## BORANG PENGESAHAN STATUS TESIS◆

**JUDUL : OPTIMIZATION OF BIODIESEL PRODUCTION FROM COOKING PALM OIL USING RESPONSE SURFACE METHOLOGY (RSM)**

**SESI PENGAJIAN : 2011/2012**

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# OPTIMIZATION OF BIODIESEL PRODUCTION FROM COOKING PALM OIL USING RESPONSE SURFACE METHODOLOGY (RSM) APPROACES

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Thesis submitted in fulfillment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering in Biotechnology

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# STUDENT’S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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# ABSTRACT

Biodiesel is one of the renewable energy resource which is suitable to replace the fossil fuel due to the depletion of fossil fuel in the future. The modeling of the design of experiment for optimization of biodiesel production from cooking palm oil is conducted by using Design Expert software version 7.1.6 (Stat Ease). This experimental design is conducted in order to optimize the biodiesel production with significant parameters that affecting the biodiesel production. The parameters that have been used are reaction temperature, methanol to oil molar ratio, catalyst concentration and reaction time. By using response surface methodology (RSM), the optimal parameters levels are determined. The optimum conditions for biodiesel production were at temperature of 72.83°C, alcohol to oil molar ratio of 9.5:1, 3.95% of catalyst concentration and 4.73 hours of reaction time, which was obtained 88.38% of biodiesel yield.

# ABSTRAK

Biodiesel merupakan salah satu daripada sumber yang boleh diperbaharui amat sesuai dijadikan bahan ganti kepada sumber galian. Perisian Design Expert versi 7.1.6 (Stat Ease) digunakan bagi merangka model penghasilan biodiesel daripada minyak masak diperbuat daripada kelapa sawit pada tahap optimum. Objektif eksperimen ini adalah untuk memaksimakan penghasilan biodiesel di bawah pengaruh parameter-parameter penting yang memberi impak terhadap penghasilan biodiesel. Parameter yang digunakan adalah suhu tindakbalas, kepekatan pemangkin, nisbah molar methanol terhadap minyak dan masa tindakbalas. Dengan menggunakan ‘response surface methodology’ dari perisian ‘Design Expert’, tahap optima setiap parameter dapat ditentukan. Optimum kondisi bagi penghasilan biodiesel adalah pada suhu 72.83°C, nisbah molar menghampiri 9.5:1, 3.95% daripada kepekatan pemangkin dan tindakbalas menggambil masa selama 4.73 jam dengan menghasilkan biodiesel sebanyak 88.38%.

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# LIST OF SYMBOLS

| | |
|---|---|
| % | Percentage |
| °C | Degree celcius |
| $+\alpha$ | High alpha point |
| $-\alpha$ | low alpha point |
| Y | biodiesel yield |
| $X_1$ | Reaction temperature |
| $X_2$ | Molar ratio |
| $X_3$ | Catalyst concentration |
| $X_4$ | Reaction time |

# LIST OF ABBREVIATIONS

| | |
|---|---|
| DoE | Design of Experiment |
| FAME | Fatty acid methyl ester |
| WCO | World Customer Organization |
| wt% | weight percent |
| $SO_2$ | Sulphur dioxide |
| $CO_2$ | Carbon dioxide |
| CO | Carbon monoxide |
| CaO | Calcium oxide |
| $Ca(OH)_2$ | Calcium hydroxide |
| $CaCO_3$ | Calcium carbonate |
| KOH | Potassium hydroxide |
| FFA | Free fatty acid |
| NaOH | Sodium hydroxide |
| ZnO | Zinc oxide |
| *et al* | and other |
| CCD | Composite central design |
| ANOVA | Analysis of variance |
| Inc. | Incorporation |
| w/w% | Weight per weight percent |
| $w/w_{oil}$ | Weight per weight oil |
| RSM | Response surface methodology |
| GC | Gas chromatography |
| GC-MS | Gas chromatography mass spectroscopy |

# CHAPTER 1

# INTRODUCTION

## 1.1 BACKGROUND OF STUDY

In last few years, worldwide energy demand increase significantly due to the needs from development of global economics and population growth (El Boulifi,N. *et al.*, 2010). There are many type of energy that uses by the global economics and population growth which are fossil energy, nuclear energy, hydroelectricity and others energy resources.

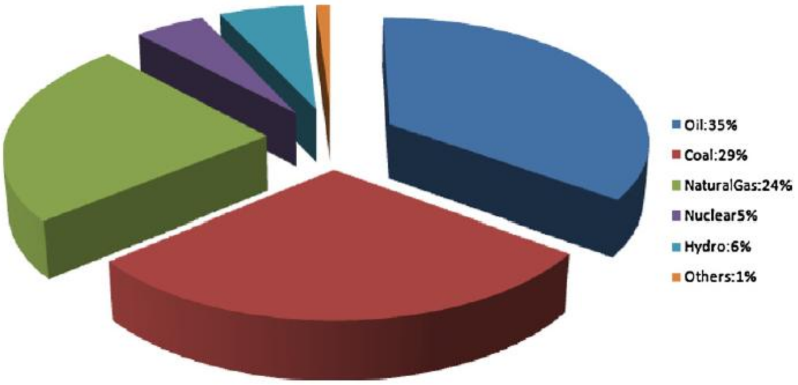


**Figure 1.1:** World Primary Energy Production in 2009 (Lin L. *et al.*, 2011)

Figure 1 shown that fossil fuels is the major fuel with 88% of world primary energy consumption that include oil (35%), coal (29%) and natural gas (24%) while nuclear energy and hydroelectricity accounted as 5% and 6% of the total primary energy consumption (Lin lin et al., 2011). Primary energy is defined as essentially raw energy which has not been subjected to any transformation or conversion process and includes natural fossil fuels and renewable energy (Steven L. and Lee K. T., 2010). Economic growth and population growth are the main factors of the growing global energydemand. Actually, there is a link between energy demand and economic output. On average, the global economy is projected to grow by 3.1% a year to 2020. Currently, world population is growing at an annual rate of 1.4% per year where the population growth among the 4.8 billion people living in the developing countries is 1.7% per annum with additional 81 million mouths to feed annually. This compares with an average 0.3% per annum in the developed countries which means that the share of the world population living in developing countries will raise from 77 today to 81% in 2020. In view of these trends, access is provide to commercial energy in developing countries will be an increasingly large and urgent challenge (Mamdouh G. S., 2003).

## 1.2 PROBLEM STATEMENT

The most growing global energy demands currently are the fossil energy sources. The problem is fossil energy resources are non-renewable, which are limited in supply and will be depleted one day (El Boulifi,N. *et al.*, 2010). Fossil fuels need millions of years to be formed from natural resources which are the fossilized remains of dead plants and animals by exposure to heat and pressure in the Earth's crust over millions of years. Because of that, fossil fuels have been categories as a non-renewable resource which is cannot be renew for the next uses. The world energy demands increase everyday make the researcher to develop another energy resource that can be renewable such as biodiesel.

The researchers and scientific community worldwide nowadays have focused on the development of biofuels, which is biodiesel, and the process of optimization to meet the standard and specifications needed in order for fuels to use commercially without compromising on the durability of the engine parts (Sharma,Y. C. *et al.,* 2008). The major issue towards widespread commercialization is the high price of biodiesel (Refaat,A. A. et al., 2007). Biodiesel is expensive because of the high price of the plant oil and some issues on the processing technologies such as the catalyst and equipment (Xin D.*et al.,* 2010).

The option in this study to reduce the price of the biodiesel is by optimize the production of biodiesel. But, it is difficult to study this optimization using classical method because a lot of parameters can affected this biodiesel production. In order to solve this problem, this study was carried out by using design of experiment (DoE) due to the ability to optimize the response with multiple variables involved.

## 1.3 RESEARCH OBJECTIVE

The main objective in this study is;

i. To optimize the biodiesel production using design of experiement (DoE) approaches.

## 1.4 SCOPE OF STUDY

To achieve the objective of this research, three scopes have been identified:

i. To optimize the biodiesel production by using design of experiment (DoE) with different of parameters (reaction time, reaction temperature, catalyst concentration and methanol to oil molar ratio).
ii. To identify the characteristics of fatty acid methyl esters (FAME) using gas chromatography.

## 1.5 RATIONAL AND SIGNIFICANCE

The finding on this study will provide the optimum conditions to carry out the transesterification process in order to maximize the biodiesel yield. With the highest biodiesel yield produced from transesterification process will reduce the production cost. Therefore, biodiesel can be commercialized as a biofuel especially for transportation usage.

# CHAPTER 2

# LITERATURE REVIEW

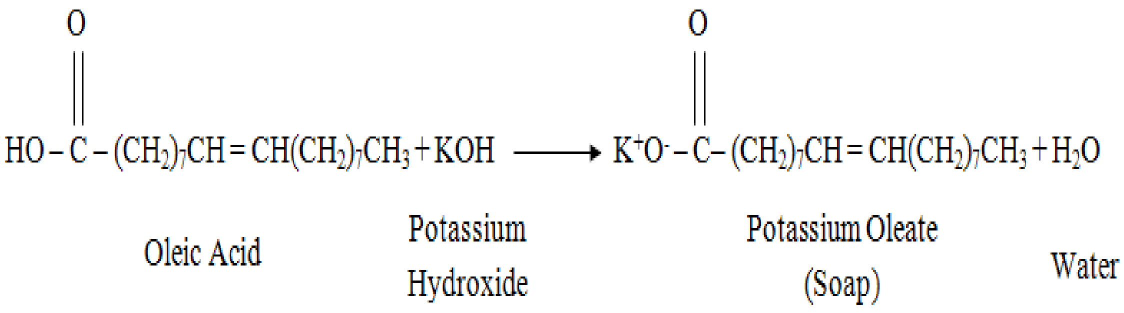
## 2.0 INTRODUCTION

Biodiesel is clean burning alternative fuel renewable resources that produced from domestic and contained no petroleum (Stalin,N. and Prabhu,H. J., 2007). Biodiesel, generally known as fatty acid methyl ester (FAME), is derived vegetable oils or animal fats produced by process of transesterification in which, oil is reacted with monohydric alcohol in presence of a catalyst (AshishK.,*et al.*, 2010). Biodiesel has been defined by World Customer Organization (WCO) as "*a mixture of mono-alkyl esters of long-chain (C16-18) fatty acids derived from vegetable oils or animal fats which is a domestic fuel for biodiesel engines and which meets the specifications of ASIM D6751*."

Biodiesel is much better than conventional diesel in terms of its flash point, sulphur content and aromatic content. The biodiesel essentially non-aromatic and sulphur free meanwhile conventional diesel can contain up to 500 ppm $SO_2$ and from 20 to 40 wt% aromatic compounds. These advantages will help reducing of urban pollution. Vehicle that used diesel as a fuel will produce black smoke and contribute to one third of the total transport that generated greenhouse gas because of the diesel is dominant for black smoke particulate together with $SO_2$ emissions. But by using biodiesel, it will decrease an average of 14% for $CO_2$, 17.1% for CO and 22.5% for smoke density (Anh, N. P. and Tan, M. P., 2008). Another advantages are bio-degradable, non-toxic in nature, has low emission profile that helps reducing global warming and hence eco-friendly (Banerjee, A. and Chakraborty, R., 2009).

## 2.1 COMPOSITION OF VEGETABLE OILS AND FATS

Animal fats and vegetable oils usually have hydrophobic properties that make them insoluble in water. Vegetable oils and animal fats consists triglycerides that will derived into biodiesel in the chemical reaction. Both 1 mol glycerol and 3 mol fatty acids combine to build up triglycerides. Fatty acids vary in terms of the length of carbon chain and number of unsaturated bonds. The chemical structure of common fatty acids is shown in Table 2.1. The saturated fatty acids consist of no double bond while the unsaturated fatty acids consist of double bonds. The saturated chains contain maximum number of possible hydrogen atoms per atom carbon. Meanwhile, unsaturated chains do not contain maximum number of possible hydrogen atoms because of the presence of double bond(s) in some carbon atoms. Natural vegetable oils and animal fats can be obtained through mechanical pressing or solvent extraction in the crude form and containing a lot of impurities such as sterol, free fatty acid and water. These free fatty acids and water content will significantly give an effect to transesterification reaction especially if it use base as catalyst. The presence of water content can reduce the yield of methyl esters. Particularly at high temperature, in the presence of water, it can hydrolyze triglycerides to diglycerides and form free fatty acid. Hydrolysis reaction has shown in Figure 2.2. These free fatty acids will subsequently react to form soap in the presence of base catalyst as shown in Figure 2.1. The formation of soap can interfere with the separation of fatty acid methyl ester (FAME) and glycerol during water washing (purification) process. (Man K. L. *et al.*, 2010).



$$HO-\overset{\overset{O}{\|}}{C}-(CH_2)_7CH=CH(CH_2)_7CH_3+KOH \longrightarrow K^+O^- -\overset{\overset{O}{\|}}{C}-(CH_2)_7CH=CH(CH_2)_7CH_3+H_2O$$

