

**PRODUCTION OF BIODIESEL FROM BIO OIL
USING CATALYTIC REACTIVE DISTILLATION**

by

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CERTIFICATION OF APPROVAL

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(Assoc. Prof. Dr. Suzana Yusup)

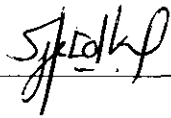
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CERTIFICATION OF ORIGINALITY

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 person



NOOR SYAHIDAH BINTI RAMLI

ABSTRACT

The advantages and the properties of biodiesel over the petroleum diesel with its conventional process are outlined. A novel process base on catalytic reactive distillation method with presence of metal oxides as heterogeneous catalyst is proposed to improve the performance of conventional method. Since bio-oil has poor volatility, high viscosity, coking and corrosiveness characteristic, it is suggested to upgrade the bio-oil. Biodiesel is one of the types for upgraded bio-oil that can be used as a green fuel. Esters from bio-oil can be converted into biodiesel through esterification / trans-esterification process by mixing bio-oil and alcohol together with presence of catalyst.

Conversion, yield and selectivity of biodiesel from bio-oil using reactive distillation approach are investigated. Selected reaction parameters were optimized, using Taguchi L9 Orthogonal Array method for design of experiments, to yield the lowest free fatty acid content in the final product. The investigated parameters include alcohol to bio-oil ratio, temperature and amount of catalyst. The effect and significance of each parameter were then studied and verified by additional experiments..

Optimum conditions for the reaction were established and effect of each variable was investigated. The optimum conditions for base transesterification which could reduce the free fatty acid content in the feedstock were at temperature of 90°C with butanol/bio-oil ratio of 3:1 and CaO at 2wt% (reactant basis). The conversion of butyl ester (biodiesel) was completed after 10 minutes with yield of 65.35% and the product quality was compared to the conventional petroleum diesel. Besides, conversion and yield produced between solid base catalyst (CaO) and acid catalyst (H₂SO₄) were also compared.

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ABBREVIATIONS AND NOMENCLATURE

BO	Bio-oil
Min	Minute
EFB	Empty fruit bunch
GCMS	Gas Chromatography Mass Spectrometer

CHAPTER 1

INTRODUCTION

1.1 Background

Biodiesel is one of the renewable energy that is currently high in demand. Biodiesel has several advantages over petroleum diesel. It is renewable, biodegradable, nontoxic, environmental friendly and has lower cost of production. It helps to reduce CO₂ emission which is a greenhouse gas that harmful to the earth. (Demirbas, 2010) state in his book of Algae energy that as an alternative fuel, biodiesel is better than petroleum diesel in terms of sulphur content, cetane number, flash point, aromatic content and its biodegradability as stated by (Demirbas A. D., 2010).

Biodiesel is known as monoalkyl, such as methyl and ethyl, ester of fatty acids (FAME) derived from a renewable lipid feedstock, such as vegetable oil or animal fat (Demirbas A. , 2009). Biodiesel from vegetable oil is no longer a new process in biodiesel industry. Corn oil, canola oil, soybean oil, sunflower oil, palm oil and rubber seed oil was introduced as source to produce biodiesel by (Mousdale, 2011) while cotton seed oil, algae oil, and coconut oil are examples of vegetables oil that has been used for biodiesel production as stated by (David M. Mousdale, 2011). Besides, base on study by (Caye M. Drapcho, 2008) poultry fat, lard and tallow are the examples of animal fat that can be used in biodiesel production where it was also stated by (Caye M. Drapcho, 2008) in their book.

Based on (Anton, Alexandre, & Gadi, 2007) nowadays, there are five major routes to produce biodiesel: 1. direct use and blending of straight vegetable oil, 2. use of microemulsions with short-chain alcohols, 3. thermal cracking (pyrolysis) of vegetable oils, 4. trans-esterification of tri-glycerides (TG) catalyzed by bases, acids or enzymes, 5. esterification of fatty acid with alcohols, using liquid (H₂SO₄) or solid acid catalysts. The conventional method for biodiesel production is trans-

esterification of glycerides, which are the main components of oils and fats used as materials, with a short chain of alcohol, usually methanol, in the presence of catalyst (Fernando, Vico-Ramirez, Juan, & Hernandez-Castro, 2011).

1.2 Problem Statement

Future energy shortage and environmental concern has boosted research alternative on renewable energy. Bio-oil (BO) from biomass is one of the alternatives that can be used as renewable energy in the future. However, as mention by (Mahmud, 2010), poor volatility, high viscosity, coking and corrosiveness of crude bio-oil have limited its applicability. So, bio-oil upgrading technologies have been proposed to improve the properties and to increase the range of possible applications.

Conventional method to produce biodiesel normally used homogenous base catalyst like Sodium Hydroxide (NaOH) and Potassium Hydroxide (KOH) for trans-esterification. Based on (Anton A. Kiss, 2007), reaction between free fatty acid (FFA) in oil with base homogenous catalyst will lead to formation of soap. This soap makes separation of biodiesel from glycerol more difficult. This situation leads to multi-step separation that reduce yield of biodiesel, thus making biodiesel as a costly alternative fuel as studied by (Suthan Turapan et. al, 2010).

In order to solve this problem, a sustainable esterification or trans-esterification process based on catalytic reactive distillation is investigated in order to convert bio-oil to biodiesel. Reactive distillation is a promising method especially for equilibrium limited and consecutive reactions. Since homogenous catalyst cannot be recovered, cannot be reuse, expensive and require neutralization as stated in the comparative study by (B. Viswanathan and A.V Ramasvamy, 2008) so it is recommended to use heterogeneous catalyst with reactive distillation method. By using metal oxides catalyst as heterogeneous catalyst in an integrated reactive distillation method, it is able to shift the chemical equilibrium to completion and preserve the catalyst activity by continuously removing the products (Anton, Alexandre, & Gadi, 2007).

1.3 Objective

1. To verify biodiesel production from bio-oil using catalytic reactive distillation with presence of metal oxide as catalyst.
2. To study the conversion, yield and selectivity of biodiesel using reactive distillation approach with presence of heterogeneous solid catalyst.
3. To compare biodiesel conversion between solid base catalyst (CaO) with acid catalyst (H₂SO₄).
4. To compare properties of biodiesel produced with conventional petroleum diesel

1.4 Scope of Study

As outline in the objectives, the main aim of this project is to produce biodiesel from bio-oil using catalytic reactive distillation method. Process involve during the conversion of bio-oil into ester is trans-esterification with the presence of base catalyst. Base on the literature review, metal oxides (heterogeneous catalyst) will be used in this project as it improves yield production compared to homogeneous catalyst. The experiment will be conducted several times using Taguchi L9 Orthogonal Array computed by design of experiment software in order to analyze conversion, yield and selectivity of the biodiesel produced. The production of biodiesel will then be analyzed by GCMS to identify the component and percentage of the component. Three parameters involve with the experiment are temperature, alcohol to bio-oil ratio and weight percentage of catalyst. Besides, comparative studies between biodiesel produced using solid base catalyst (CaO) and acid catalyst (H₂SO₄) will be analyzed. Next, biodiesel produced from the experiment will be compared with the commercial petroleum diesel to observe the fuel properties.

1.5 Significant of the Project

Since Malaysia is a large producer of oil palm waste, it is beneficial to produce biodiesel from bio-oil generated from EFB because of the feed stock availability. Besides, it helps to improve Malaysia's economy from research and development aspect. From technical point of view, this novel method helps to improve conventional method throughout biodiesel production. It helps the conversion of bio-oil to biodiesel as it equilibrium will go to the product side. Therefore time can be saved and greater yield can be obtained. Besides, it also saves time and money because of the availability and criteria for catalyst is met.

CHAPTER 2

LITERATURE REVIEW

Biomass is one of the promising renewable energy sources, and is utilized as solid, liquid and gas fuels. Especially, lignocellulosic biomass wastes are attracting interest worldwide, because of its non edible characteristic. (Suzana Y et.al, 2009) states that availability of oil palm wastes in Malaysia is the best among biomass wastes. Since the availability of biomass in Malaysia is high, so it is beneficial if this type of waste can be converted into valuable energy for future generations.

2.1 Biodiesel

Basically, biodiesel was produced by using trans-esterification or esterification of free fatty acid. Basic process of trans-esterification and esterification was shown in Figure 2.1 below.

