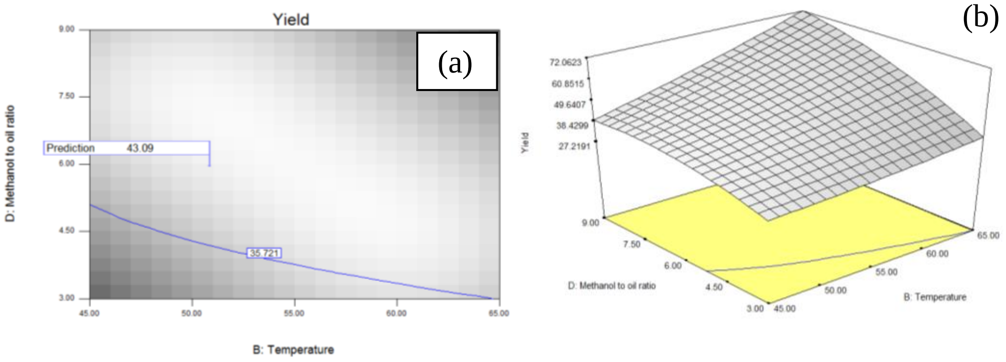


Figure 12: Effect of methanol to oil ratio and temperature in (a) contour plot (b) 3D surface plot

The reaction between the ratio of methanol and oil with catalyst concentration also gives a significant effect to biodiesel yield. Figure 13 show that the yield of biodiesel increases along with the increase of both parameters value.

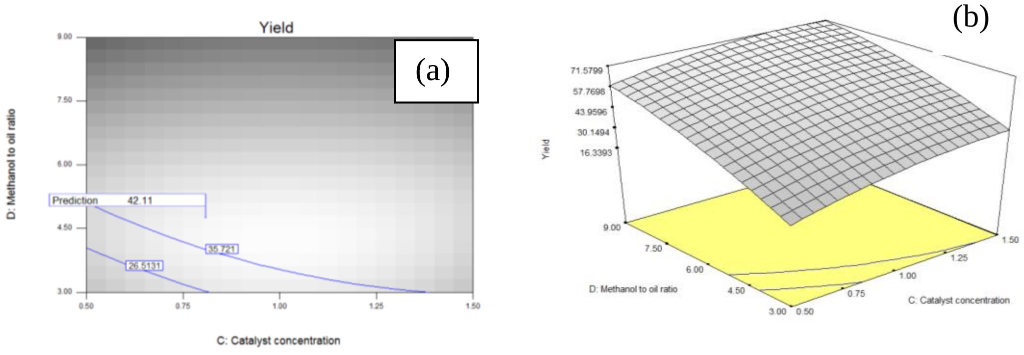


Figure 13: Effect of methanol to oil ratio and catalyst concentration in (a) contour plot (b) 3D surface plot

4.5 Characterization of Catalyst

The anatase crystalline form of Titanium Dioxide and Cerium Oxide is confirmed through Raman spectra analysis in Fig. 14. Based on the plot, some bands are resolved at 130.90 cm-1, 188.74 cm-1, 392.69 cm-1, 514.46 cm-1, 642.31 cm-1 and 800.61 cm-1. The result shows the higher the loading, the band resolves at higher value. This also proves the anatase crytalline form of titanium dioxide and cerium oxide. This was already established that anatase crystalline structure titanium gives improved catalytic activity owing to the anatase provides more vacant active sites on the surface.

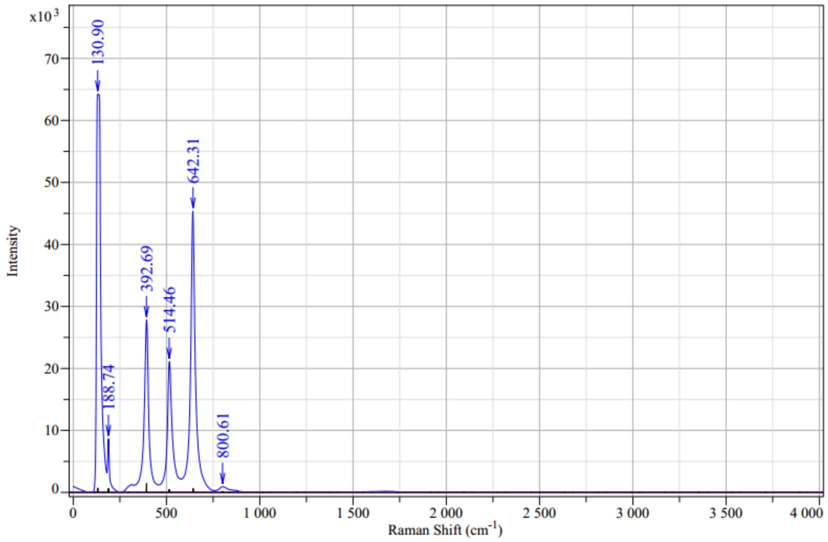


Figure 14: Raman Spectra Analysis

The first part of the spectra indicates the bands for single bond, hydroxyl group, in this case H-O-H bond as shown in Fig. 15. 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 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, 1050.75, 695.88 and 550.72 cm-1 for the CeO2-TiO2 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.