**Figure 2.1:** Formation of soap from reaction of free fatty acid and base catalyst

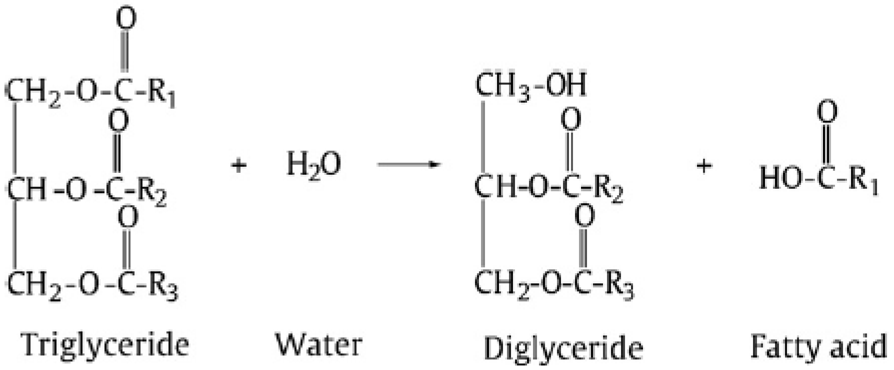


**Figure 2.2:** Hydrolysis reaction

**Table 2.1:** Chemical structure of common free fatty acids

| Name of Fatty Acid | Chemical Name of Fatty Acids | Structure (xx:y) | Formula |
|---|---|---|---|
| Lauric | Dodecanoic | 12:0 | $C_{12}H_{24}O_2$ |
| Myristic | Tetradecanoic | 14:0 | $C_{14}H_{28}O_2$ |
| Palmitic | Hexadecanoic | 16:0 | $C_{16}H_{32}O_2$ |
| Stearic | Octadecanoic | 18:0 | $C_{18}H_{36}O_2$ |
| Oleic cis-9- | Octadecanoic | 18:1 | $C_{18}H_{34}O_2$ |
| Linoleic cis-9,cis- | Octadecadienoic | 18:2 | $C_{18}H_{32}O_2$ |
| 12- | cis-9,cis-12,cis-15- | 18:3 | $C_{18}H_{30}O_2$ |
| Linolenic | Octadecatrienoic | 20:0 | $C_{20}H_{40}O_2$ |
| Arachidic | Eicosanoic | 22:0 | $C_{22}H_{44}O_2$ |
| Behenic | Docosanoic | 22:1 | $C_{22}H_{42}O_2$ |
| Erucle | cis-13-Docosenoic | 24:0 | $C_{24}H_{48}O_2$ |
| Lignoceric | Tetracosanoic | | |

Source: S. P. Singh and Dipti Singh, 2009

## 2.2 BIODIESEL COMPOSITION

Biodiesel is a mixture of fatty acid alkyl esters that produced by using alcohol as a reactant. However, methanol is widely used because of its availability and low cost. Production of biodiesel will have different composition of FAME due to the different used of feedstock. Table 2.2 show a FAME composition that commonly found in biodiesel (Man K. L. *et al.*, 2010)

**Table 2.2:** Common composition of FAME

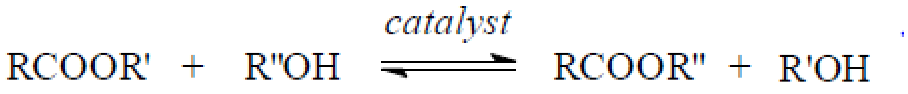
| Methyl Ester | Formula | Common Acronym | Molecular Weight |
|---|---|---|---|
| Methyl palmitic | $C_{17}H_{34}O_2$ | C16:0 | 270.46 |
| Methyl stearate | $C_{19}H_{38}O_2$ | C18:0 | 298.51 |
| Methyl oleate | $C_{19}H_{36}O_2$ | C18:1 | 296.50 |
| Methyl linoleate | $C_{19}H_{34}O_2$ | C18:2 | 294.48 |
| Methyl linolenate | $C_{19}H_{24}O_2$ | C18:3 | 292.46 |

Source: Man K. L. *et al.*, 2010

## 2.3 BIODIESEL DERIVATION TECHNIQUE

It is not possible to use directly from vegetable oils and animal fats as combustible fuel is not suitable due to their high kinematic viscosity and low volatility. It can posed serious problem in their long terms used such as deposition, ring sticking and injector chocking in the engine. To overcome this problem, the vegetable oils and animal fats must be subjected to chemical reaction in order to reduce the viscosity of the oils (Man K. L.*et al.*, 2010). The problems, causes and potential solutions for directly use vegetable oils in diesel shown in Table 2.4.

There are 5 techniques that used in this derivation which are dilution, micro-emulsion, pyrolysis, antransesterification modification techniques and supercritical methanol. Micro-emulsion is a technique where are using with an additional of alcohols that have been prepared to overcome the problem of high viscosity of vegetable oils. Pyrolysis is a cleavage to smaller molecules by thermal energy, of vegetable oils over catalyst. The most famous technique that has used in biodiesel processing technologies is transesterification technique (Amish P. V.*et al.*, 2010). In that technique, the triglycerides are converted into fatty acid methyl ester (FAME) with glycerol as byproduct in the presence of short chain alcohol, such as methanol, and catalyst, such as alkali or acid. Figure 2.3 has shown a general equation of transesterification reaction. Table 2.3 has summarized the advantages and disadvantages of each technique.



$$RCOOR' + R''OH \xrightleftharpoons{catalyst} RCOOR'' + R'OH$$

**Figure 2.3:** General equation of transesterification reaction

**Table 2.3:** Comparison of advantages and disadvantages between techniques

| Technique | Advantage | Disadvantage |
|---|---|---|
| Dilution / micro-emulsion | • Simple process | • High viscosity<br>• Bad volatility<br>• Bad stability |
| Pyrolysis | • Simple process<br>• No polluting | • High temperature is required<br>• Equipment is expensive<br>• Lowpurity |
| Tranesterification | • Fuel properties is closer to biodiesel<br>• High conversion efficiency<br>• Low cost<br>• It is suitable for industrial production | • Low free fatty acid and water content are required (for base catalyst)<br>• Pollutants will be produced because products must be neutralized and washed<br>• Accompanied by side reactions<br>• Difficult reaction products reaction |
| Supercritical methanol | • No catalyst<br>• Short reaction time<br>• High conversion<br>• Good adaptability | • High temperature and pressure required<br>• Equipment cost is high<br>• High energy consumption |

Source: Lin *et al.*, 2011

**Table 2.4:** Problems, causes and potential solutions for directly use vegetable oils in diesel

| Problem | Cause | Potential Solution |
|---|---|---|
| Short term | | |
| 1. Cold weather starting. | High viscosity, low cetane, and low flash point of vegetable oils. | Pre-heat fuel prior to injection. Chemically alter fuel to an ester. |
| 2. Plugging and gumming of filters, lines and injectors. | Natural gums (phosphatides) in vegetable oil. Other ash. | Partially refine the oil to remove gums. Filter to 4 μm. |
| 3. Engine knocking. | Very low cetane of some oils, improper injection timing. | Adjust injection timing. Use higher compression engines. Pre-heat fuel prior to injection. Chemically alter to an ester. |
| Long term | | |
| 4. Coking of injectors on piston and head of engine. | High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part loads with vegetable oils. | Heat fuel prior to injection. Switch engine to diesel fuel when operation at part loads. Chemically alter the vegetable oil to anester. |
| 5. Carbon deposits on piston and head of engine. | High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part loads with vegetable oils. | Heat fuel prior to injection. Switch engine to diesel fuel when operation at part loads. Chemically alter the vegetable oil to an ester. |
| 6. Excessive engine wear. | High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part loads with vegetable oils. Possibly free fatty acids in vegetable oil. Dilution of engine lubricating oil due to blow-by of vegetable oil. | Heat fuel prior to injection. Switch engine to diesel fuel when operation at part loads. Chemically alter the vegetable oil to an ester. Increase motor oil changes. Motor oil additives to inhibit oxidation. |
| 7. Failure of engine lubricating oil due to polymerization. | Collection of polyunsaturated vegetable oil blow-by in crankcase to the point where polymerization occurs. | Heat fuel prior to injection. Switch engine to diesel fuel when operation at part loads. Chemically alter the vegetable oil to an ester. Increase motor oil changes. Motor oil additives to inhibit oxidation. |

Source: Mustafa B. and Havva B.( 2008)

## 2.4 TRANSESTERIFICATION

Transesterification is an equilibrium reaction and it occurs essentially by mixing of two reactants (fatty acid methyl ester and alcohol). The adjustment of the equilibrium can accelerate by applying the presence of catalyst on the reaction typically either a strong acid or base (Ulf S.*et al.*, 1998). Three common kinds of catalysts that use in this process are lipase catalyst, acid catalyst, and base or alkali catalyst (Lin L.*et al.*, 2010).

## 2.5 ALKALI CATALIZED TRANSESTERIFICATION

A base-catalyzed transesterification process is normally use in biodiesel production because alkaline metal alkoxides and hydroxide are more effective than acid catalyst (Yusuke A.*et al.*, 2009). The speed of base-catalyzed transesterification process is higher than using acid catalyst. However, these types of transesterification process are very sensitive to the presence of water and free fatty acids and also needs a lot of alcohols in its reaction (Lin L.*et al.*, 2010). Figure 2.4 has shown the mechanism of the base catalyst transesterification.

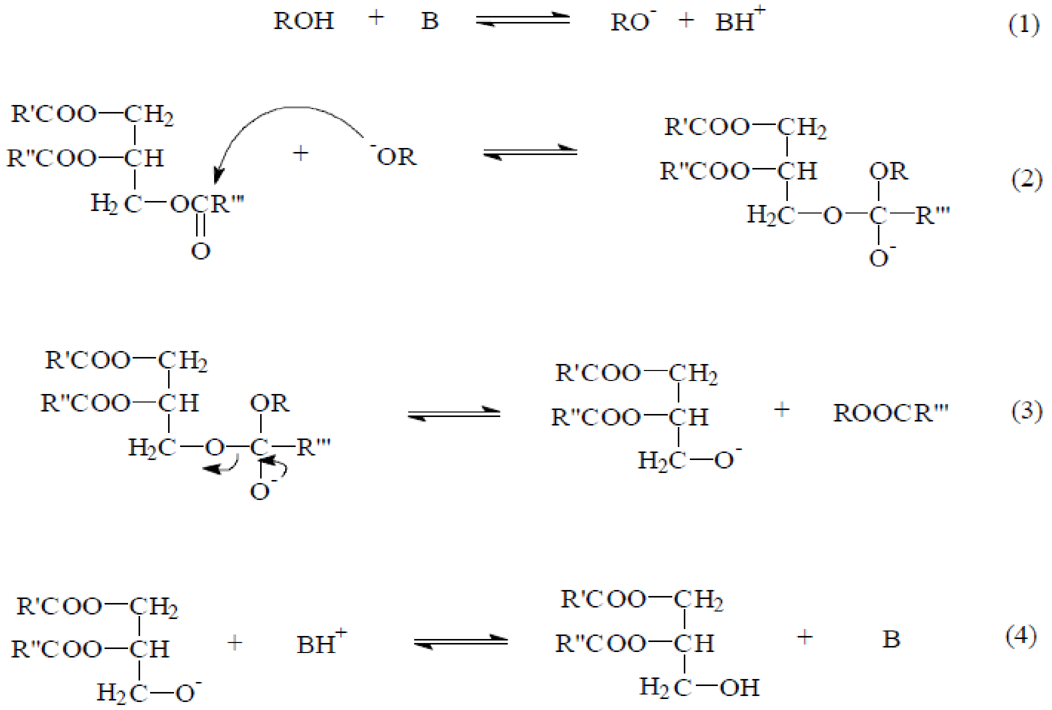


**Figure 2.4:** The mechanism of the base catalyst transesterification

Masato *et al.* had studied about solid base catalyst for biodiesel production with environment benignity and found that by using CaO as catalyst had yield 93% of fatty acid methyl ester in 1 hour duration time better than $Ca(OH)_2$ and $CaCO_3$. But after 2 hour of reaction time with CaO as catalyst, fatty acid methyl ester yield more than 99% but the portion of catalyst had changed into calcium soap by reacting with free fatty acids included with waste cooking oil in the initial stage of transesterification. Meher,L. C. *et al.* had found that 98% of methyl ester had yield from karanja oil by using alkaline transesterification under optimal condition which are 1% of KOH concentration, 6:1 of molar ratio, rate of mixing 360 rpm at 65˚C of reaction temperature for 3 hour period of time.

Umer R. and Farooq A. had studied the optimization of rapeseed oil through alkaline-catalyzed transesterification and they found that the best yield and quality produced are at methanol/oil molar ratio, 6:1; potassium hydroxide catalyst concentration, 1.0%; mixing intensity, 600 rpm and reaction temperature 65°C. by using calcined sodium silicate as a solid base catalyst, Feng G.*et al.* found that transesterification of soybean oil had yield almost 100% of biodiesel under optimum condition which are sodium silicate of 3.0 wt.%, a molar ratio of methanol/oil of 7.5:1, reaction time of 60 min, reaction temperature of 60°C, and stirring rate of 250 rpm.

## 2.6 PARAMETER STUDIES IN OPTIMIZATION PROCESS

There many parameters that used by the researchers in order to study the optimization of biodiesel production, such as agitation speed, pH, free fatty acid (FFA) content, reaction temperature, etc. Table 2.5 shows the parameters used by the researchers to optimize the biodiesel production from various feedstocks.