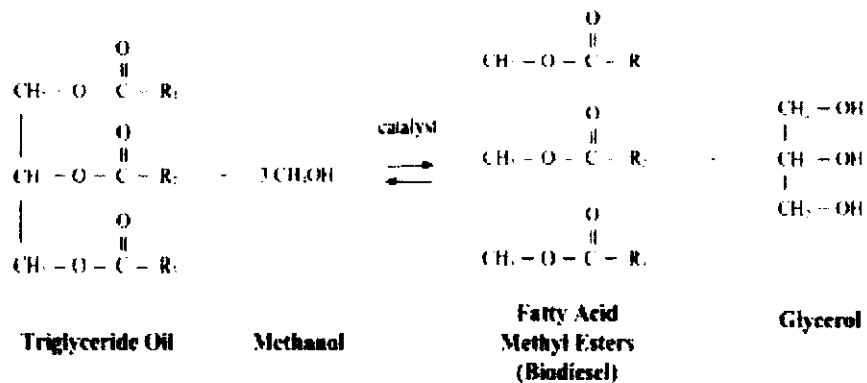


Figure 2.1 : Trans-esterification Process

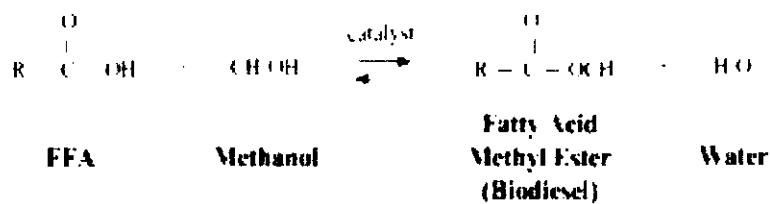


Figure 2.2 : Esterification Process

Free fatty acid was converted into ester and glycerol with presence of alcohol and catalyst for transesterification process while the end products of esterification process after the reaction were water and ester. (Anton A. Kiss, 2007) reported that biodiesel has many advantages over the petroleum diesel as it has higher cetane number and also higher flash point mean it has better and safer performance. Even though biodiesel was a renewable fuel and it has many advantages over the petroleum diesel, (Anton A. Kiss) mentioned that it has one big disadvantage which was NO_x emission. This NO_x emission was related to the density of biodiesel.

fuel property	diesel	biodiesel
fuel standard	ASTM D975	ASTM D6751
fuel composition	C ₁₀ –C ₂₁ HC ^a	C ₁₂ –C ₂₂ FAME ^a
kinetic viscosity, mm ² /s (at 40 °C)	1.3–4.1	1.9–6.0
specific gravity, kg/L	0.85	0.88
boiling point, °C	188–343	182–338
flash point, °C	60–80	100–170
cloud point, °C	–15 to 5	–3 to 12
pour point, °C	–35 to –15	–15 to 10
cetane number (ignition quality)	40–55	48–65
stoichiometric air/fuel ratio (AFR)	15	13.8
life-cycle energy balance (energy units produced per unit energy consumed)	0.83/1	3.2/1

^a HC, hydrocarbons; FAME, fatty acid methyl esters.

Figure 2.3: Petroleum Diesel and Biodiesel Comparison

Source: Biodiesel by Catalytic Reactive Distillation Powered by Metal Oxides
(Anton A. Kiss, 2008)

In (Demirbas, 2005) book entitled A Biodiesel Production for Vegetables Oils via Catalytic and Non Catalytic Supercritical Methanol Trans-esterification Method, he reported that most of the biodiesel currently being produced is mainly dependent on edible oil sources like soybean oil and palm oil where it leads to competition with

cooking oil industry. It might give effect to cooking oil price in the future as biodiesel was generated from edible oil. Therefore, biodiesel was suggested to be produced from non-edible oil like bio-oil to prevent insufficient stock of edible oil.

2.2 Bio-oil

Bio oil was produced through pyrolysis process where biomass from agricultural product was converted into oil. Electricity and heat can be generated from biomass and it was an attractive alternative of renewable energy source. Using biomass feedstock such as wood, the pyrolysis process results in “net zero” carbon dioxide emissions and no sulphoxide emissions. Like petroleum oil, bio-oil can be refined and molded into a wide variety of fuels and chemicals.

Bio oil was dark brown, free flowing liquids, with an acid or smoky odour. They were complex mixtures of compounds derived from the depolymerisation of cellulose, hemicelluloses and lignin. Chemically, they have high water content, more or less solid particles and hundreds of organic compounds that belong to acids, alcohols, ketones, aldehydes, phenols, ethers, esters, sugars, furans, nitrogen compounds and multifunctional compounds (Mohan,2006).The main acid content inside Bio oil was acetic acid. Alkyl acetate was produced from reaction of acetic acid and alcohol. Below is the figure showing organic compound of artificial bio-oil.

No	Organic Group	Chemical	Wt%	Density (g/cm ³)
1	Carboxylic Acid	Acetic Acid	26.54	1.0490
2	Ketone	Ethyl Methyl Ketone	23.63	0.8050
3	Phenol	Phenol	16.98	1.0700
4	Ester	Methyl acetate	7.17	0.9320
5	Furan	Tetrahydro-Furan	6.31	0.8892
6	Alcohol	Methanol	5.55	0.7918
7	Aldehydes	2-Furaldehyde	5.12	1.1600
8	Water	Water	8.7	1.0000

Figure 2.4: Artificial Bio-Oil Compound

Source: GC analysis of artificial bio oil for FYP entitled biodiesel

(Mohemed Afiq Ramli, 2010)

2.3 Catalytic Reactive Distillation

Reactive distillation is a combination of reaction and distillation within one unit operation. This combination provides advantages over the conventional, sequences process. As mention by (Sven & Jurgen, 2003) the most important equilibrium limited reactions that are suitable for reactive distillation are esterification, esterhydrolysis reactions, trans-esterification, and etherifications. Both esterification and trans-esterification are a process of producing ester with different by-product. Esterfication leads to formation of water while trans-esterification leads to formation of glycerol. Etherification is a process of forming ether from alcohol while esterhydrolysis is a process where hydrolysis of ester involves hydroxide ions.

A reactive distillation includes a distillation column, flashers, strippers and condensers. Based on (Arvnder, 2004) the main objective of reactive distillation is to dramatically reduce the use of excess alcohol in the feeding steam, which reduces the cost in downstream alcohol recover processes, and meanwhile maintain a high alcohol-to-oil molar ratio inside of the RD reactor, which ensures the completion of the esterification of bio-oil to bio-diesel.

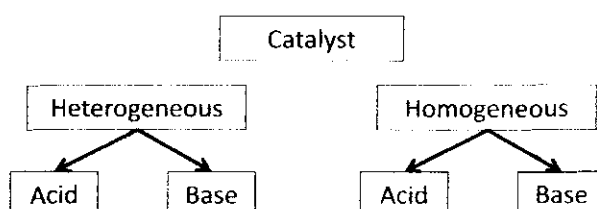
The combination (reactor and distillation) is advantages as when the rate of chemical is decreased by the reaction equilibrium resulting into poor yield, selectivity and conversion. (Chee, 2009) mentioned that combination of separation process within the reactor induces better reaction products removal from the reaction zone thus improving the overall yield, selectivity and conversion compared to a conventional process

There are several parameters that affect performance of the esterification / trans-esterification process such as molar ratio alcohol:vegetable oil, type and quantity of

catalyst, reaction time, reaction temperature and even feed stock properties and mixer identities. Normally, excess alcohol is needed to drive the reaction equilibrium to the product side and this excess alcohol must be recovered in order to reutilize and purify the biodiesel. So, reactive distillation may be advantageous for liquid-phase reaction systems when the reaction must be carried out with large excess of one or more of the reactants, when a reaction can be driven to completion by removal of one or more of the products as they are formed or when product recovery or by-product recycle scheme is complicated or made infeasible by azeotrope formation (Santandera, 2010).