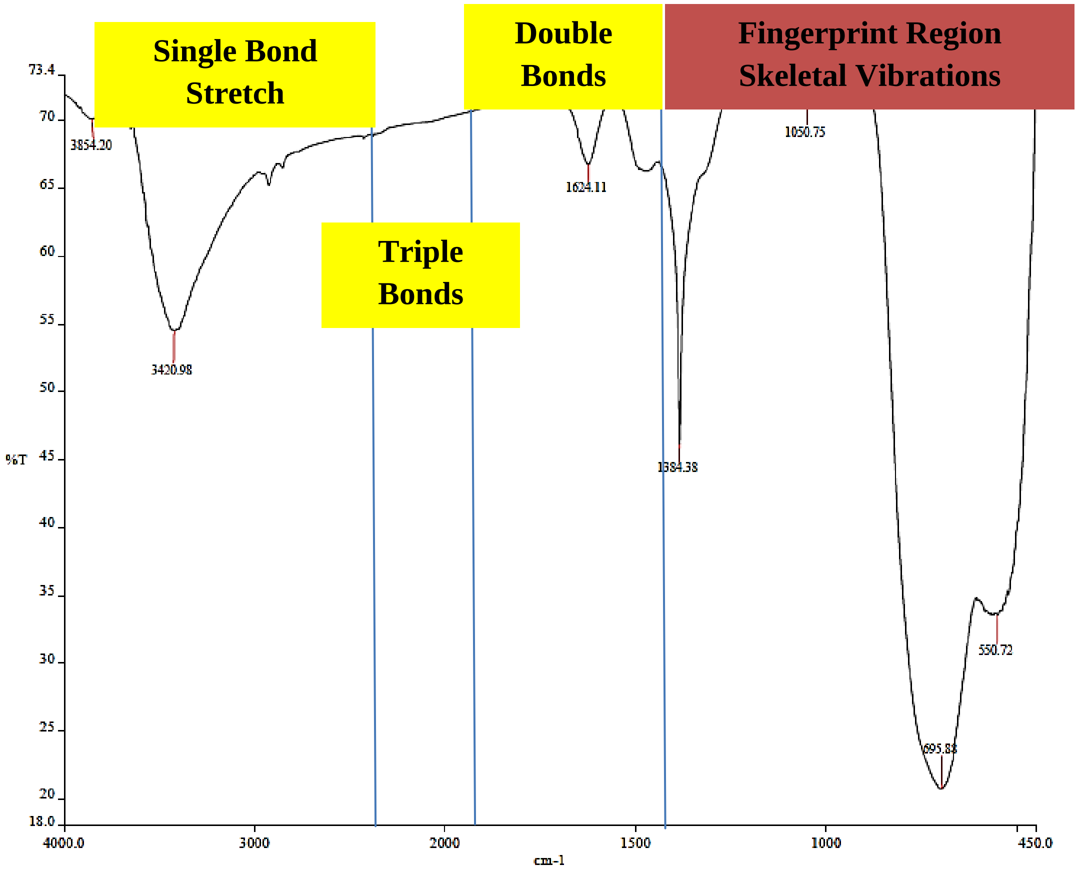


Figure 15: FTIR Analysis

These images were taken from Variable Pressure Field Emission Scanning Electron Microscope for cerium oxide doped titanium dioxide nanomaterial as shown in Figure 16. 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 oC as it can ruin the catalytic structure of the catalyst.