**Table 2.5:** Parameters used to optimize the biodiesel production

| Feedstock | Parameter | Biodiesel Yield (%) | Reference |
|---|---|---|---|
| Crude canola oil | ▪ Reaction temperature: 50°C<br>▪ Weight catalyst at 0.2 mol/mol: 1.59% by weight<br>▪ Methanol to oil molar ratio: 4.5:1 | 95.8 | Singh *et al.*, 2006 |
| Crude cottonseed oil | ▪ Methanol to oil molar ratio: 7.9:1<br>▪ Reaction temperature: 53°C<br>▪ Reaction time: 45 minutes<br>▪ Catalyst concentration: 1.0%<br>▪ Mixing rate: 268 rpm | 97.0 | Xiaohu *et al.*, 2011 |
| Animal fats, restaurant waste oil and frying oil | ▪ Amount of methanol: 40% by volume<br>▪ Catalyst concentration: 0.3% by weight<br>▪ Reaction temperature: 65°C<br>▪ Reaction time: 90 minutes | 80 | Math *et al.*, 2010 |
| *Jatropha curcas* L. | ▪ Methanol to oil molar ratio: 6:1<br>▪ Catalyst concentration: 1% by weight<br>▪ Reaction temperature: 60°C<br>▪ Reaction time: 40 minutes | 98.6 | Nakpong and Wootthikanokkhan, 2010 |

**Table 2.5:-**Continued

| Feedstock | Parameter | Biodiesel Yield (%) | Reference |
|---|---|---|---|
| Palm oil | ▪ Reaction time: 3 hours<br>▪ Reaction temperature: 127°C<br>▪ Methanol to oil molar ratio: 8:1<br>▪ Catalyst concentration: 6% by weight | 83.3 | Yee and Lee, 2008 |
| Waste cooking palm oil | ▪ Methanol to oil molar ratio: 29:1<br>▪ Catalyst concentration: 2.7% by weight<br>▪ Reaction time: 87 minutes<br>▪ Reaction temperature: 115.5°C | 79.7 | Nadyaini and Aishah, 2011 |
| Jojoba oil | ▪ Catalyst concentration: 1.35%<br>▪ Reaction temperature: 25°C | 83.5 | Bouaid et al., 2007 |

## 2.7 FACTORS AFFECTING THE PRODUCTION YIELD OF BIODIESEL

There are several conditions or parameters that affect the biodiesel production yield such as pH, agitation speed and reaction temperature. According Hary *et al.* (2008), the main factors that affecting the transesterification process are alcohol to oil molar ratio, catalyst concentration, reaction temperature and reaction time.

### 2.7.1 Effect of Reaction Temperature

Reaction temperature is one of the important parameters in the biodiesel production. Demirbas and Karslioglu (2007) said that the increasing of reaction temperature, especially to supercritical conditions, had favourable influence in the yield of ester conversion. Math et al. (2010) mentioned that the reaction temperature also give an influence toward rate of reaction. Normally, catalytic methanolysis is experimented near to methanol boiling point. Hary *et al.* (2008) observed that the increasing of the conversion was less than 3% with the increasing of the reaction temperature from 30°C to 70°C and the effect of temperature on the conversions of triglyceride were less pronounce.

According to Carlos *et al.* (2010), the assessment made on the difference between the dispersion of the results from one temperature to another to improve the correlation and establish more precisely the effect of temperature on FAME production. Mathiyazhagan and Ganapathi (2011) found out that the higher reaction temperature increased the reaction rate and shortened the reaction time due to the reduction in viscosity of oils. But, the increasing in the reaction temperature beyond the optimal level leads to decrease of biodiesel yield because of the higher reaction temperature accelerates the saponification of triglycerides. Usually, the reaction temperature should be below the boiling point of alcohol in order to avoid the alcohol evaporation.

### 2.7.2 Effect of Alcohol to Oil Molar Ratio

Another important factor that affected the production of biodiesel is alcohol to oil molar ratio. Stoichiometrically, the methanolysis process requires three moles of methanol for each mole of oil. Because of the reversible reactions of transesterification of triglycerides, the excess methanol is required in order to shift the equilibrium towards the direction of ester formation (Amish *et al.*, 2011). According to Demirbas and Karslioglu (2007), the yield of alkyl ester increased with the increasing molar ratio of alcohol to oil. Meanwhile, according to Nakpong and Wootthikanokkhan (2010), the transesterification reaction was slower with the lower methanol to oil ratio, whereas shorter time was required for a higher methanol to oil molar ratio to get same methyl ester content.

Hossain and Mazen (2010) found that soybean oil to methanol molar ratio of 1:1 gave the higher yield of biodiesel, which is 71.2%, than 3:1 oil to methanol molar ratio. Nakpong and Wootthikanokkhan (2010) observed that the methyl ester content for a methanol to Jatropha oil ratio of 6:1 was 93.1% w/w after 20 minutes, whereas the same content was obtained with a methanol to Jatropha oil molar ratio of 8:1 after 10 minutes and a methanol to Jatropha oil molar ratio 10:1 after 5 minutes. Ramadhas *et al.* (2005) said that maximum conversion efficiency was achieved very close at methanol to rubber seed oil molar ratio of 6:1 compare to methanol to rubber seed oil molar ratio of 3:1 and 5:1. Hossain *et al.* (2010) found that methanol to oil molar ratio of 1:1 has higher biodiesel yield than methanol to oil molar ratio of 1:2, 1:3 and 1:4.

### 2.7.3 Effect of Catalyst Concentration

The catalyst is one of important feedstock used in the process of transesterification of the fatty acids. A catalyst aims at speeding up the process by aiding the rapid breaking of triglyceride bonds (Kafuku and Mbarawa, 2010). According to Amish *et al.* (2011), the conversion yield increased with the increasing of catalyst amount. But, with further increase in catalyst amount will decreased the conversion yield due to soap formation. Kafuku and Mbarawa (2010) also mentioned that with higher catalyst concentrations after reached optimal levels, the yield would decreased and more soap was formed because the excess catalyst favouring the process of saponification.

Edward *et al.* (2001) found that ester yield increased as the catalyst concentration increased and the highest yield of 82% was obtained using acid catalyst concentration of 5%. Keera *et al.* (2011) said that the NaOH catalyst concentration was observed from between 0.5 to 1.5 w/w% gave optimal yield at 1.0 w/w% but higher than the NaOH catalyst concentration of 1.0 w/w% will decrease the yield of biodiesel production. Highina *et al.* (2011) studied the ZnO catalyst concentrations of 0.25%, 0.5%, 1.0% and 1.5%, and found the highest yield of biodiesel was at ZnO concentration of 1.5%. Hary et al. (2008) found that optimum yield was at KOH concentration of 1.0% and further increasing of KOH concentration would caused the decreasing of production yield.

### 2.7.4 Effect of Reaction Time

According to Hawash *et al.* (2011) mentioned that the decreasing of reaction time will decrease the percentage of yield. Ilgen and Akin (2008) found that in the 1 hour of reaction time FAME yield increased significantly and reached 57.75% and with further increase in reaction time, FAME yield increased and highest FAME yield of 82.29% was obtained after 9 hours of reaction time. Hayyan *et al.* (2010) said that the conversion of FFA to FAME increased with the increasing of reaction time and the highest conversion after 1 hour reaction which is 90.9%. Chonkhong et al. (2007) found an increasing in the conversion yield with the increase of reaction time up to 3 hours. Ranganathan *et al.* (2011) found that when the reaction time increased, the biodiesel production increased and reached maximum at 8 hours, and then biodiesel production decreased with the increasing of reaction time. This was due to the fact of that the tendency of soap formation increases with the increase in reaction time.

## 2.8 DESIGN OF EXPERIMENT (DOE)

Design of experiments is a methodology for systematically applying statistics to experimentation. It also can be defined as a series of tests in which purposeful changes are made to the input variables of a process or output response (Tanco *et al.*, 2008). This technique is a proven technique that is used extensively in many industrial-manufacturing processes. Their application of experimental design also well documented. The application of the design of experiments which uses more than a single design in sequence is less frequent (Sullivan and Cockshott, 2001).

The advantage of the experimental design is, it would increase the amount of information in every experiment way better than the ad hoc approach. Secondly, it also can provide an organized approach towards analysis and interpretation of results, thus facilitate communication. The ability of DoE in identifying the interaction among the factors, leads to the more reliable prediction of response in the areas which are not directly covered by experimentation. DoE also gives benefits in the assessment of information reliability in light of experimental and analytical variation (Chambers and Swalley, 2009). Through DoE technique, the total number of the experiments can be reducedby evaluating the more relevant interaction between variables (Farhana, 2010).

## 2.9 RESPONSE SURFACE METHODOLOGY (RSM)

The approached toward Design of Experiment (DoE) began in 1950's when Box and Wilson developed the RSM. Their methodology allowed the chemical industry to apply the DoE as well as in others industries (Tanco *et al.*, 2008). Response surface methodology (RSM) is a collection of statistical and mathematical techniques that useful for modelling and analysis of the problems in which the response of interest is influenced by several variables and the objective is to optimize this response (Montgomery, 2005). The response surface designs are type o f designs that used for fitting response surface. The objectives of studying the RSM can be achieved by understanding the topography of response surface (local maximum, local minimum, ridge lines) and finding the region where the optimal response occur in order to move rapidly and efficiently along the path to get maximum or minimum response so that response has been optimized (Nuran Bradley, 2007).

According to Kathleen *et al.* (2004), the most extensive applications of RSM are in the particular situations where several input variables potentially influence some performance measure or quality characteristic of the process. Different values of operating conditions comprise the factors for each experiment. Some may be a categorical, such as supplier of raw material, and others may quantitative, such as pH, temperature and feed rates. In practice, the categorical variables must be handled separately by comparing the best operating conditions with respect to quantitative variables across different combinations of categorical ones. The quantitative variables' fundamental methods involve fitting first order (linear) or second order (quadratic) functions of the predictors to one or more response variables, and then examining the characteristics of the fitted surface to decide the appropriate actions (Russell, 2009).

According to Farhana (2010), and Chambers and Swalley (2009), the response surface designs are used to model the response of a curved surface to a range of continuous variable. The non-inclusion of categorical variables is limited to RSM; hence, it is used for optimization process and not in the initial screening process. RSM provides a more complete understanding of the significant factors involved and is capable to identify whether minimum or maximum response exist within the model.

## 2.10 CONCLUSION

Biodiesel also known as fatty acid methyl ester is derived from vegetable oils or animal fat by transesterification process with additional of alcohol in presence of catalyst. Cooking palm oil is used as a research subject in biodiesel synthesis because of its potential to extract amount of FAME from its oils. Base catalyst transesterification process has been choosing in order to produce the biodiesel because it more effective than acid catalyst transesterification.

# CHAPTER 3

# METHODOLOGY

## 3.1 FLOWCHART OF BIODIESEL PRODUCTION

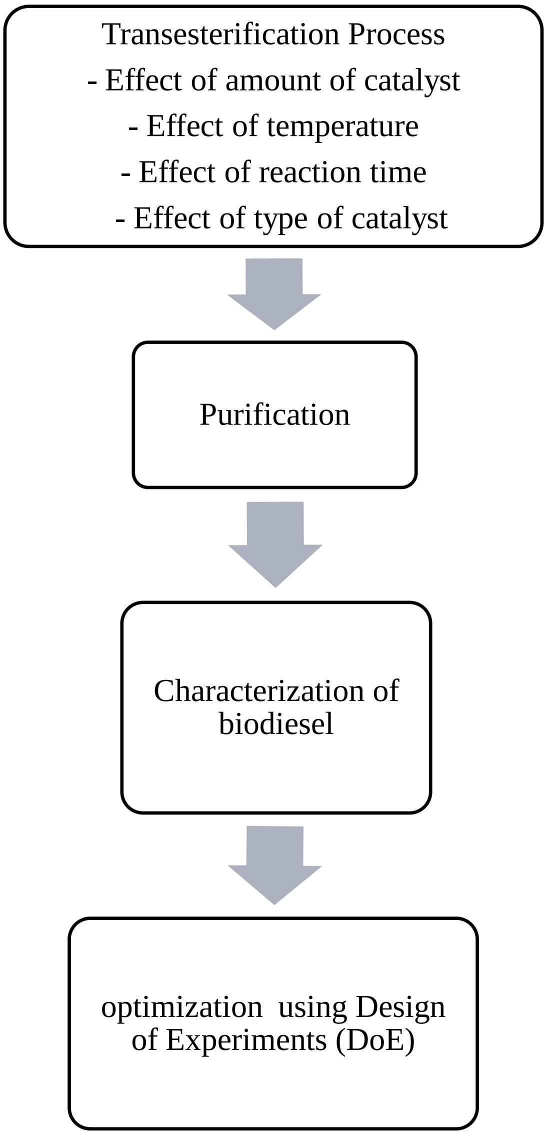


**Figure 3.1:** Flowchart of production process

## 3.2 BIODIESEL PRODUCTION BY USING TRANSESTERIFICATION TECHNIQUE

The experiment is set up by equipped 250 ml glass three-necked flask batch reactor with reflux condenser, thermometer and mechanical stirrer, immersed in constant temperature. 200 ml of cooking palm oil is taken in reactor and placed in water or oil bath at desired temperature (Ashish K.*et al.*, 2010). A reflux condenser is connected to the reactor as a function to prevent alcohol from loss to surrounding (Suzana Y. and Modhar A. K., 2010). The molar ratio of methanol to cooking palm oil is set to 6:1. 4 ml of n-hexane is stirred with 40 ml of methanol for 10 minute and then, the solution is mixed with cooking palm oil in the reactor. The reaction time is set for 2 hour duration (El Boulifi,N. *et al.*, 2010). Then, the mixture is transferred carefully to separating funnel to separate glycerol by gravity. The experiment is repeated by changing the reaction time with 3, 4, 5 and 6 hours. The another experiment is employed by using different catalyst concentration from 1 to 5% ($w/w_{oil}$) in step of 1%, different reaction temperature from 50°C to 90°C in step of 10°C (Ashish K.*et al.*, 2010) and different methanol to oil molar ratio which are 8:1, 10:1, 12:1 and 14:1.