2.4 Catalyst

Catalyst is a substance that speeds up the chemical reaction without reacting with the chemicals. Since catalyst is not consumed by the chemical reaction, hence it can be recovered unchanged at the end of the reaction. The catalyst efficiency depends on several factors such as specific surface area, pore size, pore volume and active concentration (Smith and Notheisz, 2006). Besides, catalyst performance is depending upon concentration of basic sites on the surface of the catalyst. Supporting of the alkali metal compound on a large surface area is an interesting option for decreasing the amount of catalyst required to obtain similar level of catalytic activity (A.A Refaat, 2011). Catalyst can be divided into two categories which are homogeneous and heterogeneous catalyst. Both categories have two sub categories which are acid catalyst or base catalyst. Each type of the catalyst has its own advantages over the other. For this project, we will focus only on heterogeneous catalyst as a catalyst used in reactive distillation method. Therefore, for the experiment purposes, metal oxides (CaO) are chosen as a catalyst.



2.4.1 Heterogeneous Catalyst

Even though heterogeneous catalyst just has moderate conversion of reaction rate, but it can be recovered after the treatment, possible to be use in continuous fix bed operation, not sensitive to water and free fatty acid, possible to reuse the catalyst and potentially cheaper compared to homogeneous catalyst as studied by (B.Viswanathan et.al, 2008) .[^{vi}] Heterogeneous catalyst is thus considered to be a green process. The process requires neither catalyst recovery nor aqueous treatment steps: the purification steps of products are then much more simplified and very high yields of methyl esters, close to theoretical value are obtained as reported by (Cao, et al., 2008) .

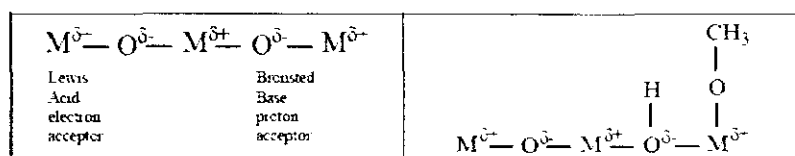


Figure 2.5 Surface Structure of Metal Oxides (G. Jorckendoff and Niemantsverdriet, 2003)

Source: Biodiesel Production using Solid Metal Oxide Catalyst (A.A Refaat, 2011)

The structure of metals oxides is made up of positive metals ions (cations) which posses Lewis acidity, i.e they behave as electron acceptors, and negative oxygen ions (anions) which behave as proton acceptors and thus Bronsted bases.

There are recent studies on metal oxides as heterogeneous catalyst. These include alkali earth metal oxides, transition metal oxides, mixed metals oxides and supported metal oxides. The structure of metal oxides is made up of positive metal ions (cations) which possess Lewis acidity, i.e they behave as electron acceptors, and negative oxygen ions (anions) which behave as proton acceptors and are thus Bronsted bases (Refaat, 2011).

Table 2.1: Summary of Past Project about Metal Oxides Catalyst (CaO)

References	Findings	Analysis
Liu et al, 2008	Small amounts of water can improve the catalytic activity of CaO and biodiesel yields because in the presence of water O^{2-} on the surface of the catalyst extracts H^+ from water molecules to form OH^- which subsequently extracts H^+ of methanol to form methoxides anions, which are the real catalyst of the trans-esterification reaction Calcium methoxide has strong basicity and high catalytic activity as a heterogeneous solid base catalyst and 98% biodiesel yield was obtained within 2hour. The order of reactivity $Ca(OH)_2 < CaO < Ca(CH_3O)_2$.	Small amounts of water can improve catalytic activity of CaO. Reactivity of metal oxides follows Lewis basic theory
Dossin et. Al, 2006	Too much water (more than 2.8% by weight of oil) is added to methanol, the fatty acid methyl ester will hydrolyze under basic conditions to generate fatty acids, which can react with CaO to form soap.	Water more than 2.8% by weight of oil leads to formation of soap
Lee et al. 2009	Calcium oxide is the metal oxides catalyst that most frequently applied for biodiesel synthesis, probably due to its cheap price, minor toxicity and high availability	CaO is high availability
A.A Refaat	The activities of the catalyst CaO and ZnO appeared to be enhanced with the addition of MgO.	Activities of CaO can be enhanced by addition of MgO

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

Before the experiment took place, research was done to ensure the smoothness of the project. Below was the research methodology for this project.

1st Stage: Project Planning Phase

Problem identification base on current issue with the significance of the project was determined. Possible techniques to improve the problem identified were outlined. Since biodiesel conversion from bio-oil needs alcohol and catalyst in the reaction, type of alcohol and catalyst used was identified.

2nd Stage: Characterization of BO and Catalyst Phase

For the characterization of BO and catalyst used, literature review was conducted. Catalyst types and characteristic was identified. Comparable studies between the type and characteristic of the catalyst was conducted. Besides, BO characterization and component of the BO was analyzed base on literature review at first.

3rd Stage: Screening and Identification Phase

Suitable catalyst used for biodiesel conversion was identified with suitable condition for experimental purposes. Basis for the selection criteria were outlined with the explanation of the catalyst chosen. Either actual bio-oil was used for the experiment..

4th Stage: Experiment Design

Equipment setup for experimental purposes was identified. Decision on the equipments and chemicals involved for the project with clear view of procedures was conducted. Equipments were identified specifically for analyzing product and chemical purposes.

5th Stage: Comparative Study

Comparative studies of conversion, selectivity and yield of biodiesel were conducted base on experimental data. These data were then analyzed and interpreted into a table foe clear information. Result was evaluated based on conceptual understanding and practicality.

3.2 Flow Chart of Experimental Procedure

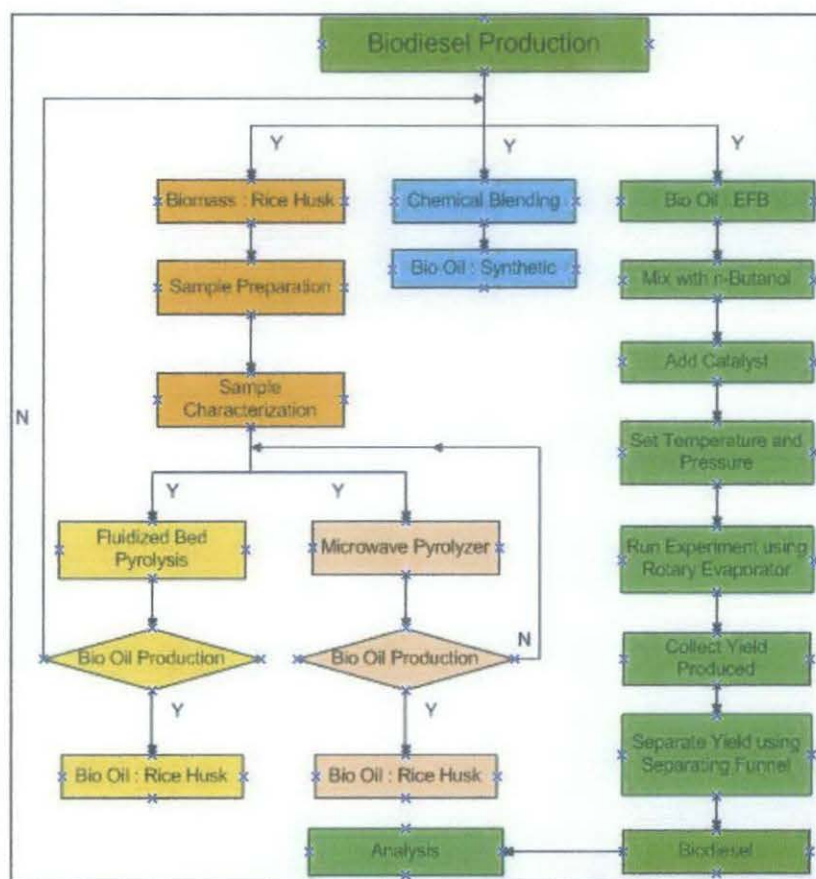


Figure 3.1: Flow Chart of Experimental Procedure

At first, bio-oil production from rice husk was conducted in order to obtain bio-oil for biodiesel production. Since the bio-oil produced by pyrolysis system was too watery, the bio-oil was neglected and the other source of bio-oil was found. Synthetic bio-oil derived from the chemical mixture was conducted to obtain bio-oil. After that, the bio-oil from EFB was arrived, and that bio-oil was used for experimental purposes.