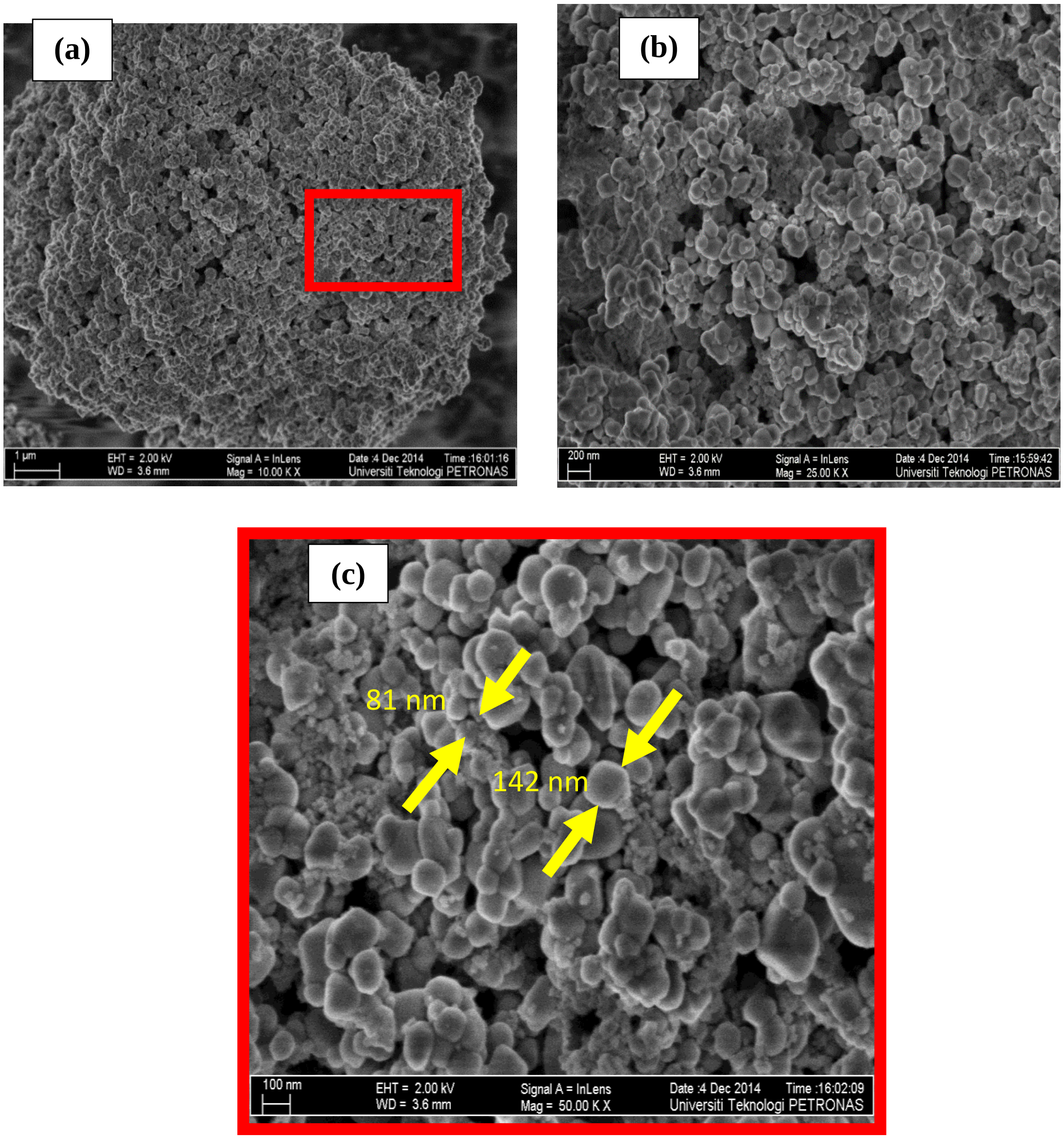


Figure 16: FESEM Analysis of CeO_2-TiO_2 nanomaterial

The specific surface area of CeO2-TiO2 is 20.6875 m2/g and average pore diameter is 15.043 nm. The pores volume of the catalyst is 0.083701 cm3/g is shown in Fig. 17. These data determined through Surface Area and Pore Size Analyzer. This analysis shows that the synthesized catalyst contain mesoporous sizes which is range of 2 to 50 nm. The cerium oxide have improved the average diameter of the pores and also the surface are as well. Studies shows that small surface are is more favourable for the reaction as increases the catalytic activity of the transesterification. So by increasing the temperature for calcination, we can reduce the surface area of the catalyst. It is because at high calcination temperature, more nitrates from cerium precursor will be removed and this will enhance the catalystic properties. The mixed titania phase is considered to contribute to enhancement of the photocatalytic activity. The difference between the conduction band edges of TiO2 and anatase phases produces charge transfer from one phase to another, which results in photo-generated charge separation. This phenomenon prevents electron hole recombination and enhances the activity of photocatalytic oxidation. The sample has an aggregated structure of anatase nanoparticles, which forms mesopores in the interspaces.