## 3.3 BIODIESEL PURIFICATION

The methyl ester is washed with lukewarm water to remove catalyst, methanol and glycerol residual after glycerol has been separate from the mixture by the separating funnel. After that, the raw biodiesel is heated to 100°C in open vessel in order to remove any water particle (Ashish K.*et al.*, 2010).

## 3.4 EVALUATION OF BIODIESEL CONVERSION

The gas chromatography mass spectrometry (GC-MS) was used for analyzing compositions of product. The oven temperature of GC was held at the initial temperature of 0°C for 3 minutes. Then, ramped to 120°C with 40°C/min and held for 3 minutes. Finally, ramped up at 10°C/min to 250°C and maintained for 5 minutes. Injector and detector temperature are used at 250°C. Hydrogen gas is used as carried at flow rate of 35 mL/min.

## 3.5 EXPERIMENTAL DESIGN AND PROCESS OPTIMIZATION

The statistical analysis for the production of biodiesel from cooking palm oil was performed by using Design Expert version 7.1.6 software. The experimental design as a function of the selected process variables was carried out using central composite design (CCD) (Razali *et al.*, 2010). It was used to study the interaction between process variables by applying the RSM. In order to obtained the optimal biodiesel yield, certain transesterification process conditions, such as reaction temperature (50°C, 60°C, 70°C, 80°C and 90°C), catalyst concentration (1%, 2%, 3%, 4% and 5%), methanol to oil molar ratio (6:1, 8:1, 10:1, 12:1 and 14:1) and reaction time (2 hour, 3 hour, 4 hour, 5 hour and 6 hour), were optimized. Each of these variables is varied over five levels which were low alpha point (-α), low fractional point (-1), central point (0), high fractional point (+1) and high alpha point (+α). Biodiesel yield (Y) was taken as a response of the design experiments. The full quadratic equation of the response variable for biodiesel production was derived by RSM as equation (3.1).

$$\begin{aligned} Y &= \beta_0 + \beta_1X_1 + \beta_2X_2 + \beta_3X_3 + \beta_4X_4 + \beta_{12}X_1X_2 + \beta_{13}X_1X_3 + \beta_{14}X_1X_4 \\ &\quad + \beta_{23}X_2X_3 + \beta_{24}X_2X_4 + \beta_{34}X_3X_4 + \beta_{11}X_1^2 + \beta_{22}X_2^2 + \beta_{33}X_3^2 \\ &\quad + \beta_{44}X_4^2 \end{aligned} \tag{3.1}$$

Where, Y is the response of biodiesel yield; $\beta_0$ is a constant; $\beta_1$, $\beta_2$, $\beta_3$ and $\beta_4$ are linear regression; $\beta_{11}$, $\beta_{22}$, $\beta_{33}$ and $\beta_{44}$ are interaction regression; $X_1$, $X_2$, $X_3$ and $X_4$ are variables.

# CHAPTER 4

# RESULT AND DISCUSSION

## 4.1 INTRODUTION

This chapter is discussing about the results which are obtained during the study on the optimization of biodiesel production based on the effect of the parameters in presence of alkali catalyst, which is n-hexane. The parameters that used in this study are reaction temperature, catalyst concentration, molar ratio of alcohol to oil and reaction time. The optimization of biodiesel production by using RSM is shows in this chapter.

## 4.2 EVALUATION OF FATTY ACID METHYL ESTER (FAME) CONTENT IN BIODIESEL

The analysis of FAME in biodiesel yield was carried out by using gas chromatography mass spectrophotometer (GC-MS). Peak area of the graph resulting from the analysis was comparing with the library database of NIST05a.L. The summary of the FAME contents was listed in the Table 4.1.

**Table 4.1:** Summary of FAME content in biodiesel yield

| FAME | Area (%) | Retention Time |
|---|---|---|
| Dodecanoic Acid | 0.64 | 5.007 |
| Methyl Tetradecanoic Acid | 2.43 | 9.088 |
| Pentadecanoic Acid | 0.12 | 11.201 |
| Hexadecanoic Acid | 39.99 | 14.137 |
| Octadecanoic Acid | 53.49 | 17.833 |
| Eicosanoic Acid | 2.99 | 20.647 |
| Tricosanoic Acid | 0.14 | 25.493 |
| Tetracosanoic Acid | 0.20 | 27.851 |

## 4.3 OPTIMIZATION USING RESPONSE SURFACE METHODOLOGY (RSM)

According to Gorkhan *et al.* (2011), RSM is an efficient statistical tool for optimization of multiple variables. In order to fully optimize the production of biodiesel from refine cooking oil made of palm oil, RSM is used to study the experimental regime from a statistical stand-point and designs a protocol. This technology is useful model for studying factors that affect the response by varying them simultaneously and it can also be used to study the relationship between one or more factors (independent variables) and responses (dependent variable) (Syafiq Eidham, 2011).

Four experimental factors, reaction temperature, catalyst concentration, molar ratio, and reaction time, are chosen for optimization of biodiesel production from cooking oil made of palm oil. Factor levels were chosen by considering the operating limits of the experimental apparatus and the properties of reactants (Vicente *et al.*, 1998). The RSM is using four factors and five level central composite designs to optimize the response variable. Each factor in this design is studies at five different level of central composite designs, which are -α, -1, 0, +1 and +α (Table 4.2). All variables were taken at central coded that has been considered as zero. Table 4.2 lists all maximum and minimum range of the variables and levels were investigated and full experimental plans designed with respect to their value in actual and coded form. The percentage of biodiesel yield was studied as response. This criterion was used in all experimental designs and analyzed with the aid of Design Expert version 7.1.6 statistical software (Stat-Ease Inc, Minneapolis, MN). The percentage of biodiesel yield was analyzed by using variance (ANOVA). The optimum levels of variables were obtained by numerical and graphical designs with the usage of Design Expert program.

**Table 4.2:** Experimental range and level coded of the process variables

| **Independent Variables** | **Unit** | **Symbol** | **Ranges and Levels** | | | | |
|---|---|---|---|---|---|---|---|
| | | | **-α** | **-1** | **0** | **+1** | **+α** |
| Reaction temperature | °C | $X_1$ | 50 | 60 | 70 | 80 | 90 |
| Molar ratio | - | $X_2$ | 6 | 8 | 10 | 12 | 14 |
| Catalyst concentration | % | $X_3$ | 1 | 2 | 3 | 4 | 5 |
| Reaction time | h | $X_4$ | 2 | 3 | 4 | 5 | 6 |

Table 4.3 shows the design matrix of the variables and the experimental results for percentage of biodiesel yield from cooking oil made of palm oil. The design independent variables and their range already classified as in Table 4.2.

By using quadratic model on the experiment data, the following second-order polynomial equation (4.1) was found to show the percentage of biodiesel yield as Y.

$$\begin{aligned} Y = {} & 77.03 + 1.64X_1 + 8.78X_2 + 12.48X_3 + 8.99X_4 + 2.13X_1X_2 - 1.51X_1X_3 \\ & + 3.47X_1X_4 - 0.89X_2X_3 + 0.78X_2X_4 + 3.77X_3X_4 - 11.89X_1^2 - 5.06X_2^2 \\ & - 5.40X_3^2 - 2.94X_4^2 \end{aligned} \tag{4.1}$$

Where, Y (%) was the response factors for percentage of biodiesel yield from cooking oil that made of palm oil. $X_1$, $X_2$, $X_3$ and $X_4$ were representing as values of independent factors, which were reaction temperature, molar ratio, catalyst concentration and reaction time, respectively.

**Table 4.3:** Central composite design (CCD) of factors with percentage of biodiesel yield as response

| Standard Order | Run | Reaction Temperature (°C) | Molar Ratio | Catalyst Concentration (%) | Reaction Time (h) | Predicted | Percentage of Biodiesel Yield (%) |
|---|---|---|---|---|---|---|---|
| 24 | 1 | 70 | 10 | 3 | 6 | 83.26 | 88.3 |
| 22 | 2 | 70 | 10 | 5 | 4 | 80.40 | 85.5 |
| 21 | 3 | 70 | 10 | 1 | 4 | 30.48 | 33.1 |
| 27 | 4 | 70 | 10 | 3 | 4 | 77.03 | 76.1 |
| 2 | 5 | 80 | 8 | 2 | 3 | 22.70 | 22.2 |
| 15 | 6 | 60 | 12 | 4 | 5 | 79.92 | 76.5 |
| 30 | 7 | 70 | 10 | 3 | 4 | 77.03 | 82.3 |
| 6 | 8 | 80 | 8 | 4 | 3 | 38.90 | 40.1 |
| 1 | 9 | 60 | 8 | 2 | 3 | 27.62 | 30.7 |
| 16 | 10 | 80 | 12 | 4 | 5 | 91.38 | 84.5 |
| 12 | 11 | 80 | 12 | 2 | 5 | 63.69 | 65.3 |
| 28 | 12 | 70 | 10 | 3 | 4 | 77.03 | 68.9 |
| 10 | 13 | 80 | 8 | 2 | 5 | 38.52 | 35.9 |
| 23 | 14 | 70 | 10 | 3 | 2 | 47.31 | 50.0 |
| 3 | 15 | 60 | 12 | 2 | 3 | 41.14 | 41.3 |

**Table 4.3:**-Continued

| **Standard Order** | **Run** | **Reaction Temperature (°C)** | **Molar Ratio** | **Catalyst Concentration (%)** | **Reaction Time (h)** | **Predicted (%)** | **Percentage of Biodiesel Yield (%)** |
|---|---|---|---|---|---|---|---|
| 8 | 16 | 80 | 12 | 4 | 3 | 57.37 | 55.1 |
| 4 | 17 | 80 | 12 | 2 | 3 | 44.75 | 36.7 |
| 14 | 18 | 80 | 8 | 4 | 5 | 69.79 | 65.7 |
| 19 | 19 | 70 | 6 | 3 | 4 | 39.23 | 38.3 |
| 11 | 20 | 60 | 12 | 2 | 5 | 46.20 | 41.2 |
| 18 | 21 | 90 | 12 | 3 | 4 | 32.76 | 39.7 |
| 17 | 22 | 50 | 10 | 3 | 4 | 26.21 | 27.0 |
| 29 | 23 | 70 | 10 | 3 | 4 | 77.03 | 81.1 |
| 26 | 24 | 70 | 10 | 3 | 4 | 77.03 | 76.3 |
| 9 | 25 | 60 | 8 | 2 | 5 | 29.55 | 27.9 |
| 5 | 26 | 60 | 8 | 4 | 3 | 49.84 | 44.3 |
| 13 | 27 | 60 | 8 | 4 | 5 | 66.85 | 71.1 |
| 25 | 28 | 70 | 10 | 3 | 4 | 77.03 | 77.5 |
| 20 | 29 | 70 | 14 | 3 | 4 | 74.35 | 83.0 |
| 7 | 30 | 60 | 12 | 4 | 3 | 59.78 | 58.6 |

## 4.4 ANALYSIS OF VARIANCE (ANOVA)

Analysis of variance method (ANOVA) is used to select significant factors (Neda *et al.*, 2002). ANOVA is widely used in the statistical evaluation and referred as the analysis of variance. ANOVA is an excellent technique in order to determine the process condition whether it has a significant effect to the process. The hypothesis of ANOVA can be used in order to identify the statistical significant variation in quality (Farhana, 2010).

Table 4.4 shows the analysis of variance for response surface quadratic model of the percentage of biodiesel yield from cooking oil.

The Model F-value of 24.80 implies the model is significant. There is only a 0.01% chance that a “Model F-Value” this large could occur due to noise. Values of “Prob > F” less than 0.05 indicate model terms are significant. In this case, $X_2$, $X_3$, $X_4$, $X_1X_4$, $X_3X_4$, $X_1^2$, $X_2^2$, $X_3^2$ and $X_4^2$ are significant model terms. Values greater than 0.10 indicate the model terms are not significant. If there are many insignificant model terms (not including those required to support hierarchy), model reduction may improved the model.

The “lack of Fit F-value” of 1.94 implies the Lack of Fit is not significant relative to the pure error. There is a 24.10% chance that a “Lack of Fit F-value” this large could occur due to noise. Non-significant lack of fit is good. Generally, P-values lower than 0.01 indicate that the model is considered to be statistically significant at the 99% confidence level (Razali, 2010).

Table 4.5 shows the analysis of fit of the polynomial model equation from the analysis of variance (ANOVA).