3.3 Procedure for Esterification/Trans-esterification Process by Catalytic Reactive Distillation

1. Bio-oil and alcohol (n-butanol) was mixed based on alcohol to bio-oil ratio into the reactor vessel.
2. Catalyst was added to the mixture of butanol and bio-oil based on the experimental design of Taguchi.
3. The mixture then heated to desired temperature.
4. The experiment was conducted until the reactant in the reactor vessel finished.
5. The experiment time was started immediately after the rotary evaporator was turned on and achieved the desired condition for the experiment needed.
6. Reaction time of the experiment was started when there was a formation of first drop of distillate in condenser.
7. Procedures 91-60 was repeated with different conditions of variables based on Taguchi L9 Orthogonal Array.
8. Yield produced from the reaction was separated into water rich phase and ester rich phase.
9. Water rich phase and ester rich phase was weighed for analysis purposes.
10. The data obtained from the experiment was then compared with experiment that used acid catalyst.

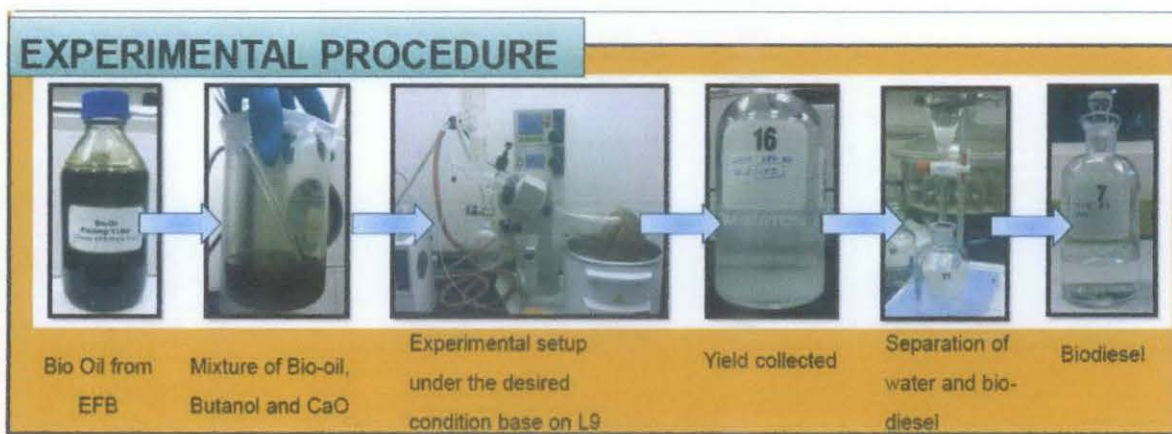


Figure 3.2: Experimental Procedure

3.4 Details on Experiment Design

3.4.1 Design of Experiment base on Taguchi L9 Orthogonal Array

Table 3.1: L9 Orthogonal Array

Trial No.	Factor 1 A: Alcohol: Bio-oil	Factor 2 B: Temperature °C	Factor 3 D: Catalyst, wt%
# 1	1 : 1	90	6
# 2	2 : 1	90	4
# 3	3 : 1	90	2
# 4	1 : 1	50	2
# 5	3 : 1	50	4
# 6	2 : 1	70	2
# 7	3 : 1	70	6
# 8	1 : 1	70	4
# 9	2 : 1	50	6

L9 Orthogonal Array that has been developed using design of expert was used for experimental purposes. Total of experiments needed to achieve the objectives outlined are nine. These nine experiments base on Taguchi method was help in analyzing the data and parameters that affect the biodiesel production. Relationship between the variables was established using design of expert software and analysis was conducted for each parameter.

3.5 Characterization and Properties Measurement

In order to obtain data for bio-oil, biodiesel and petroleum diesel properties, the characterization analysis was conducted. Properties that have been analyzed throughout the experiment were:

1. Density
2. Specific Gravity
3. Calorific Value
4. pH
5. Pour Point
6. GCMS

3.6 Equipments and Materials for Experiments

3.6.1 Equipments

1. Rotary evaporator (consist of water bath as temperature controller, vacuum pump and distillation column).
2. Three-neck round bottom glass flask (250ml) equipped with:
 - i. Magnetic stirrer
 - ii. Thermometer
 - iii. Water bath
 - iv. Refrigerator
 - v. Personal protective equipment (PPE)
3. Gas chromatography mass spectrometer
4. pH meter
5. ISL's automated Mini Cloud & Pour Point Analyzer MPP5G's
6. Bomb Calorimeter
7. Liquid Density Meter

3.6.2 Materials

1. Alcohol, (n-butanol)
2. Bio-oil
3. Metal oxide : CaO

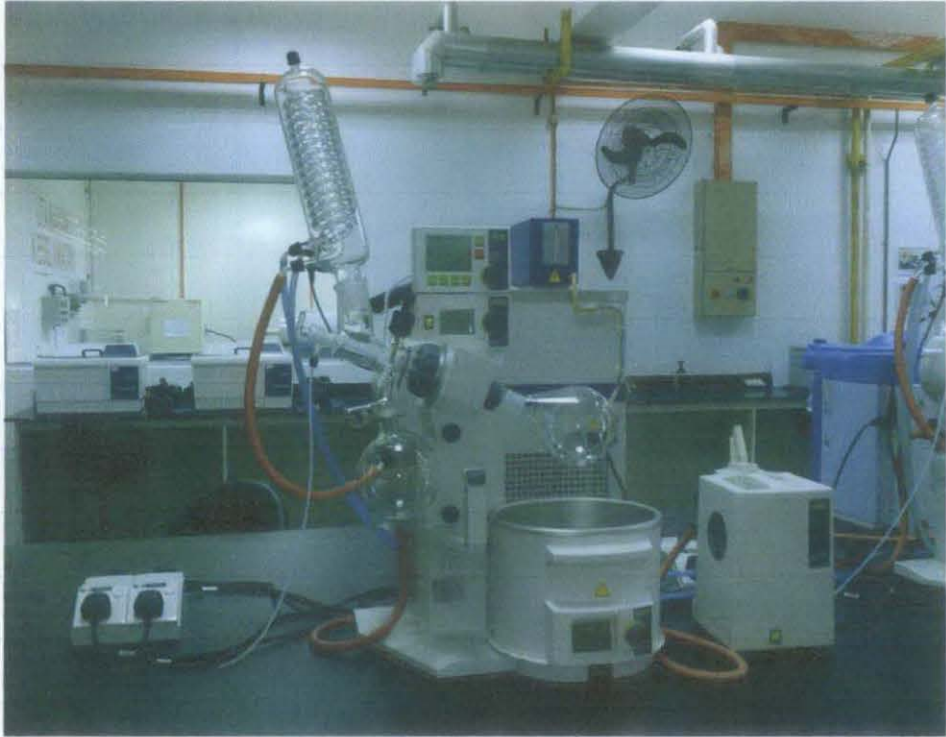


Figure 3.3: Equipment Rotary Evaporator

CHAPTER 4

RESULT AND DISCUSSION

4.1 Biodiesel Production Base on Taguchi (L9) Orthogonal Array

Table 4.1: Base Transesterification Reaction Variables

Trial No.	Factor 1 A: Alcohol: Bio-oil	Factor 2 B: Temperature °C	Factor 3 D: Catalyst, wt%	Biodiesel, wt%
# 1	1 : 1	90	6	34.32
# 2	2 : 1	90	4	44.47
# 3	3 : 1	90	2	65.35
# 4	1 : 1	50	2	16.12
# 5	3 : 1	50	4	13.97
# 6	2 : 1	70	2	35.41
# 7	3 : 1	70	6	32.93
# 8	1 : 1	70	4	20.62
# 9	2 : 1	50	6	10.57

Table 4.2: Conversion, Selectivity and Yield of Ester and Water Rich Phase

Trial No.	Total feed		Conversion		Selectivity				Yield	
	A		B+C		B		C		B	C
	weight (g)	wt%	weight (g)	wt%	weight (g)	wt%	weight (g)	wt%	wt%	wt%
#1	56.21	100	32.73	58.23	19.29	58.94	13.44	41.06	34.32	23.91
#2	79.96	100	46.75	58.47	35.56	76.06	11.19	23.94	44.47	13.99
#3	102.74	100	76.34	74.30	67.14	87.95	9.20	12.05	65.35	8.95
#4	53.97	100	17.15	31.78	8.70	50.73	8.45	49.27	16.12	15.66
#5	104.89	100	26.64	25.40	14.65	54.99	11.99	45.01	13.97	11.43
#6	78.36	100	42.15	53.79	27.75	65.84	14.40	34.16	35.41	18.38
#7	107.12	100	49.26	45.99	35.27	71.60	13.99	28.40	32.93	13.06
#8	55.09	100	22.63	41.08	11.36	50.20	11.27	49.80	20.62	20.46
#9	81.66	100	18.09	22.15	8.63	47.71	9.46	52.29	10.57	11.58