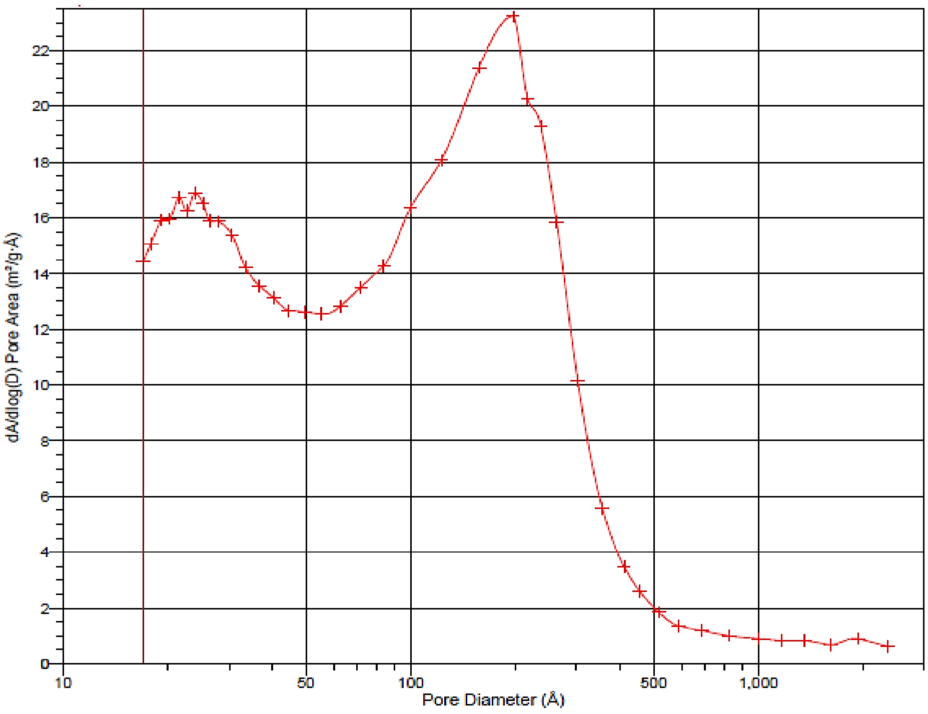


Figure 17: Pores mean diameter distribution of CeO_2-TiO_2

4.6 Effect of parameters in biodiesel yield

- Temperature effect

Figure 18, shows that as the temperature increase the yield of biodiesel increases. It reaches its maximum yield at 90°C which is approximately 72.1%. So this shows that at optimum temperature of 90°C of transesterification process, the yield reaches its maximum.

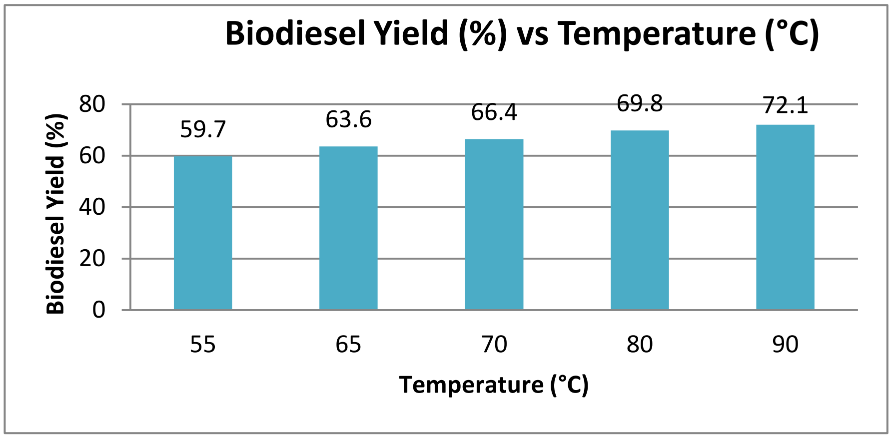


Figure 18: Biodiesel yield vs Temperature

- Reaction Time Effect

The plot below shows that as the reaction time increases the yield of biodiesel increases and reaches platitude at 180 min in Figure 19. The maximum yield of biodiesel is approximately about 72.2% at 180 min. Therefore this proves that sufficient reaction time is essential for the transesterification process to completely occur and the conversions to occur.

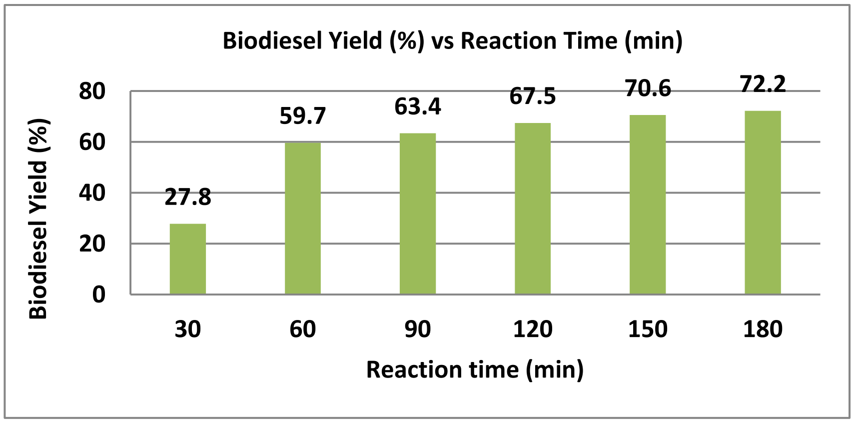


Figure 19: Biodiesel yield vs Reaction Time

- Catalyst Dosage Effect

Figure 20 shows the graph of biodiesel yield against catalyst dosage. Based on the plot, it shows that the biodiesel achieves its maximum yield (71.5%) at 4wt% catalyst dosage. On 5wt% and so on the yield begins to be constant. So this shows that the optimum catalyst dosage is 4wt%.