**Table 4.4:** Analysis of variance (ANOVA) for response surface quadratic model of percentage of biodiesel yield from cooking oil

| Source | Sum of Square | Degree of Freedom | Mean Square | F-value | P-value Prob > F | Result |
|---|---|---|---|---|---|---|
| Model | 12,645.63 | 14 | 903.26 | 24.80 | < 0.0001 | Significant |
| $X_1$ - Temperature | 64.35 | 1 | 64.35 | 1.77 | 0.2036 | |
| $X_2$ - Molar Ratio | 1,849.77 | 1 | 1,849.77 | 50.78 | < 0.0001 | |
| $X_3$ - Catalyst Concentration | 3,737.51 | 1 | 3,737.51 | 102.61 | < 0.0001 | |
| $X_4$ - Reaction Time | 1,938.60 | 1 | 1,938.60 | 53.22 | < 0.0001 | |
| $X_1X_2$ | 72.68 | 1 | 72.68 | 2.00 | 0.1782 | |
| $X_1X_3$ | 36.30 | 1 | 36.30 | 1.00 | 0.3340 | |
| $X_3X_4$ | 192.52 | 1 | 192.52 | 5.29 | 0.0363 | |
| $X_2X_3$ | 12.78 | 1 | 12.78 | 0.35 | 0.5624 | |
| $X_2X_4$ | 9.77 | 1 | 9.77 | 0.27 | 0.6122 | |
| $X_3X_4$ | 227.26 | 1 | 227.26 | 6.24 | 0.0246 | |
| $X_1^2$ | 3,875.33 | 1 | 3,875.33 | 106.39 | < 0.0001 | |
| $X_2^2$ | 702.68 | 1 | 702.68 | 19.29 | 0.0005 | |
| $X_3^2$ | 799.51 | 1 | 799.51 | 21.95 | 0.0003 | |
| $X_4^2$ | 236.51 | 1 | 236.51 | 6.49 | 0.0223 | |
| Residual | 546.37 | 15 | 36.42 | | | |
| Lack of Fit | 434.31 | 10 | 43.43 | 1.94 | 0.2410 | Not significant |
| Pure Error | 112.05 | 5 | 22.41 | | | |
| Cor. Total | 13,192.00 | 29 | | | | |

**Table 4.5:** Analysis of fit of the polynomial model equation

| | | | |
|---|---|---|---|
| **Standard Deviation** | 6.04 | **R-Squared** | 0.9586 |
| **Mean** | 56.81 | **Adjusted R-Squared** | 0.9199 |
| **C. V. %** | 10.62 | **Predicted R-Squared** | 0.7981 |
| **PRESS** | 2,663.01 | **Adequate Precision** | 16.0930 |

The quality of fit of the polynomial model equation was expressed by correlation coefficient as $R^2$, adjusted $R^2$ and adequate precision. According to Syafiq Eidham (2011), the $R^2$ value provided a measure of how much variability in the observed response values can be explained by the experimental factors and their interactions. The $R^2$ value always lied between 0 and 1. The closer $R^2$ value to 1.00, the stronger the model was and the better it predicted the response.

In this case, the $R^2$ is 0.9586. It shows that 4.14 percent of total variables were not explained by the model. The “Predicted R-Squared” of 0.7981 is in agreement with the “Adjusted R-Squared” of 0.9199. “Adequate Precision” measures the signal to noise ratio. The ratio of 16.093 indicates an adequate signal. This model can be used to navigate the design space. According to Farhana (2010), the fitted polynomial equation was used to visualize the relationship between the response and the experimental levels of each factor used in the design as three-dimensional surface plots.

Figure 4.1 illustrated the plots of predicted versus experimental data for the percentage of biodiesel yield from cooking oil.