*A = Mixture of Bio-oil, alcohol (n-butanol) and catalyst (CaO)

*B = Biodiesel (Ester Rich Phase)

*C = Water Rich Phase

Results of the test conducted base on the design of experiment (DOE) L9 Orthogonal Array are shown in Table 4.1 above. Ester and water rich phase has been analyzed base on the conversion, selection and yield after the reaction occurred. The conversion, selectivity and yield produced were calculated base on the formula below:

$$\text{Conversion} = \frac{\text{Total Weight of B + C}}{\text{Total Weight of Feed (A)}} \times 100$$

$$\text{Selectivity} = \frac{\text{Total Weight of B}}{\text{Total Weight of Conversion (B + C)}} \times 100$$

$$\text{Yield} = \frac{\text{Percentage of Conversion (B)} \times \text{Percentage of Selectivity (B)}}{100}$$

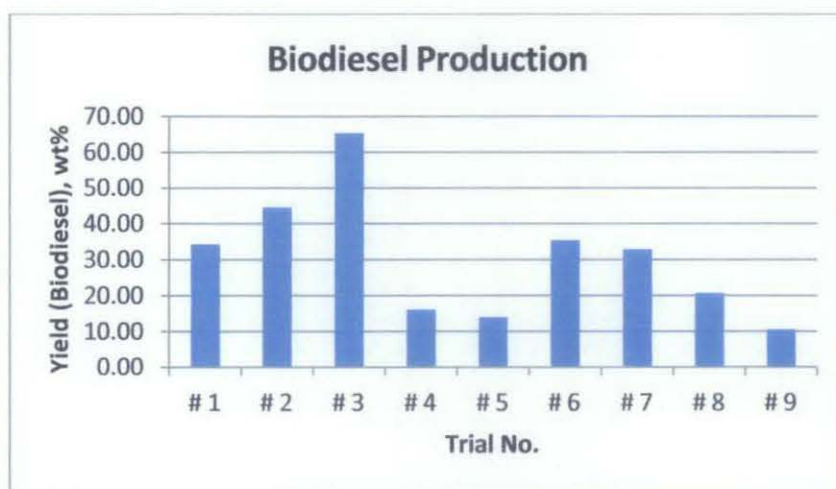


Figure 4.1: Biodiesel Production in wt%

From the data obtained in Table 4.1, run number #3 shown the highest production of ester rich phase. The optimum condition for base esterification was determined by running the reaction at constant mixing rate of 35rpm, ratio 1:3 of bio-oil: alcohol, temperature at 90°C and at 2wt% of catalyst as shown in Figure 4.1 above. Percentage of ester rich phase obtained at run number #3 was 65.35% which was the highest production of ester compared to the other runs while percentage of ester rich phase obtained at run number #9 was the lowest production.

4.1.2 Effect of Bio-oil : Alcohol Ratio and Temperature

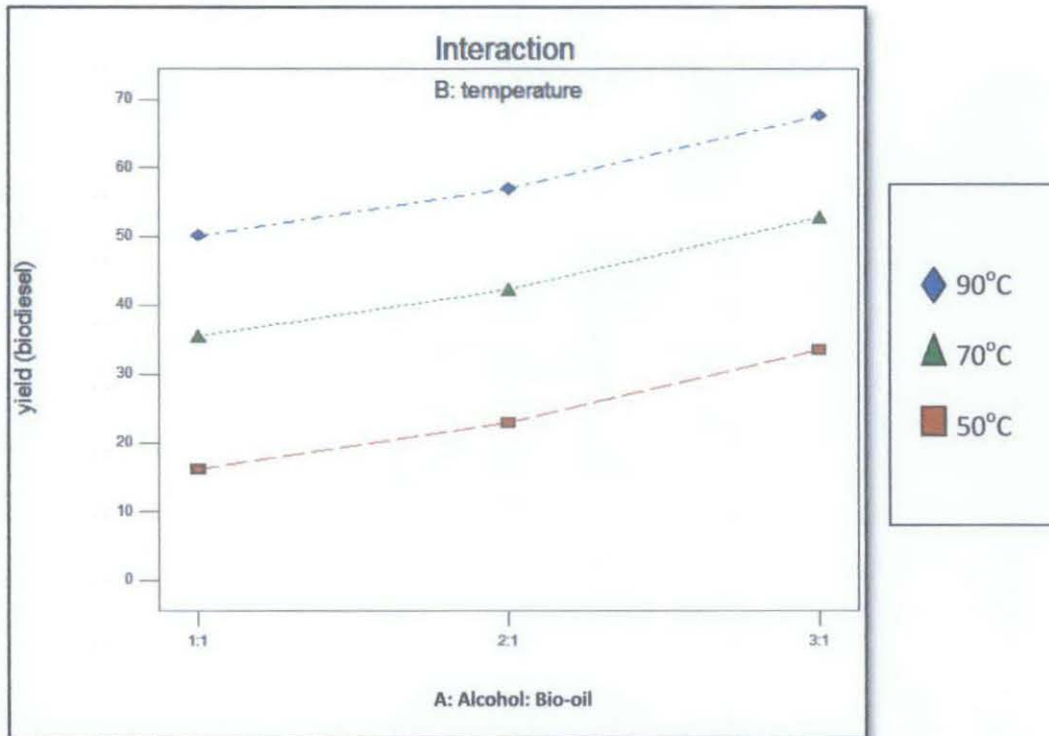


Figure 4.2: Interaction between Temperature and Ratio of Bio-oil to Alcohol with Presence of 2wt% Catalyst

2 wt% of catalyst (CaO) was used for the above interaction between temperature and ratio of alcohol to bio-oil. By taking catalyst as control variables for the above graph, the interaction of temperature and alcohol to bio-oil ratio for biodiesel production can be clearly seen.

Ratio of bio-oil to alcohol was varied across the experiments which was introduced to shift the equilibrium towards the product. By increasing the ratio of alcohol to bio-oil ratio, it was observed to result in higher production especially at 3:1 alcohol to bio-oil ratio. Temperature was also varied across the experiments.

By increasing the temperature, it was noticed to result in higher production especially at 90°C. Besides, by increasing temperature resulted in decreasing amount of free fatty acid esterification products. This lead to conclusion that increasing the heat increases the conversion rate of free fatty acid, which leads to reduction of acid value in bio-oil and increasing of ester in biodiesel.

Ratio of 3:1 was found to be sufficient in reducing amount of fatty acid inside the bio-oil at temperature of 90°C and 2wt% of catalyst. Besides, it was found to be an easy product separation as well. This was the temperature at atmospheric pressure using butanol before exceeding the alcohol boiling point avoiding excessive reactants losses. Below are the other graph that shown the interaction between temperature and alcohol to bio-oil ratio at specific constant value of catalyst.