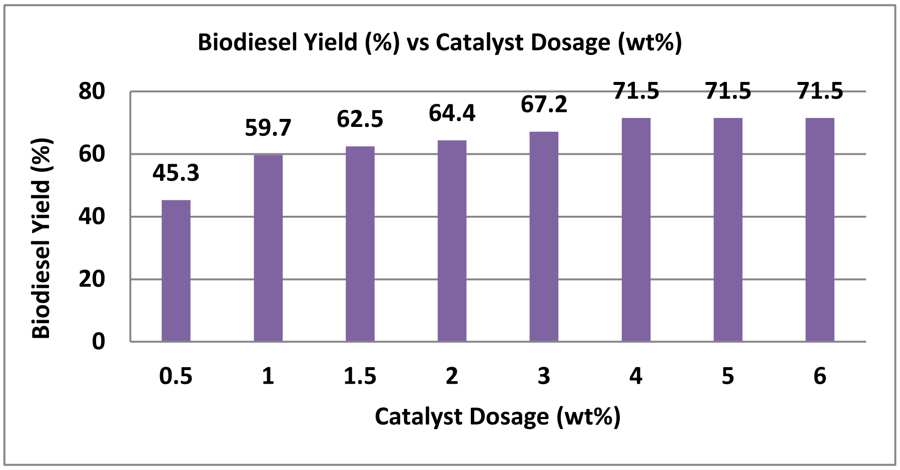


Figure 20: Biodiesel yield vs Catalyst dosage

- Reusability Effect

The reusability of the catalyst was tested by using the optimized parameters and CeO_2 –TiO_2 catalyst in Figure 21. The experiment was repeated for 6 runs using the same catalyst. For each run the catalyst has been washed with alcohol and again dried at 100°C and calcinated at 300°C before use it again for next run, to maintain purity and fuel properties of biodiesel. As the runs goes on the yield of the biodiesel begins to decrease. This might be because of catalytic property of the catalyst getting decrease after each run. But the decrement