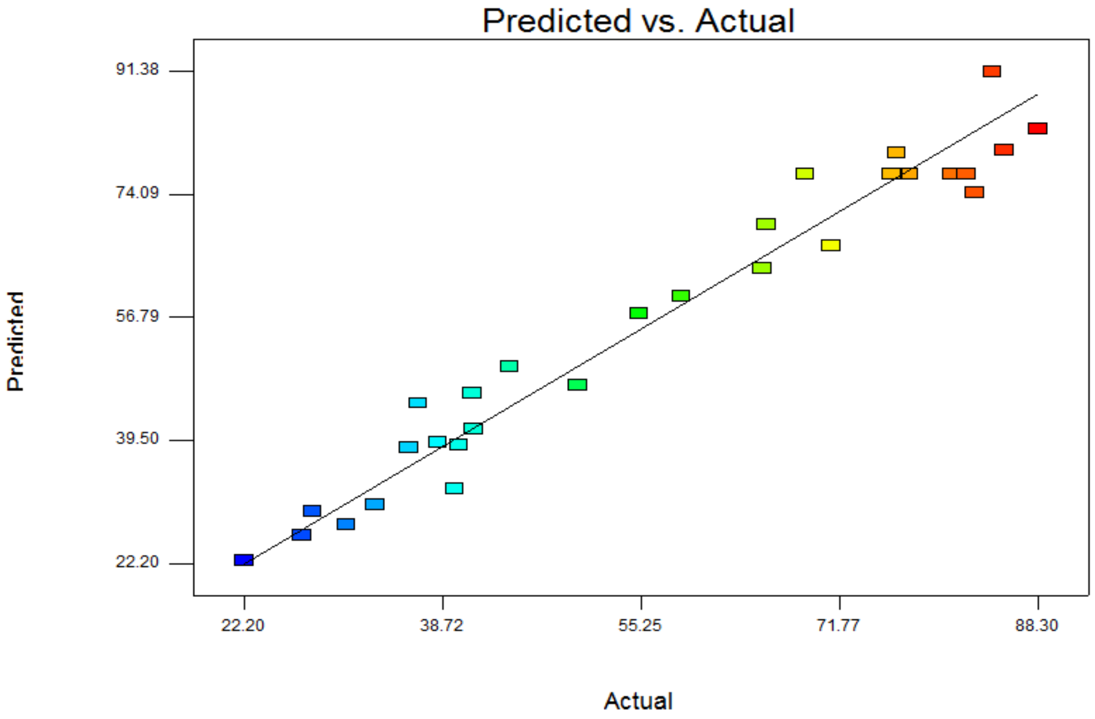


**Figure 4.1:** Plots of predicted versus experimental data of the percentage of biodiesel yield

## 4.5 EFFECT OF ONE FACTOR

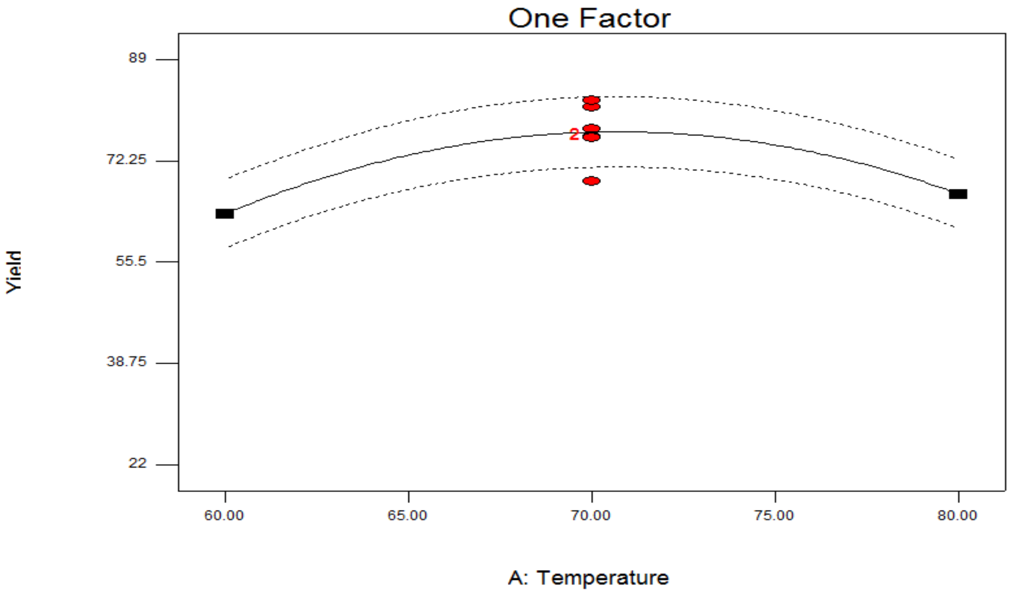


**Figure 4.2:** Effect of reaction temperature toward percentage of biodiesel yield

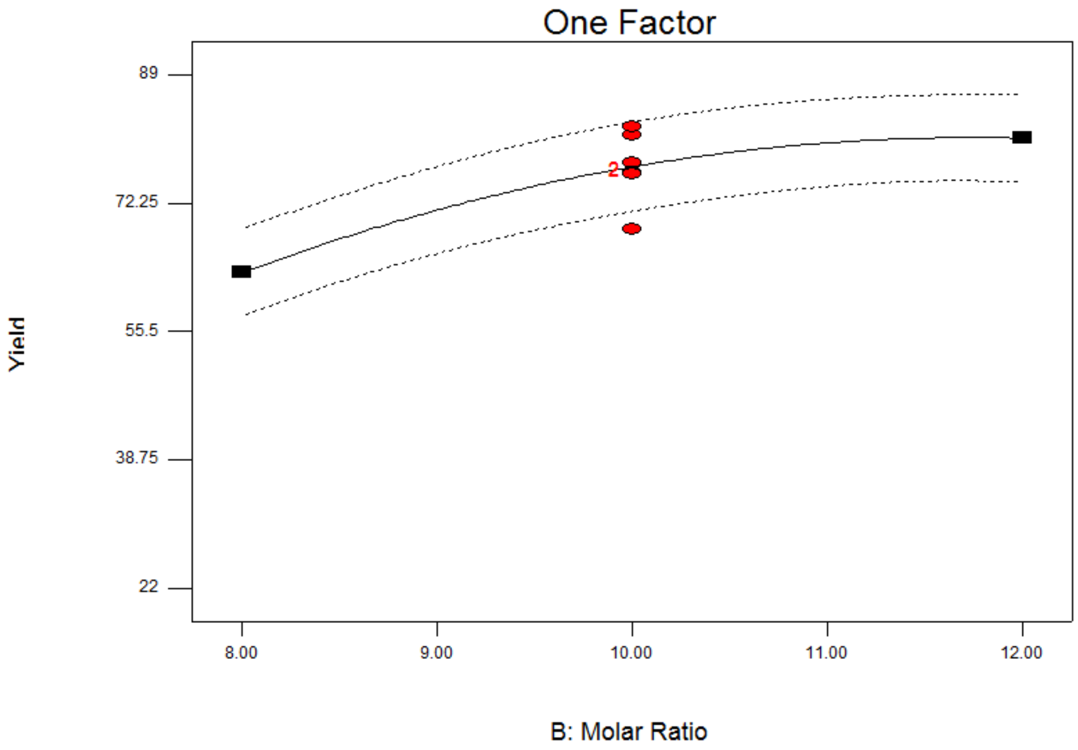


**Figure 4.3:** Effect of molar ratio toward percentage of biodiesel yield

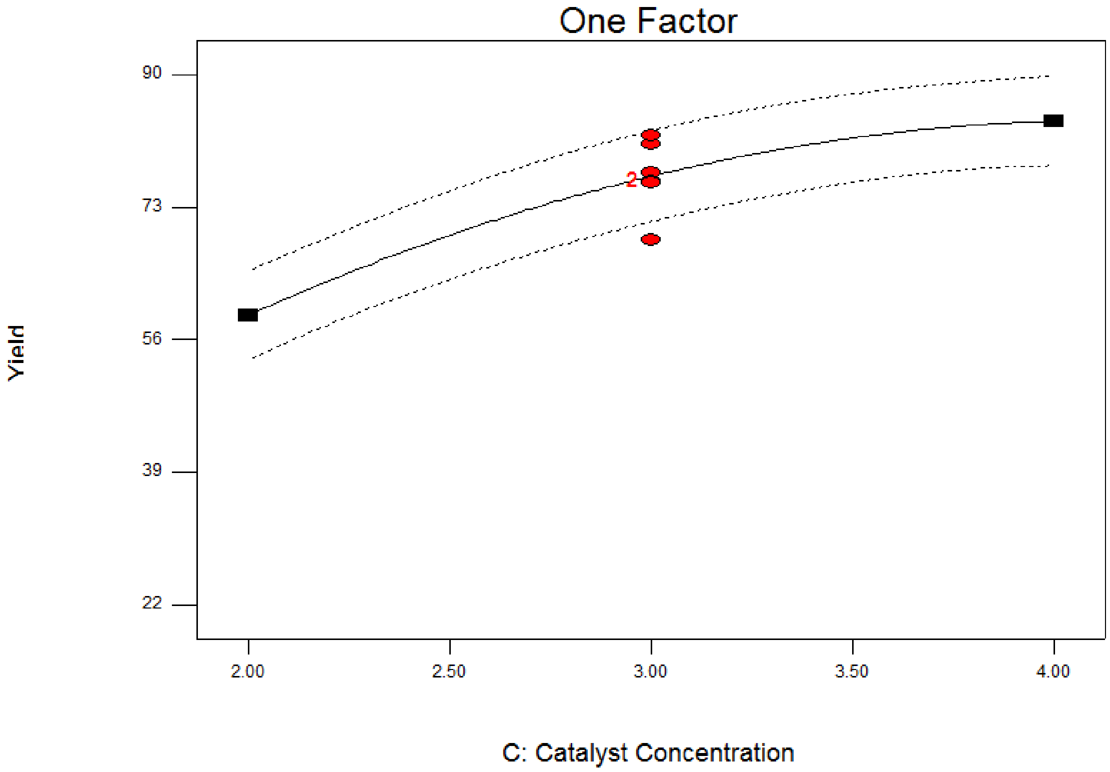


**Figure 4.4:** Effect of catalyst concentration toward percentage of biodiesel yield

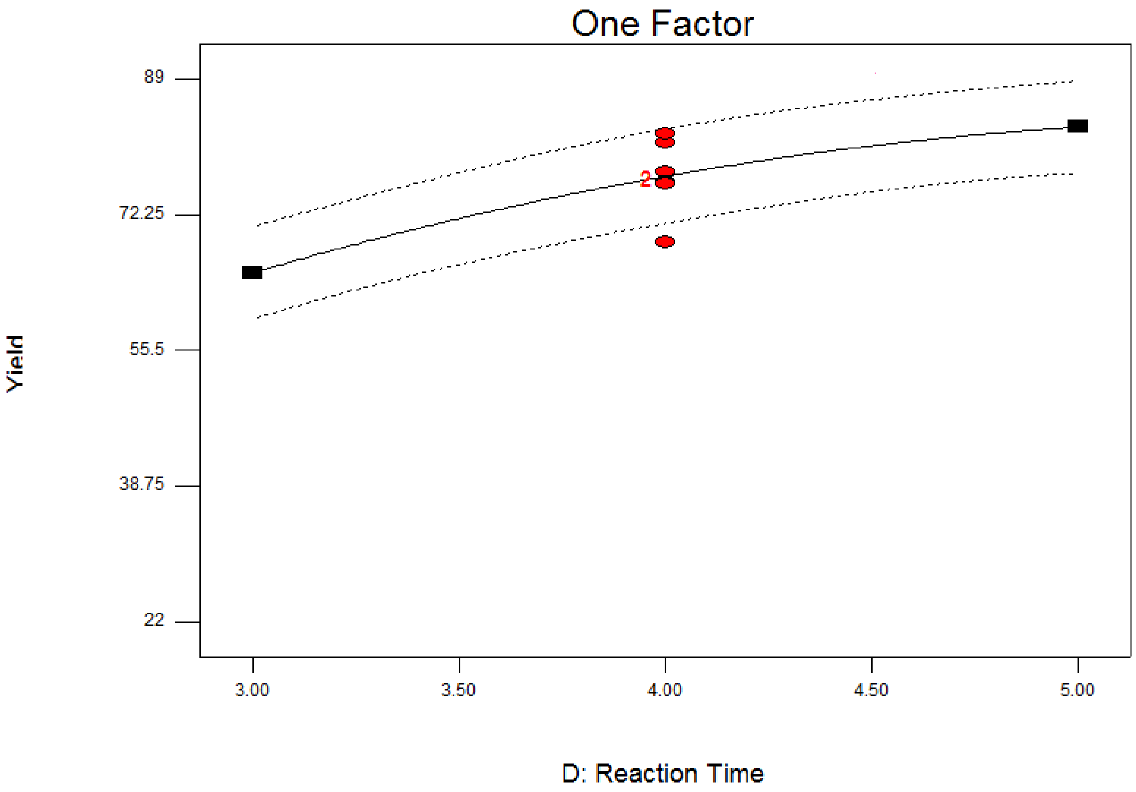


**Figure 4.5:** Effect of reaction time toward percentage of biodiesel yield

Figure 4.2, 4.3, 4.4, and 4.5 illustrated the effect of the individual factor toward the percentage of biodiesel yield. These all factors show positive effects except for factor of reaction temperature. The biodiesel yield increased with the increasing of reaction temperature until it reached at optimal temperature. After that the biodiesel yield decrease. According to Ganapathi (2011), further increase in reaction temperature will accelerate the saponification of triglycerides.

The figure 4.3, 4.4 and 4.5 indicates that the biodiesel yield will increased with the increasing of these three factors. This shows that these factors give positive influence toward biodiesel yield. This is must be due to the positive values of the factors in the quadratic model as in equation (4.1). It is also indicates that the experimental must be runs at the highest value of these factors in order to maximize the biodiesel yield. However, the interaction factors must also be considered as the effect of individual factors plots does not show the information regarding the interaction involved.

## 4.6 INTERACTION OF THE PARAMETERS

The three-dimensional response surface curves were plotted in order to study the interaction of different parameters toward biodiesel yield and to study the optimization of the biodiesel yield.

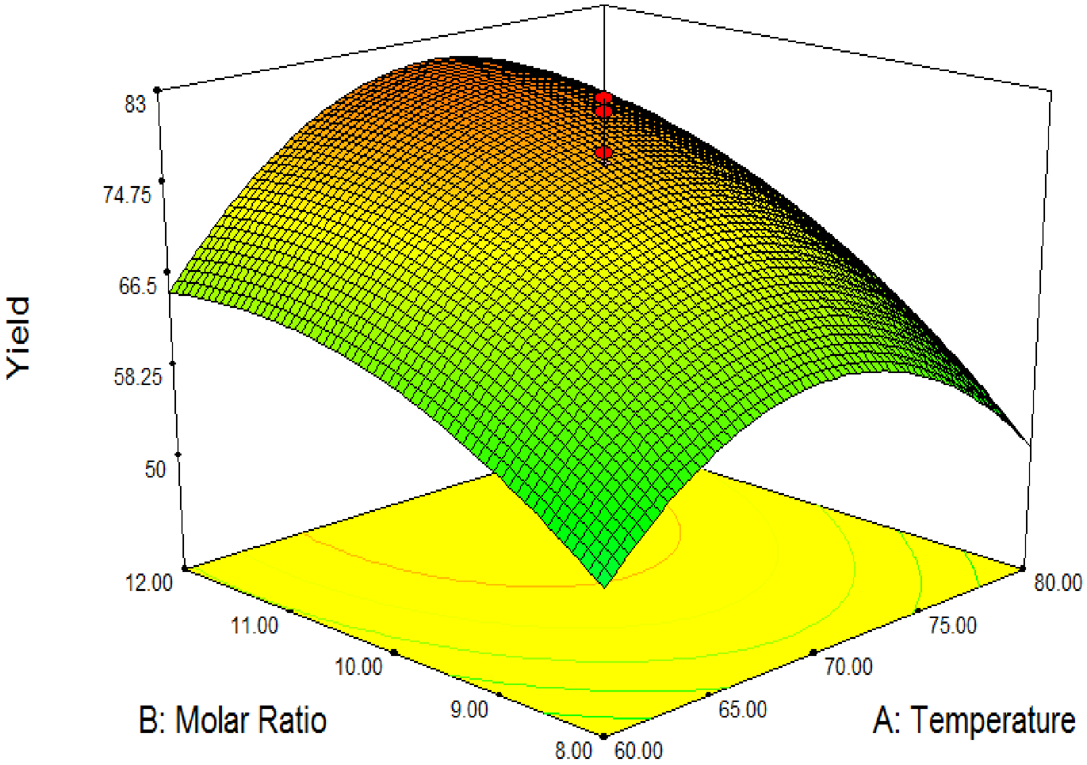


**Figure 4.6:** Interaction of temperature and molar ratio toward biodiesel yield

Figure 4.6 shows the interaction between reaction temperature and molar ratio toward response of biodiesel yield. The highest biodiesel yield in figure 4.6 was obtained at temperature of 70°C with alcohol to oil molar ratio of 14:1 that induce biodiesel yield to 83%. However, the biodiesel yield tends to reduce along with the increasing of the temperature to 90°C. Meanwhile, biodiesel yield slightly decrease as the alcohol to molar ratio increased to 14:1.

According to Hary *et al.* (2008), the transesterification process or catalytic methanolysis that has carried out at near the boiling point of methanol give the highest biodiesel yield. According to Mathiyazhagan and Ganapathi (2011), the increasing of temperature beyond the optimum level will leads to decrease the biodiesel yield because of acceleration of the saponification of triglycerides that give favourable towards soap formation.

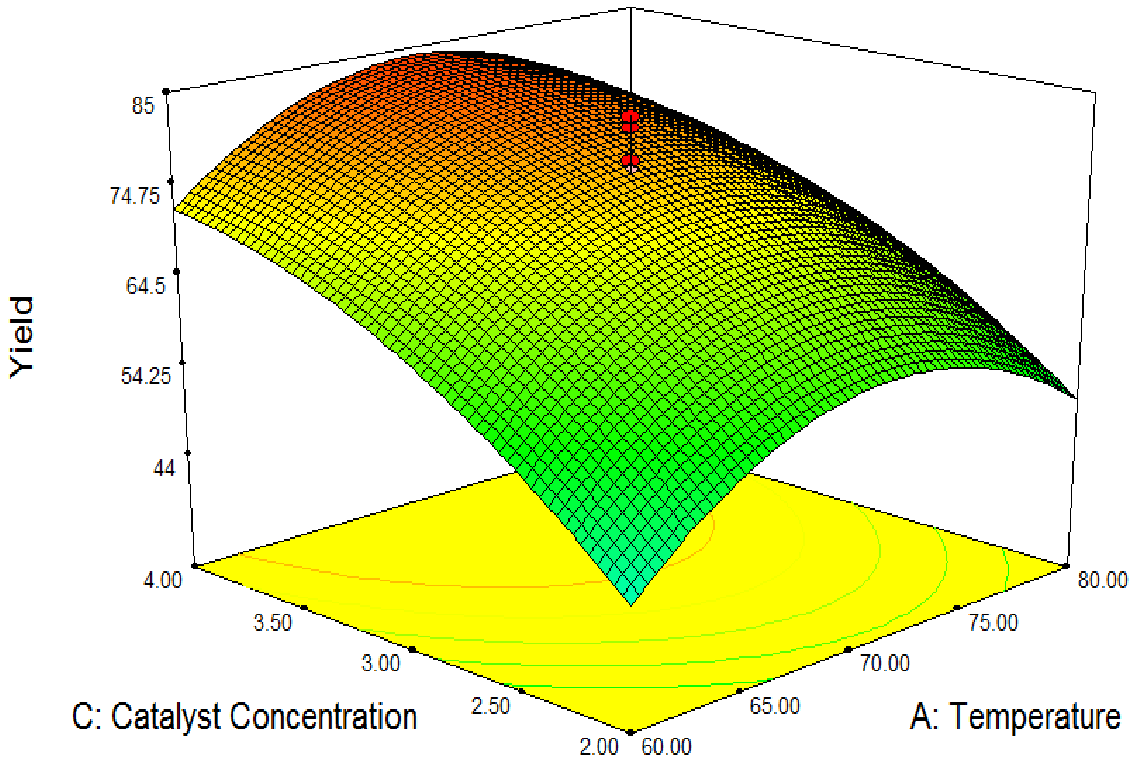


**Figure 4.7:** Interaction of temperature and catalyst concentration toward biodiesel yield

Figure 4.7 shows the response of biodiesel yield toward reaction temperature and catalyst concentration. The highest biodiesel yield in Figure 4.7 was found at temperature of 70°C with the presence 5% of catalyst concentration, which is induce 85.5% biodiesel yield. As mentioned previously, the biodiesel yield tends to decrease with the increasing of temperature beyond the optimal levels. However, the biodiesel yield increase with the increasing of catalyst concentration.

According to Kafuku and Mbarawa (2010), a catalyst is used to speed up the transesterification process by aiding the rapid breaking of triglyceride bonds. This shows that with the increasing of catalyst concentration will speed up the breakdown of triglyceride bonds that leads to highest biodiesel yield. However, according to Ashish *et al.* (2010), the higher catalyst concentration used beyond the optimal levels will the reduce biodiesel yield because of the soap formation.

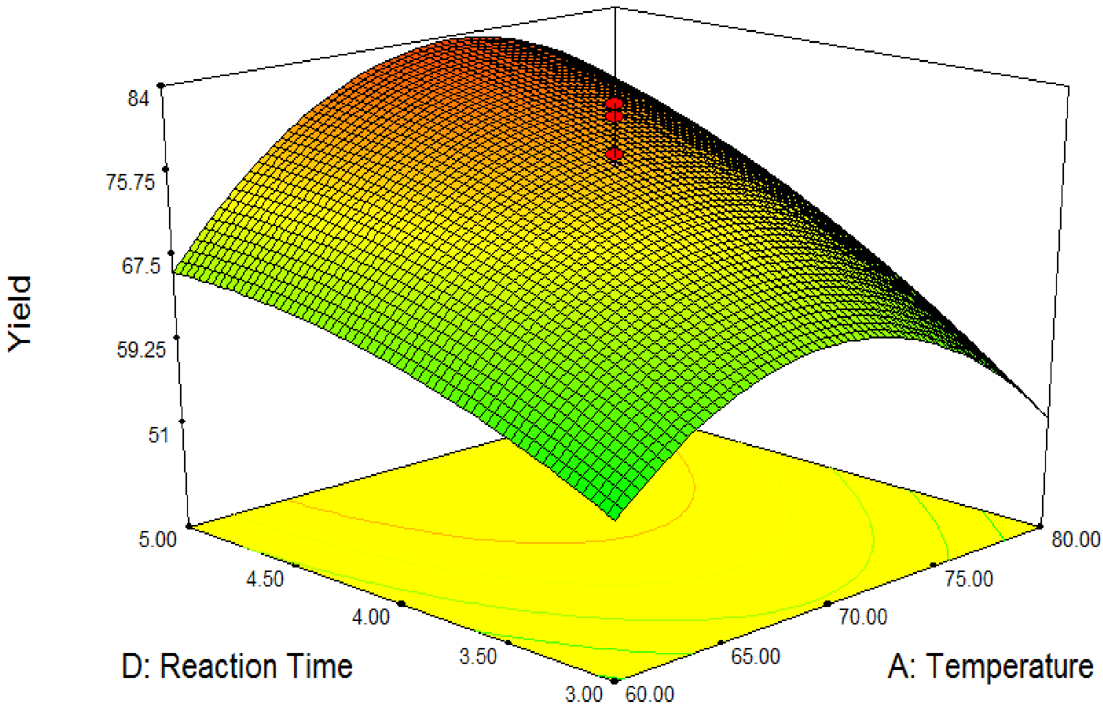


**Figure 4.8:** Interaction of temperature and reaction time toward biodiesel yield

Figure 4.8 illustrated the relation between reaction temperature and reaction time toward response of biodiesel yield. The highest biodiesel yield in Figure 4.8 was found at temperature of 70°C with 6 hours reaction time, which is 88.3% of biodiesel yield. As mentioned previously, the biodiesel yield tends to decrease with the increasing of temperature beyond the optimal levels. However, the biodiesel yield is slightly decreased with the increasing of reaction time. The reaction starts very fast in first hour. The reaction started become slower after that and reached steady state. According to Ranganathan *et al.* (2011), the decreasing of biodiesel yield is due to the fact that the tendency of soap formation increases with the increase of reaction time.