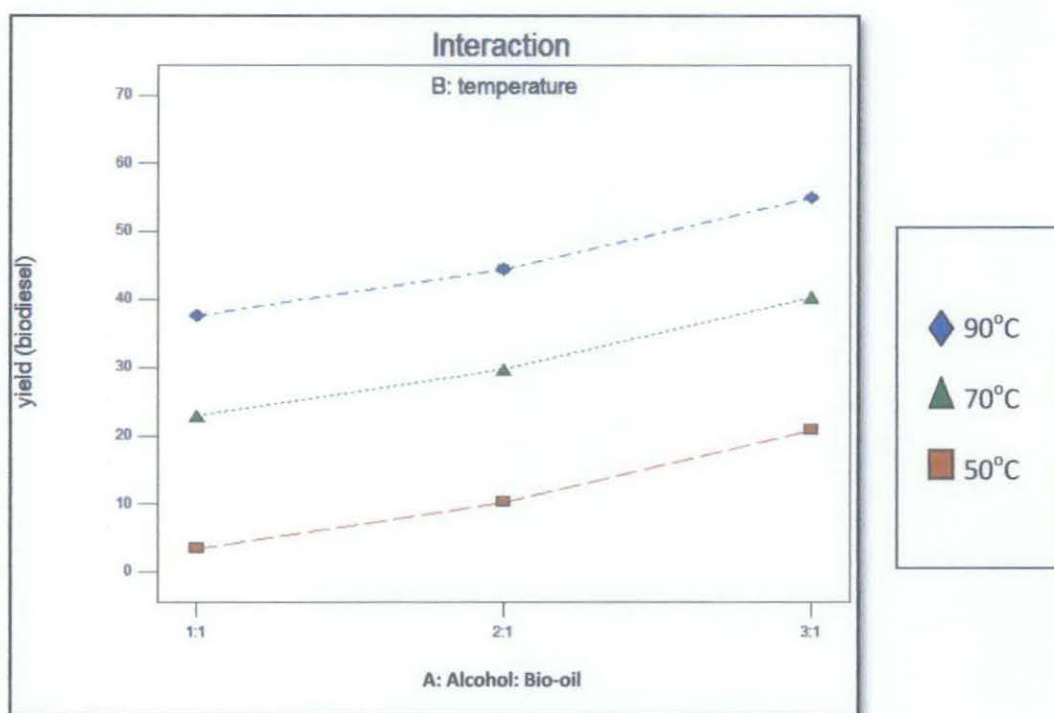


Figure 4.3: Interaction between Temperature and Ratio of Bio-oil to Alcohol with Presence of 4wt% Catalyst

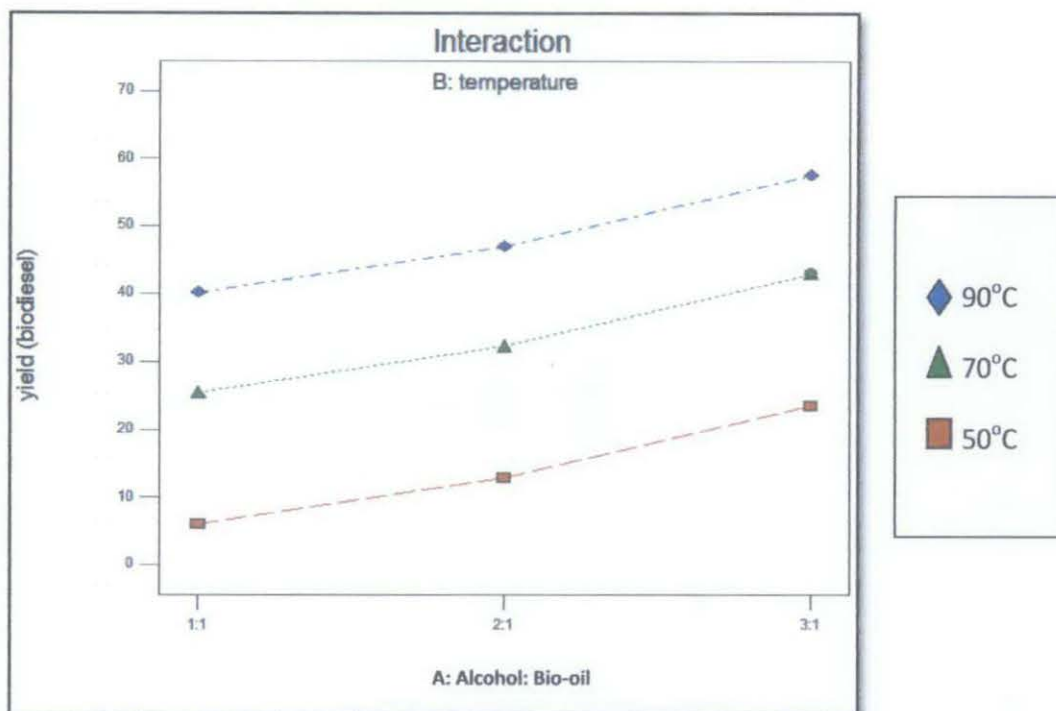


Figure 4.4: Interaction between Temperature and Ratio of Bio-oil to Alcohol with Presence of 6wt% Catalyst

4.1.3 Effect of Catalyst (wt %)

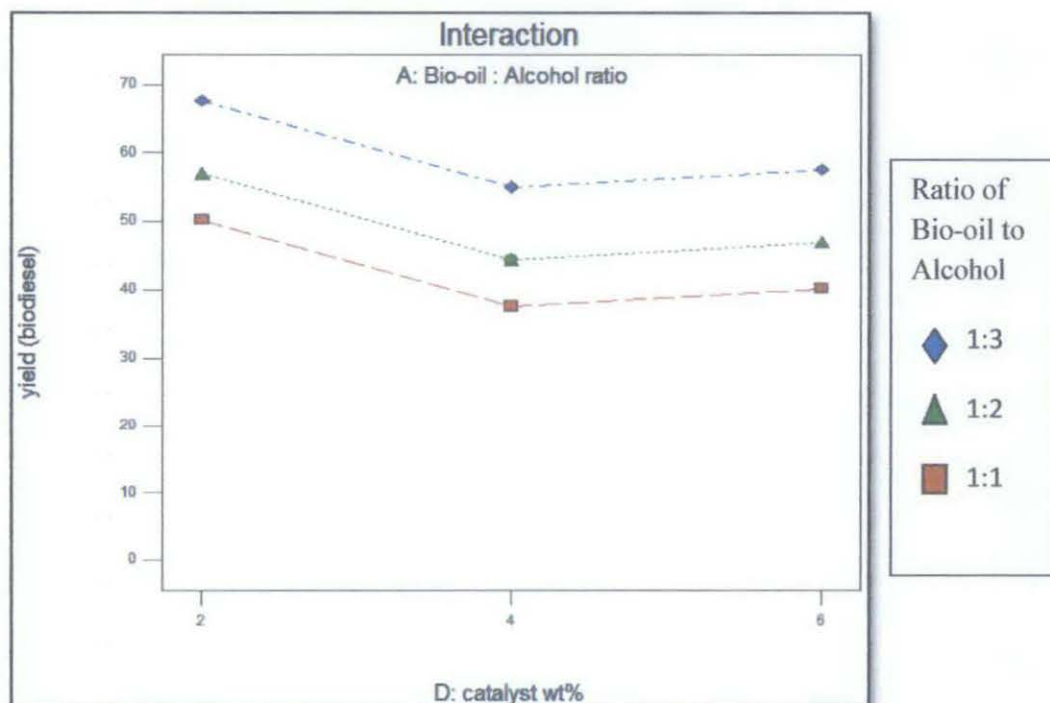


Figure 4.5 Interaction between Ratio of Bio-oil to Alcohol and Catalyst wt% at Temperature of 90°C

Catalyst amount was varied at 2,4 and 6wt% on total feed basis. The highest recorded conversion was at 2wt% catalyst as shown in Figure 4.6. The production of

biodiesel was decreased at 4wt% catalyst then it was increased at 6wt% catalyst. The increasing ranking of biodiesel production base on catalyst wt% was catalyst at 4wt%, 6wt% then 2wt%. Base on the theory, amount of catalyst used should increase the reaction time as it helps to increase the reaction rate of the reactant. But, the outcome base on the experiment conducted was differ compared to the theory. At ratio alcohol to bio-oil of 3:1 and at temperature 90°C, the reaction time needed to finish the reaction was fluctuated according to the ranking of biodiesel production. This might be due to solid catalyst surface area that not contacted with the reactant smoothly.

4.2 Additional Experiment on Optimum Condition

Additional experiment was conducted to verify optimum condition of biodiesel production. Base on Taguchi L9 Orthogonal Array; run no #3 gave the highest yield production which was 65.35% of biodiesel that have been converted from free fatty acid inside the bio-oil.

Instead of to verify the biodiesel production at optimum condition, the other purpose to conduct this experiment was to observe reaction time taken for the reactant to finish its reaction. Below is a graph of the relation between reaction time and yield production at optimum condition.