in yield of biodiesel for 6 runs is just between 2.5% to 5.68%. In order to maintain recover the maximum amount of catalyst, phosphoric acid has been used. This will enhance the separation by forming 3 layers which is at top is Free Fatty Acids, in middle is glycerol and methanol and at bottom is the catalyst. For industrial applications CeO_2 – TiO_2 heterogeneous catalyst has the capability to be reused as this would be cost efficient. By this we also can prove that this heterogeneous catalyst has capacity to be recycled with the minimum decrement which is less than 5%.

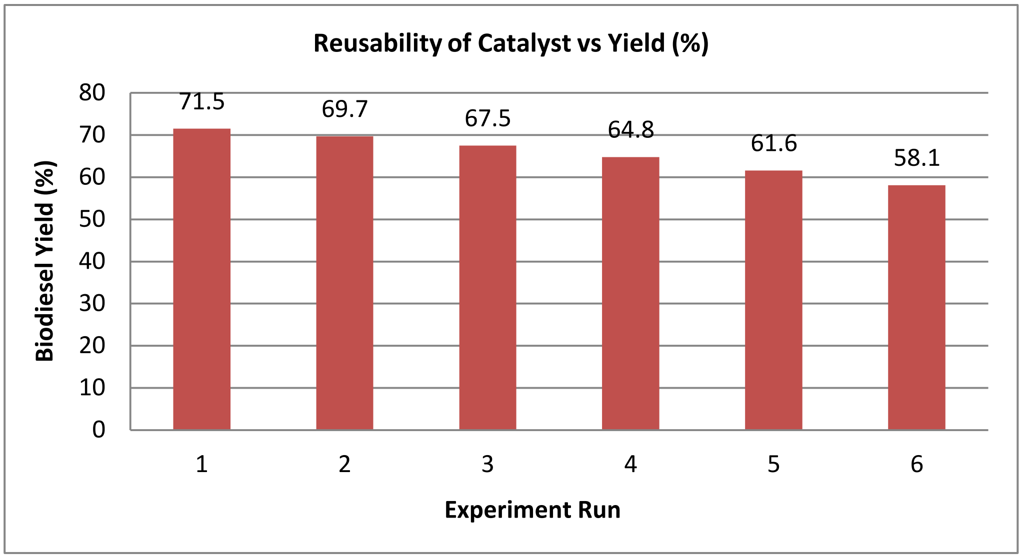
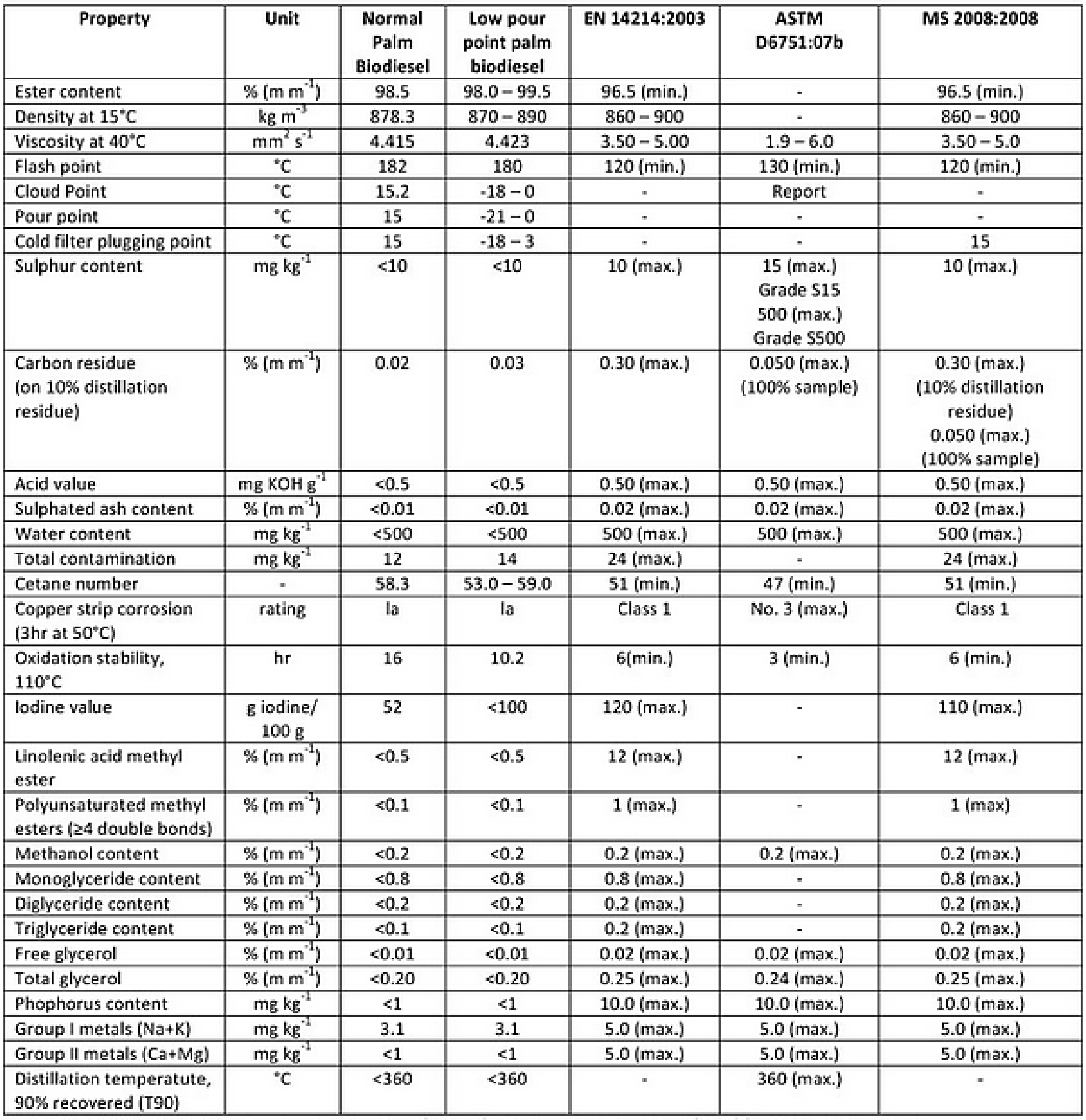