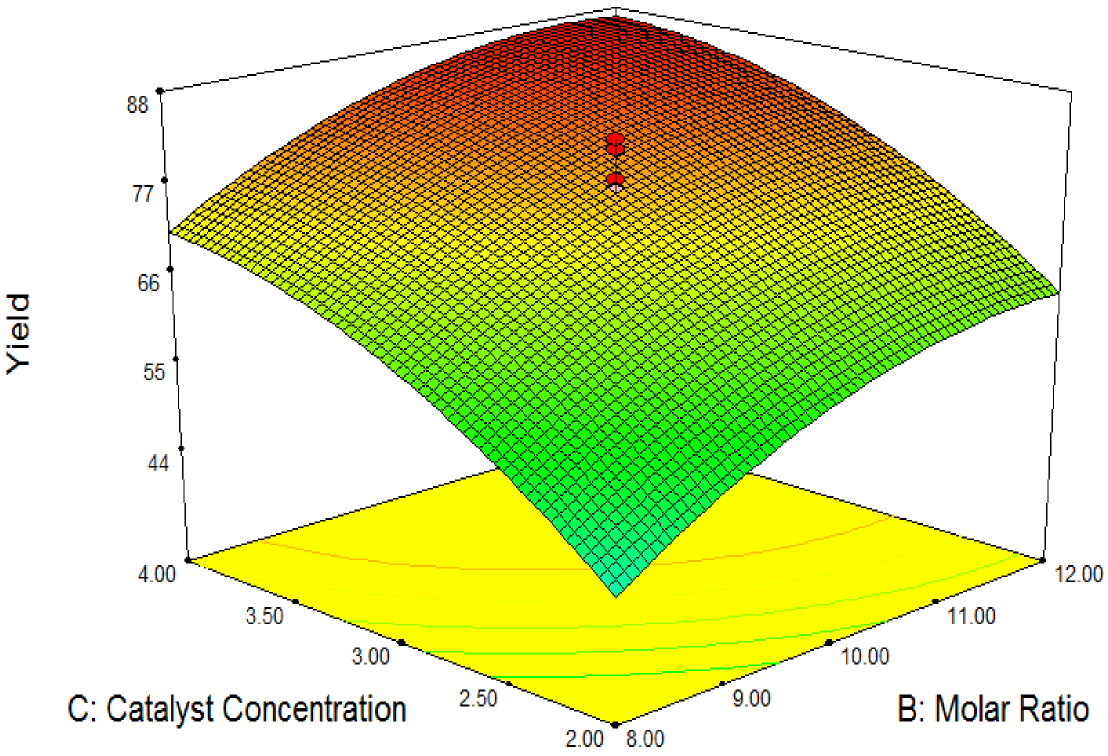


**Figure 4.9:** Interaction of molar ratio and catalyst concentration toward biodiesel yield

Figure 4.9 shows the response of biodiesel yield with the respect of alcohol to oil molar ratio and catalyst concentration. The highest biodiesel yield in Figure 4.9 was found at 5% of catalyst concentration with alcohol to oil molar ratio of 10:1, which is induce the biodiesel yield at 85.5%. As mentioned previously, the increasing of molar ratio will increase the biodiesel yield. Same goes to catalyst concentration. The increasing of catalyst concentration will leads to the increasing of biodiesel yield. However, the further increase will decrease the biodiesel yield due to the formation of soap.

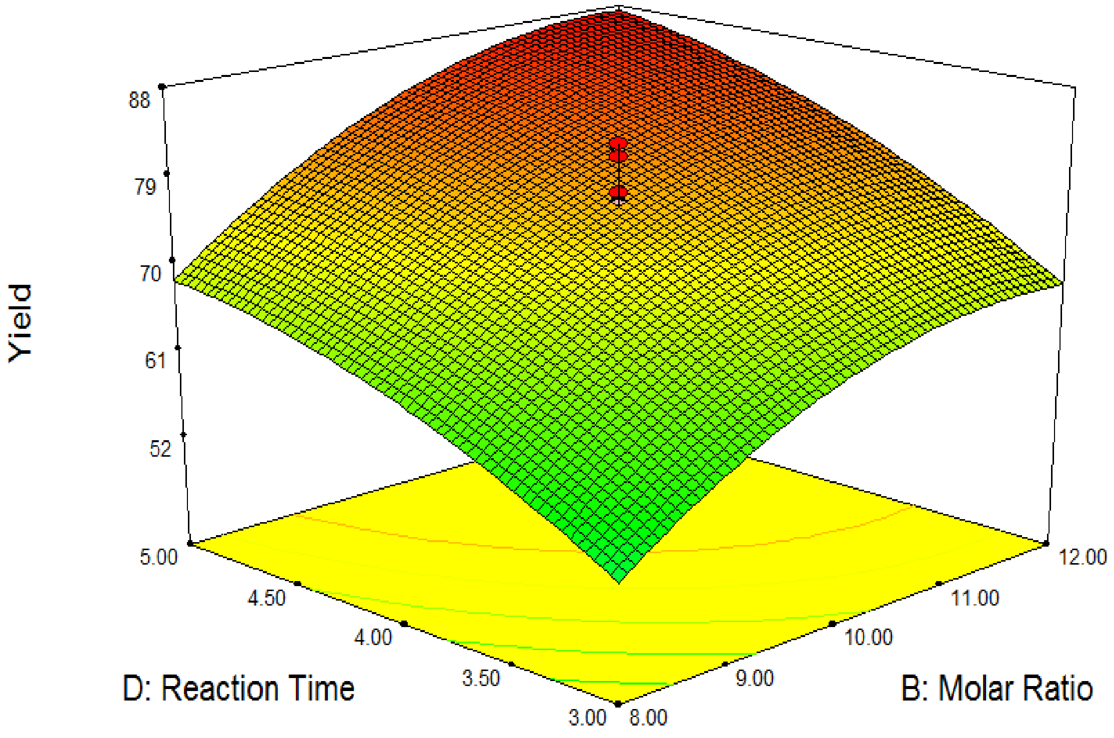


**Figure 4.10:** Interaction of molar ratio and reaction time toward biodiesel yield

Figure 4.10 illustrated the interaction of alcohol to oil molar ratio and reaction time toward the response of biodiesel yield. The highest biodiesel yield in Figure 4.10 was found at 6 hours of reaction time with alcohol to oil molar ratio of 10:1, which is induce the biodiesel yield at 88.3%. As mentioned previously, the increasing of molar ratio will increase the biodiesel yield. Same goes to reaction time. The increasing of reaction time will leads to the increasing of biodiesel yield. However, the further increase in reaction time can leads toward the decreasing of biodiesel yield due to the favourable of soap formation in the reaction process.

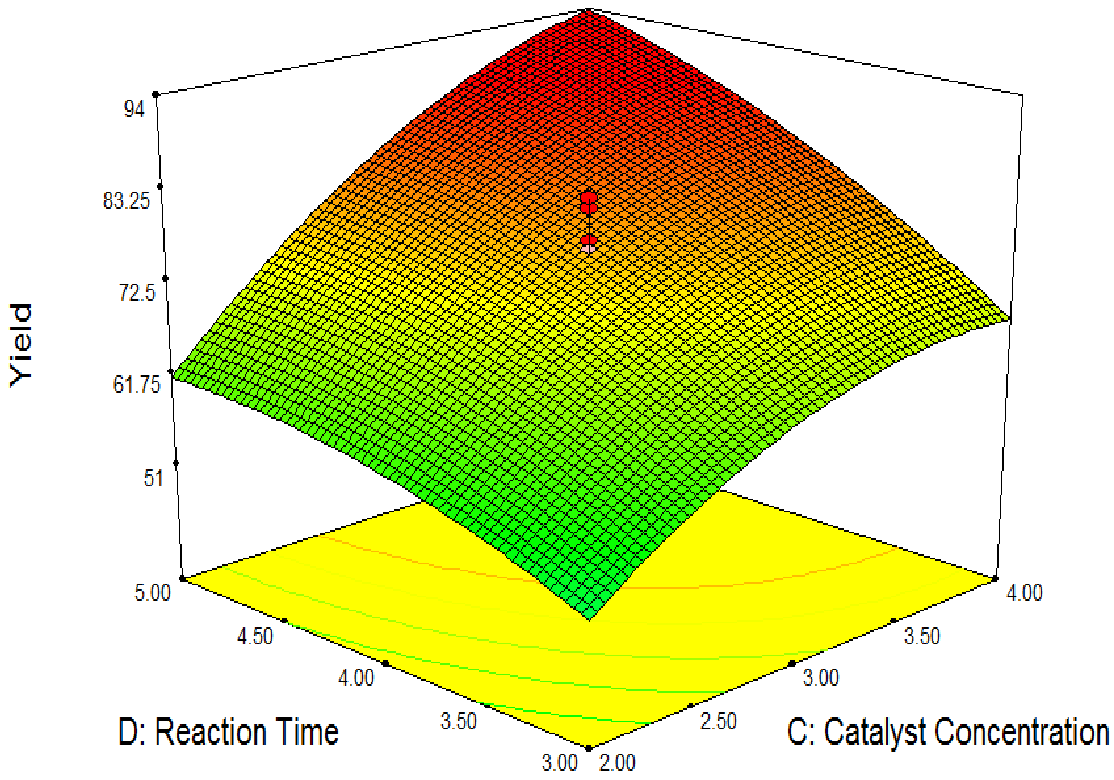


**Figure 4.11:** Interaction of catalyst concentration and reaction time toward biodiesel yield

Figure 4.11 illustrated the relationship between the catalyst concentration and reaction time toward the response of biodiesel yield. The highest biodiesel yield in Figure 4.11 was found at 6 hours of reaction time with 3% of catalyst concentration that induce the biodiesel yield at 88.3%. As mentioned previously, the increasing of reaction time will leads to the increasing of biodiesel yield. However, the further increase in reaction time can leads toward the decreasing of biodiesel yield. Same goes to catalyst concentration. The increasing of catalyst concentration will increase the biodiesel yield until it reached at optimal levels and then, the biodiesel yield tends to decrease with the further increasing in catalyst concentration due to the formation of soap in the reaction process of tranesterification.

## 4.7 VALIDATION OF DATA

In order to validate the adequate of the model equation (4.1), the total three verifications of experiments for biodiesel production were carried out under several of reaction process conditions as shown in Table 4.6. The verification of the results was achieved by carrying out the experiments under optimal conditions at temperature of 70°C, 4% of catalyst concentration, alcohol to oil molar ratio of 11:1 and 5 hours of reaction time.

**Table 4.6:** Validation of data and models constructed for biodiesel production

| **Run** | **Parameters** | | | | **Yield (%)** | | |
|---|---|---|---|---|---|---|---|
| | **Temperature (°C)** | **Catalyst Concentration (%)** | **Molar Ratio** | **Reaction Time (h)** | **Actual** | **Predicted** | **Error** |
| 1 | 70 | 4 | 11 | 5 | 90.82 | 89.43 | 0.016 |
| 2 | 70 | 4 | 11 | 5 | 88.54 | 89.43 | 0.010 |
| 3 | 70 | 4 | 11 | 5 | 89.78 | 89.43 | 0.004 |

The optimum condition of the biodiesel yield was constructed by the RSM. Table 4.7 shows the optimum condition that designed by RSM.

From 47 solutions constructed by the RSM, the selected condition with the highest biodiesel yield can be obtained from the condition at temperature of 72.83°C, alcohol to oil molar ratio of 9.50, catalyst concentration of 3.95% and 4.73 hours of reaction time.