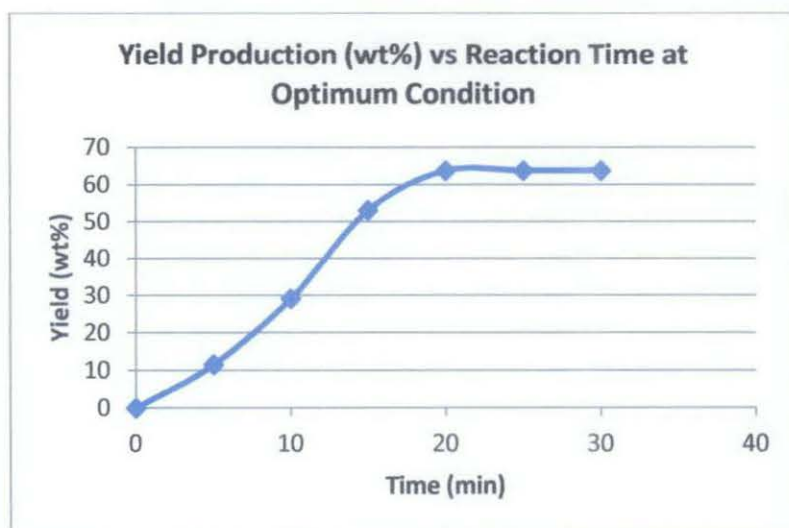


Figure 4.6 Yield Production (wt %) vs Reaction Time at Optimum Condition

During the course of reaction, 6 readings for biodiesel conversion were obtained from samples withdrawn from the yield vessel. Time intervals at which samples are withdrawn were 0, 5,10,15,20 and 25 minutes. Results are shown in Figure 4.6 representing biodiesel conversion over time. Biodiesel conversion surged in initial reaction period which covers 15 minutes while it started to slow down after 15 minutes until a stable conversion curve was noticed to be dominant in the last few readings. Conversion at 20 minutes was not far from 17 minutes as it shown the conversion of the biodiesel nearly finished and the maximum reaction time was achieved.

4.3 Comparison of Yield Production (wt%) for Different Type of Catalyst

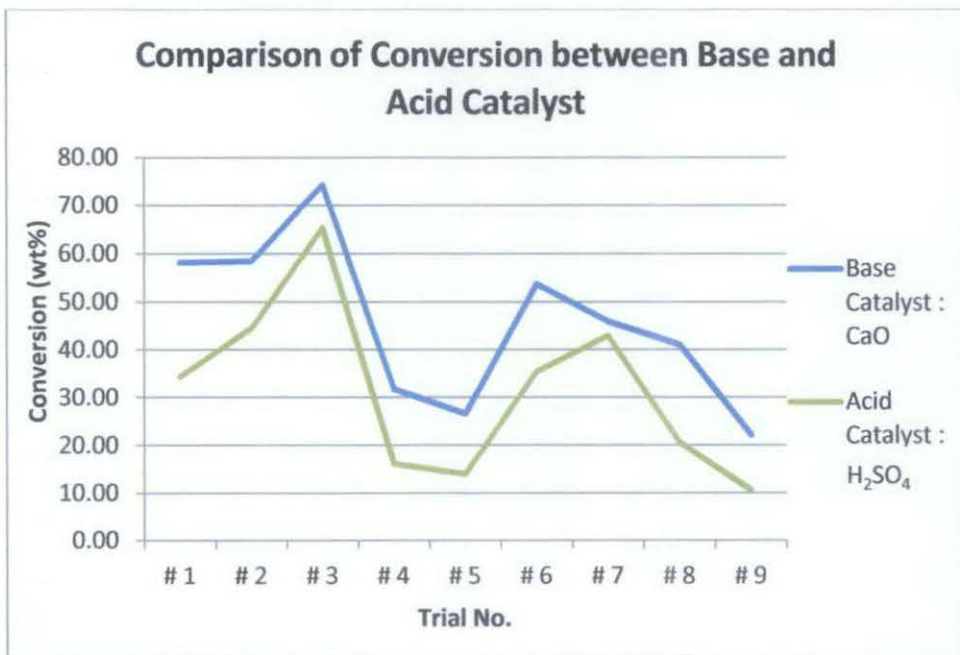


Figure 4.7: Comparison of Conversion between base and Acid Catalyst

Acid and base catalyst was used during the experiment conducted to identify the difference between the conversions. Base on the experiment conducted, conversion for base catalyst gave higher percentage compared to acid catalyst. The highest conversion was shown by trial number #3 with the percentage of 74.30% for base catalyst and 65.35% for acid catalyst.

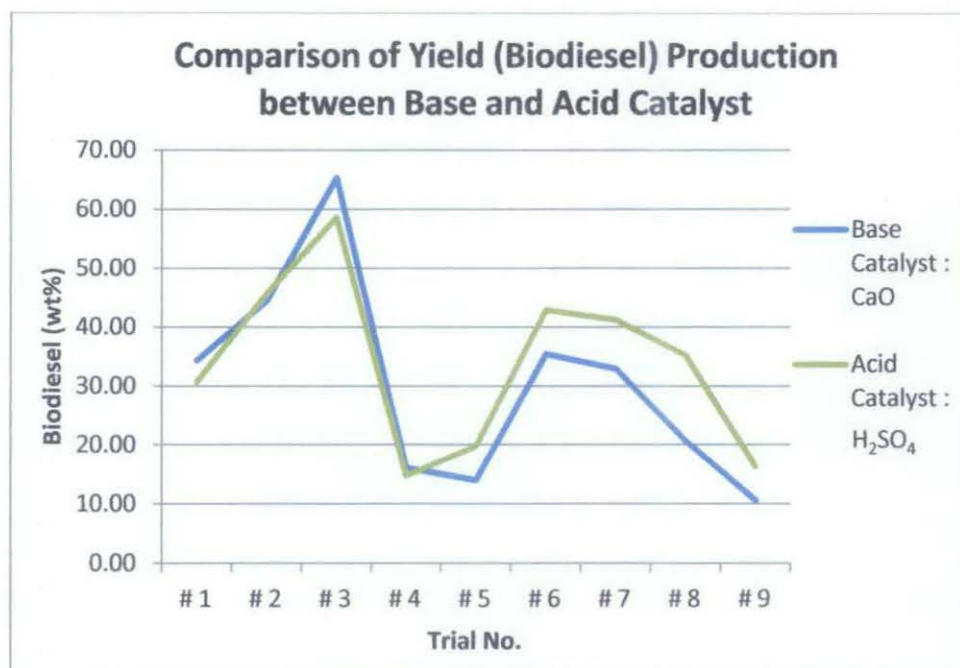


Figure 4.8: Comparison of Yield (Biodiesel) production between Base and Acid Catalyst

Biodiesel production was observed after the separation of water rich phase from the total conversion. The highest production of biodiesel was noticed at trial no #3. Base on the observation in Figure 4.8, the used of base catalyst gave higher percentage of biodiesel production compared to acid catalyst at trial no. 3. Base on the pattern above, trial no. 3 is the only trial that gave higher biodiesel production percentage for base catalyst. This was due to the theory of type of catalyst where acid catalyst promotes high production rate compared to base catalyst. After the separation of water rich phase for both base and acid catalyst, the water rich phase volume for base catalyst was higher than acid catalyst. This can be shown by figure 4.8, where the yield of biodiesel for acid catalyst was higher compared to base catalyst.

4.4 Comparison of Properties Analysis

4.4.1 pH Analysis

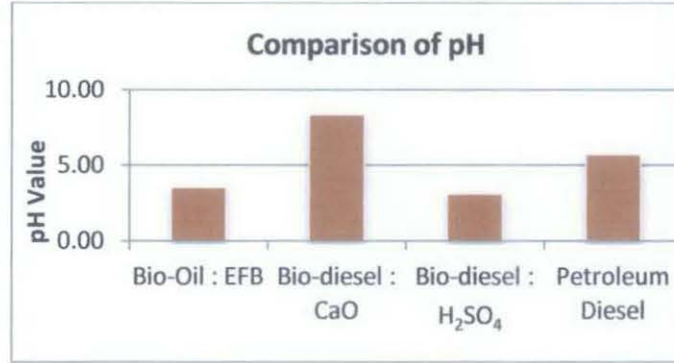


Figure 4.9: Comparison of pH

Biodiesel produced by using base catalyst (CaO) was noticed to have pH of 8.4 which was in alkali range while the biodiesel produced using acid catalyst was acidic. The pH for conventional petroleum diesel was observed to be in acidic range with the pH value of 5.75. pH for bio-oil used was 3.58 and after the conversion using base catalyst, the value of pH was increased. The ideal range for biodiesel was from 8.00 to 9.00 and the biodiesel produced using CaO was in that range.