Figure 21: Biodiesel yield vs reusability

4.7 Fuel Properties

According to Malaysian Palm Oil Board (MPOB), Table 14 are the fuel properties for normal and low pour point palm oil biodiesel [24].

Table 11: 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	la	la	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 standards as tabulated Table 15. Most of the values of properties for the palm oil biodiesel produced with NaOH catalyst is close to the standard is shown in the Table 12. However, the properties for palm oil biodiesel produced with CeO_2-TiO_2 catalyst deviates slightly from the standards in Table 11. 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.

Table 12: 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	10.7 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	-	-

4.8 Utilization of Biodiesel By-product

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 as shown in Figure 22. 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] .

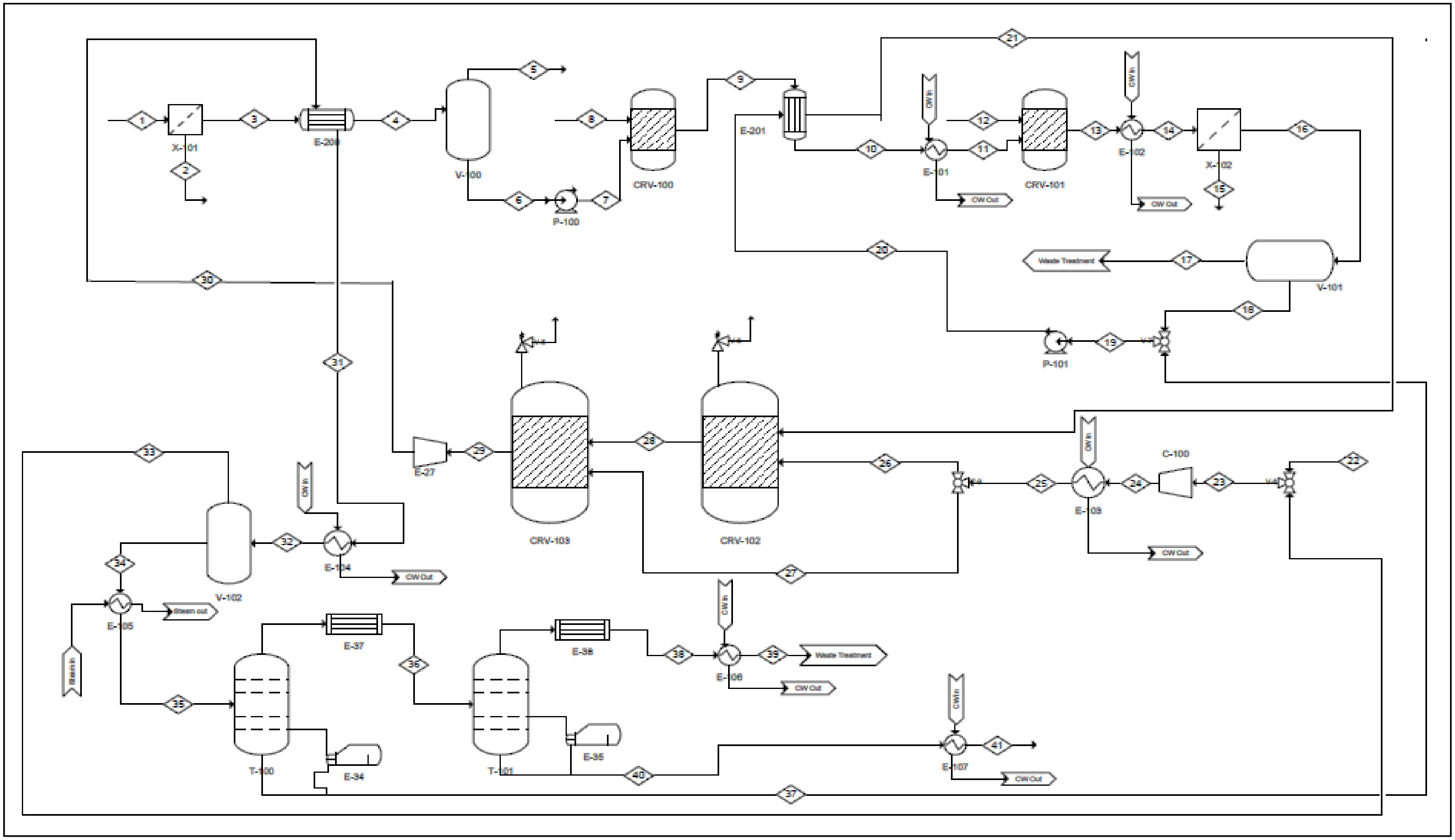


Figure 22: Process Flow Diagram of 1,2-propanediol Production

This production process consists 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 as shown in Figure 21. 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.

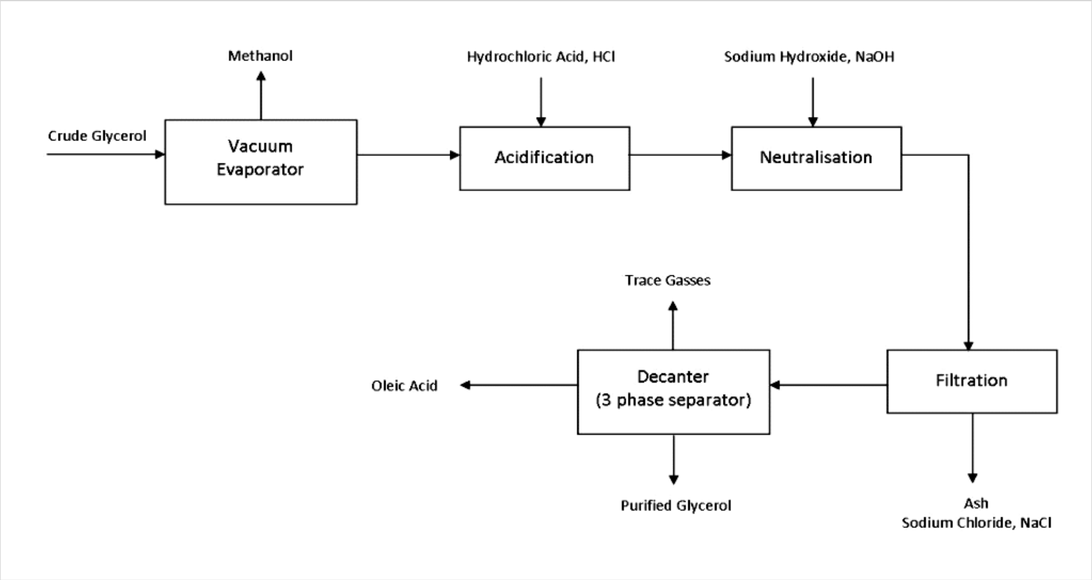


Figure 23: Block Diagram of Crude Glycerol Purification

First, the crude glycerol is fed into vacuum evaporator to remove methanol as shown in Figure 24. 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].