**Table 4.7:** Optimum condition design by the response surface methodology (RSM)

| **constrains** | | **Lower Limit** | **Upper Limit** | **Lower Weight** | **Upper Weight** | **Importance** |
|---|---|---|---|---|---|---|
| **Name** | **Goal** | | | | | |
| Reaction Temperature | Is in range | 60.0 | 80.0 | 1 | 1 | 3 |
| Molar Ratio | Is in range | 8.0 | 12.0 | 1 | 1 | 3 |
| Catalyst Concentration | Is in range | 2.0 | 4.0 | 1 | 1 | 3 |
| Reaction Time | Is in range | 3.0 | 5.0 | 1 | 1 | 3 |
| Yield | Maximize | 22.2 | 88.3 | 1 | 1 | 3 |
| **Solution Number** | **Reaction Temperature (°C)** | **Molar Ratio** | **Cat. Conc. (%)** | **Reaction Time (h)** | **Yield (%)** | **Desirability** |
| 1 | 72.83 | 9.50 | 3.95 | 4.73 | 88.8391 | 1 (Selected) |
| 2 | 75.09 | 11.21 | 3.34 | 4.84 | 90.4748 | 1 |
| 3 | 67.38 | 10.96 | 3.78 | 4.44 | 89.4185 | 1 |
| 4 | 69.76 | 9.52 | 3.86 | 4.85 | 89.6152 | 1 |
| 5 | 70.57 | 10.05 | 3.45 | 4.78 | 88.5697 | 1 |
| 6 | 68.27 | 11.67 | 3.34 | 4.85 | 89.9445 | 1 |
| 7 | 73.11 | 10.99 | 3.67 | 4.64 | 92.3116 | 1 |
| 8 | 68.44 | 11.92 | 3.87 | 4.18 | 88.3831 | 1 |
| 9 | 77.08 | 11.43 | 3.44 | 4.69 | 88.7512 | 1 |
| 10 | 67.50 | 10.00 | 3.91 | 4.83 | 90.6334 | 1 |

# CHAPTER 5

# CONCLUSION

## 5.1 CONCLUSION

As a conclusion, this study of optimization of biodiesel production from cooking oil palm oil based by using design of experiments (DoE) has successful achieved its objective requirement. The objective of this study is to optimize the biodiesel production by using design of experiments (DoE) with usage of different parameters that mainly affect the biodiesel yield.

Based on the design model, the best range value for temperature of 72.83°C, alcohol to oil molar ratio of 9.5:1, 3.95% of catalyst concentration and 4.73 hours of reaction time in order to obtain highest biodiesel yield. These ranges of data were obtained from the point prediction by using response surface methodology (RSM). Design of experiment is act as tool in order to provide the framework for the unravelling complex relationships between a response and multiple factors.

## 5.2 RECOMMENDATIONS

In order to establish the data error and to minimize the percentage error of the design model, it is recommended to use mechanical stirrer instead of magnetic stirrer. This is due to improper mixing of reactants by usage of magnetic stirrer. The mixing of reactants is important because the reactants can fully reacts with each other so biodiesel yield can obtained at optimum values.

For the further studies, it is recommended to study the characterization of physical and chemical properties of biodiesel production. It is important to determine whether the yield that produced from the reaction process is content biodiesel or not. It is also can be used in future reference for further studies.

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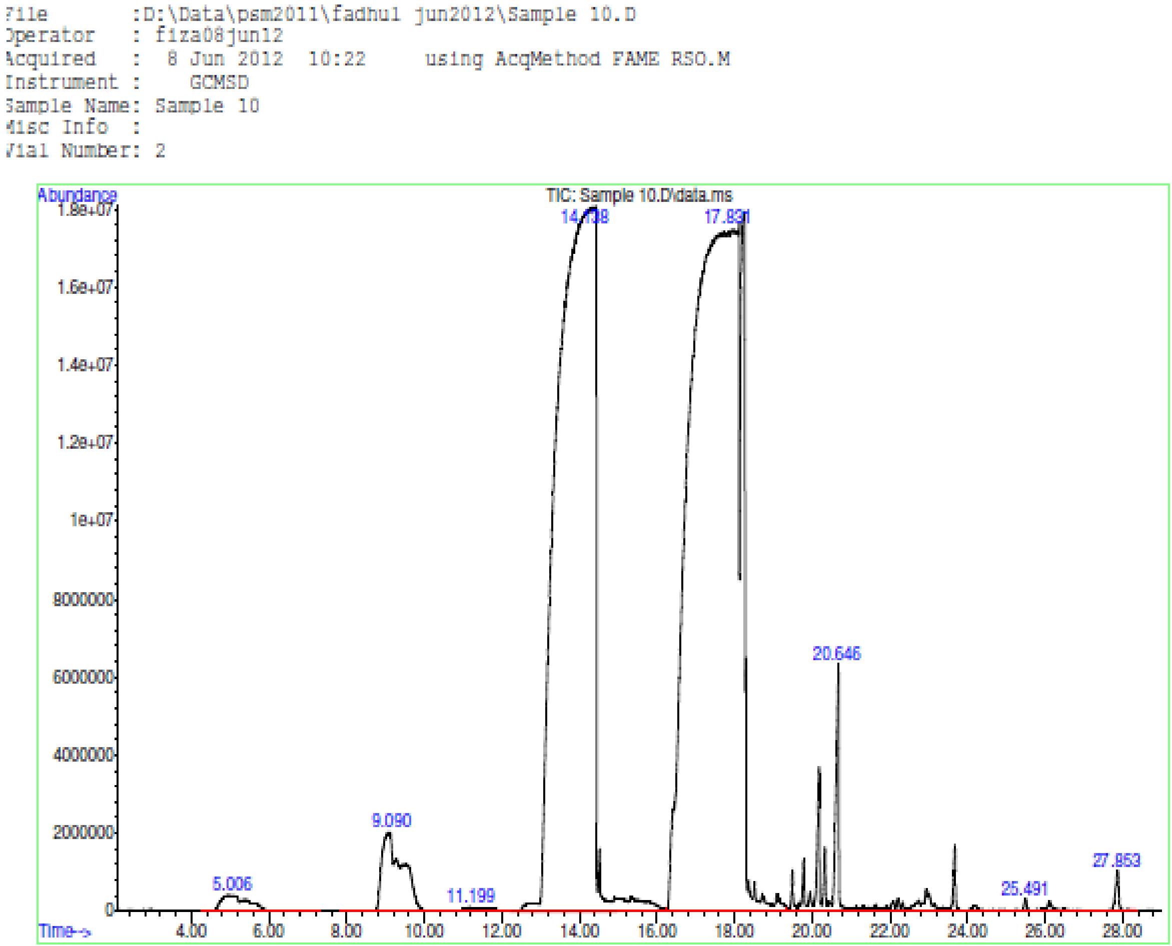
# APPENDIX A



```
ile         :D:\Data\psm2011\fadhul jun2012\Sample 10.D
perator    : fiza08jun12
cquired    :  8 Jun 2012  10:22     using AcqMethod FAME RSO.M
Instrument :    GCMSD
ample Name: Sample 10
isc Info  :
ial Number: 2
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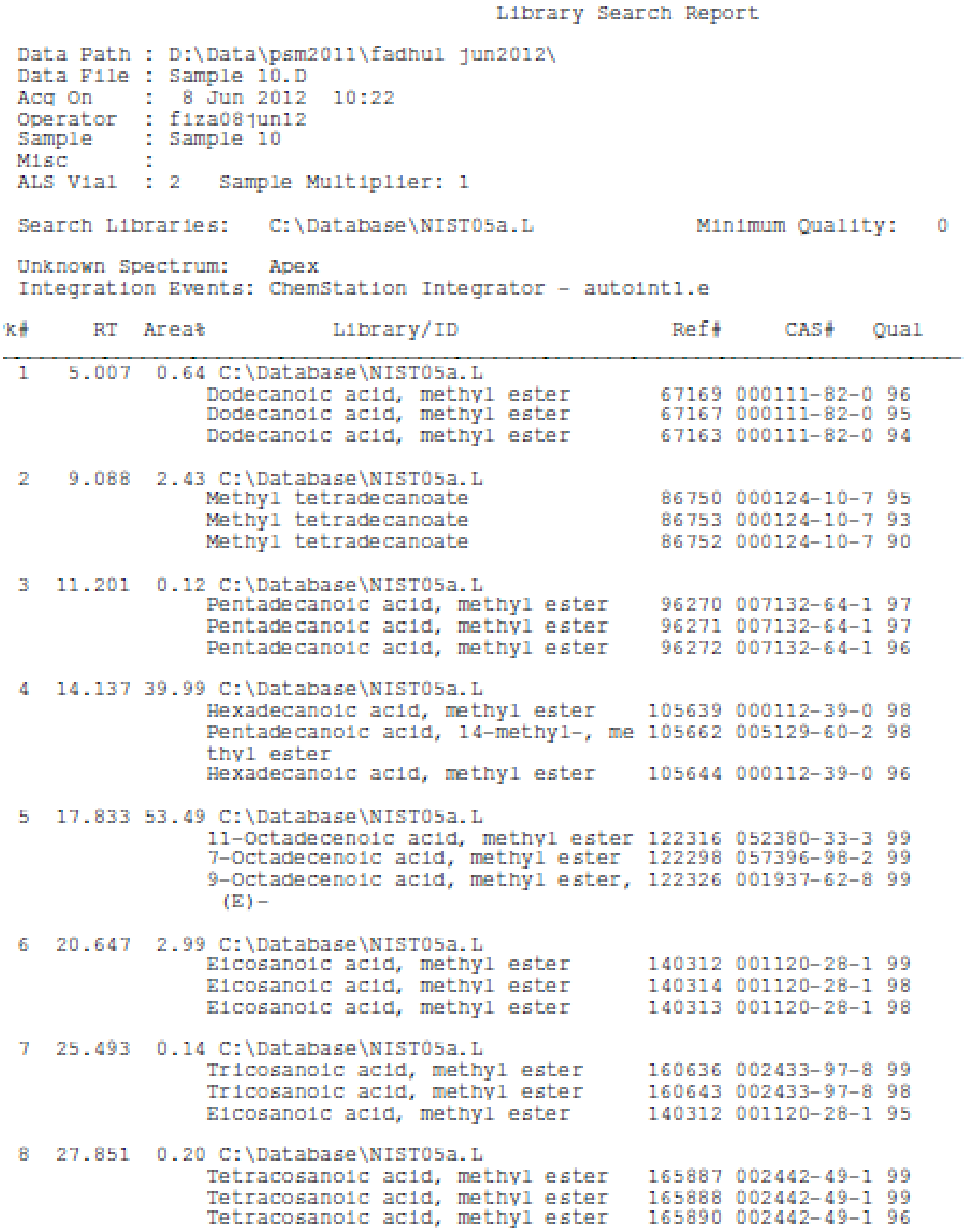
**Figure A.1:** Graph of FAME contents in biodiesel yield



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                                     Library Search Report

Data Path : D:\Data\psm2011\fadhul jun2012\
Data File : Sample 10.D
Acq On    :  8 Jun 2012  10:22
Operator  : fiza08jun12
Sample    : Sample 10
Misc      :
ALS Vial  : 2   Sample Multiplier: 1

Search Libraries:   C:\Database\NIST05a.L            Minimum Quality:   0

Unknown Spectrum:   Apex
Integration Events: ChemStation Integrator - autoint1.e

k#     RT  Area%          Library/ID                  Ref#     CAS#   Qual
_____________________________________________________________________________

 1   5.007  0.64 C:\Database\NIST05a.L
                    Dodecanoic acid, methyl ester       67169 000111-82-0 96
                    Dodecanoic acid, methyl ester       67167 000111-82-0 95
                    Dodecanoic acid, methyl ester       67163 000111-82-0 94

 2   9.088  2.43 C:\Database\NIST05a.L
                    Methyl tetradecanoate               86750 000124-10-7 95
                    Methyl tetradecanoate               86753 000124-10-7 93
                    Methyl tetradecanoate               86752 000124-10-7 90

 3  11.201  0.12 C:\Database\NIST05a.L
                    Pentadecanoic acid, methyl ester    96270 007132-64-1 97
                    Pentadecanoic acid, methyl ester    96271 007132-64-1 97
                    Pentadecanoic acid, methyl ester    96272 007132-64-1 96

 4  14.137 39.99 C:\Database\NIST05a.L
                    Hexadecanoic acid, methyl ester    105639 000112-39-0 98
                    Pentadecanoic acid, 14-methyl-, me 105662 005129-60-2 98
                    thyl ester
                    Hexadecanoic acid, methyl ester    105644 000112-39-0 96

 5  17.833 53.49 C:\Database\NIST05a.L
                    11-Octadecenoic acid, methyl ester 122316 052380-33-3 99
                    7-Octadecenoic acid, methyl ester  122298 057396-98-2 99
                    9-Octadecenoic acid, methyl ester, 122326 001937-62-8 99
                     (E)-

 6  20.647  2.99 C:\Database\NIST05a.L
                    Eicosanoic acid, methyl ester      140312 001120-28-1 99
                    Eicosanoic acid, methyl ester      140314 001120-28-1 98
                    Eicosanoic acid, methyl ester      140313 001120-28-1 98

 7  25.493  0.14 C:\Database\NIST05a.L
                    Tricosanoic acid, methyl ester     160636 002433-97-8 99
                    Tricosanoic acid, methyl ester     160643 002433-97-8 98
                    Eicosanoic acid, methyl ester      140312 001120-28-1 95

 8  27.851  0.20 C:\Database\NIST05a.L
                    Tetracosanoic acid, methyl ester   165887 002442-49-1 99
                    Tetracosanoic acid, methyl ester   165888 002442-49-1 99
                    Tetracosanoic acid, methyl ester   165890 002442-49-1 96
```

**Figure A.2:** Comparison of FAME contents with library database of NIST05a.L

**Table A.1:** The condition of the gas chromatography

| | |
|---|---|
| **Temperature column** | Initially held at 0°C for 3 min, then ramped to 120°C with 40°C/min (held for 3 min), and finally ramped up at 10°C/min to 250°C and maintained for 5 min. |
| **Injector and Detector temperature** | 250°C |
| **Injection size** | 1.0μL (10:1 split) |
| **Hydrogen flow** | 35mL/min |
| **Air flow** | 450mL/min |
| **Nitrogen make up** | 35mL/min |
| **Carrier gas** | Hydrogen, compressed air, $H_2$, $N_2$ |
| **Type of Column** | DB wax |