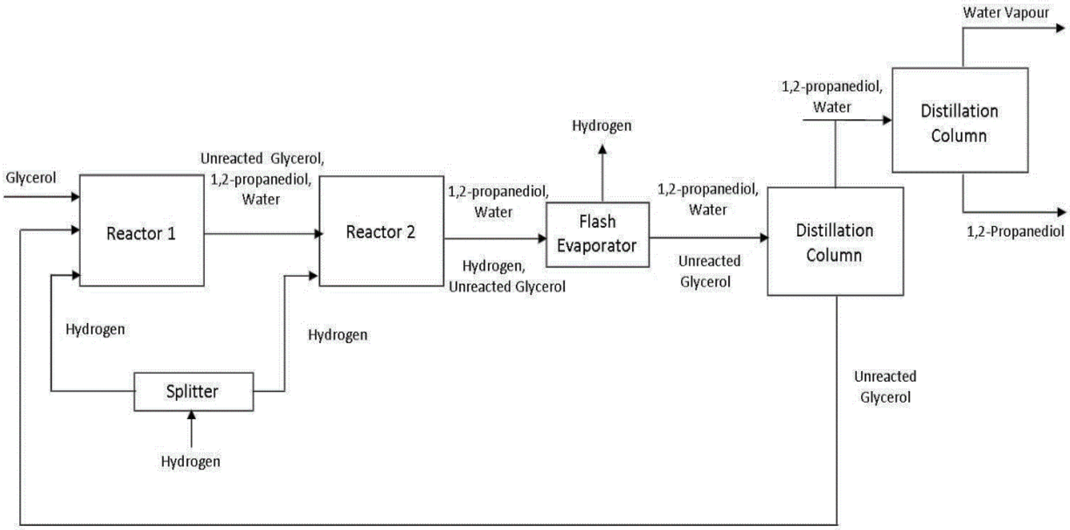


Figure 24: Hydrogenolysis Block Diagram

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 in Figure 25 and Table 13.

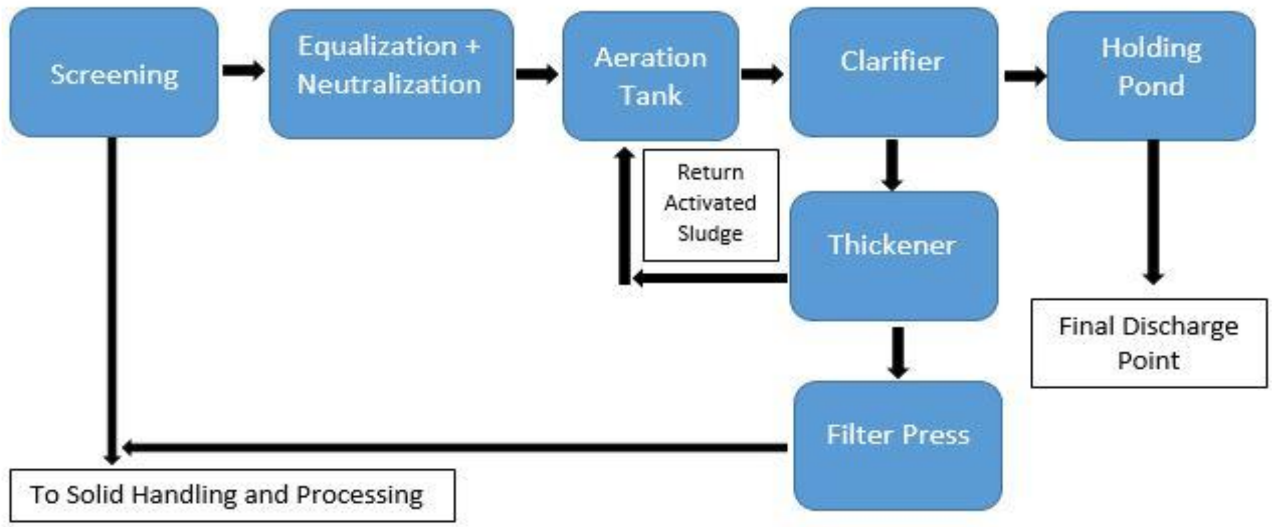


Figure 25: Example of Waste Water Treatment Process

Table 13 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

CHAPTER 5

CONCLUSION AND RECOMMENDATION

Overall the objectives of this project have been achieved. The catalyst was synthesized by Cerium Oxide doped Titanium Dioxide nanomaterials. So in this study, titanium dioxide nanoparticles are experimented as a catalyst in biodiesel production. In order to improve the tranesterification process in biodiesel production these catalyst are blend by metal oxides to improve its catalytic effects. 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

The characterization of catalyst was also done by using FTIR, FESEM, Raman Spectrometer and Surface area and Pore Analyzer. 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.

Titanium dioxide doped Cerium Oxide catalyst were studied and applied to the transesterification process. The data obtained from response surface methodology of Design Expert Software is used as the reference to determine the optimum parameter conditions. The catalyst with loading of 0.4wt% Cerium Oxide doped with Titanium dioxide was calcined under 300 ^oC. Based on the studies conducted, the optimized condition for biodiesel production is temperature at 180 ^oC, reaction time at 180 minutes, catalyst dosage at 4 wt% and methanol to oil ratio is 11:1. At this condition the yield of biodiesel is approximately about 72%. For the reusability of $CeO-TiO_2$ catalyst, it shows that the decrement of the yield is just 3% to 6% even after 6 runs of experiment. The used catalyst has been washed before tested for each run. Overall this study or the reseach proves that when the reaction time and catalyst dosage increases, the yield of biodiesel is increases as well and will become constant at it’s maximum concentration (at certain point). This can be said as the longer reaction time provides enough time for the catalyst to boost up the transesterification process.

In the nut shell, we can conclude that all the objectives of this project can be accomplished. Due to environmental issues, in industrial applications, homogeneous catalysts have to be substituted by heterogeneous catalyst. There are very high chances for titanium dioxide nanoparticles to be one of the possible substitutes in the fabrication of biodiesel. The exploitation of cerium oxide and ionic liquids in synthesizing Titanium Dioxide nanoparticles will help in recovering the yield of biodiesel. This substance can be used extensively in industries with more enhanced research. So these kind of studies are recommended for future uses.

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