4.4.2 Density Analysis at 20°C

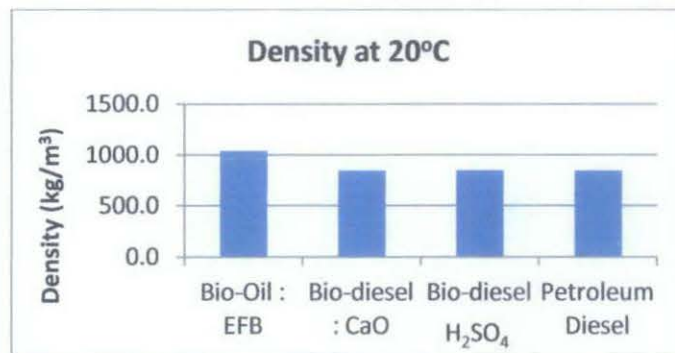


Figure 4.10; Comparison of Density at 20°C

Based on the theory, since the alcohol used was n-butanol that has longer chain length, so the biodiesel produced has less density compared to shorter chain length saturated esters. The relation between biodiesel density and NO_x emission was parallel to each other. As the density of biodiesel increased, the more NO_x emission will be produced. Based on Figure 4.10, the density of bio-oil was decreased from 1037.2 kg/m³ to 846.2 kg/m³ using base catalyst after the conversion of biodiesel. Biodiesel that has been produced using base and acid catalyst have density value near to petroleum conventional diesel which was around 850 kg/m³.

4.4.3 Specific Gravity at 20°C

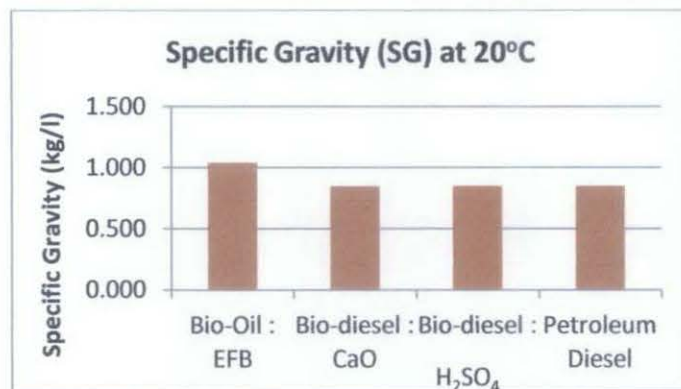


Figure 4.11: Specific Gravity at 20°C

Specific gravity (SG) for bio-oil was decreased after the conversion of biodiesel from 1.039 kg/l to 0.848 kg/l using base catalyst. Specific gravity was related to the density of biodiesel as it is a comparison of its density with density of water. Both biodiesel and petroleum diesel was observed to have similar specific gravity value.

4.4.4 Calorific Value

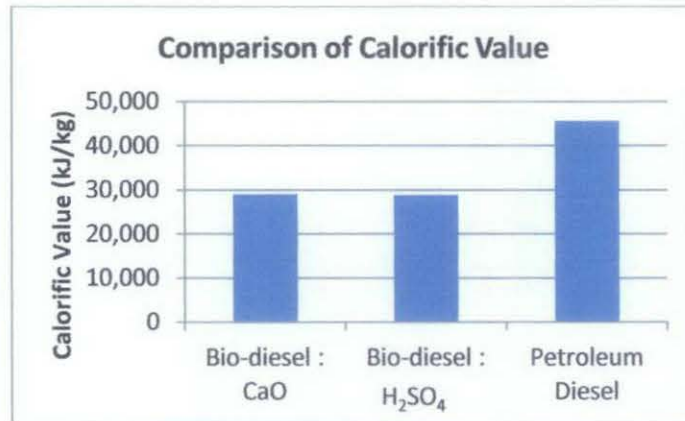


Figure 4.12: Comparison of Calorific Value

Calorific value of the biodiesel was observed to be less than conventional petroleum diesel. This might be due to the calorific value of the type of biomass that has been used to produce the bio-oil. Besides, since the bio-oil used was watery, it might reduce the heat of combustion of the substance. Steps to improve the calorific value must be implemented in order to gain high calorific value of biodiesel that can produce more heat of combustion.

4.4.5 Pour Point

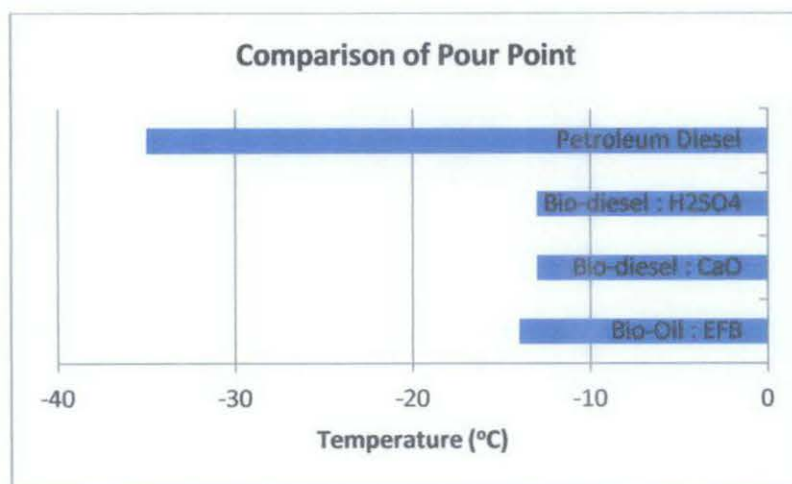


Figure 4.13: Comparison of Pour Point

Conventional petroleum diesel has lower pour point value compared to biodiesel produced. With pour point of -35°C , petroleum diesel does not have problems when it was used at cold countries since the pour point value was low. Biodiesel produced that has pour point of -13°C will have difficulties to flow the biodiesel at low temperature. This pour point is the lowest temperature at which oil will flow or readily pumpable. Type of catalyst does not affect the pour point value as both biodiesel from base and acid catalyst have the same value of pour point. The pour point value will determine paraffin content inside the oil as it increases with increasing of pour point value.

4.5 GCMS Analysis

The purpose of gas chromatography mass spectrometer analysis was to validate the existence of alkyl ester which is biodiesel in the sample of the product. The actual composition of bio-oil, biodiesel and diesel was detected by GC. These data was evaluated to verify the experiment conducted.

4.5.1 Component Analysis of Bio-Oil from EFB

Table 4.3: Component of Bio-oil from EFB

No of Peak	Composition	Concentration (%)
1	Furan,2,4-dimethyl	0.876
2	phenol	21.333
3	1,3-Dioxolane, 2-(1,1-dimethyl 1) -2-methyl-	1.454
4	2-Cyclopenten-1-one,2-hydroxy-3methyl	7.176
5	2-cyclopentene-1-one, 2 hydroxy -3,4-dimethyl	0.872
6	Tetrahydrofuran,2-propyl	2.01
7	Phenol, 2-methoxy	1.071
8	Hexanal,5,5-dimethyl	2.903
9	2-cyclopenten-1-one, 3-ethyl-2-hydroxy	2.262
10	Benzothiazole,4,5,6,7-tetrahydro-2-amino	1.398
11	Tetrahydrofuran,2-methyl-5-pentyl	6.52
12	2-(Trifluoromethyl) propenoic acid	0.852
13	2-propenoic acid, 2-methyl-5-pentyl	3.04

14	1,2-Benzenediol, 3-methoxy	3.626
15	3(2H)-Pyridazinone, 6-methyl	3.983
16	Phenol,2,6-dimethoxy	25.624
17	2,2,5,5 - Tetramethyl-3-hexanone	2.029
18	4-methoxy-2-methyl-1-(methylthio)benzene	2.245
19	Phenol,3-[(trimethylsilyloxy)-	2.066
20	(4-methoxy-phenyl)-(2-nitrocyclohexyl)-methanol	2.082
21	1-Butanone,1-(2,4,6-trihydroxy-3-methyl phenyl)	1.581
22	1,2-Benzenedicarboxylic acid,butyl 8-methanonyl ester	1.173
23	1,2-Benzenedicarboxylic acid,mono (2-ethylhexyl) ester	3.823

Bio-oil from EFB that has been used for biodiesel production has total of 3.892% of propenoic acid that can be converted into butyl ester (biodiesel) with reaction of alcohol.

4.5.2 Component Analysis of Ester Rich Phase

Table 4.4: Component of Ester Rich Phase

No of Peak	Composition	Concentration (%)
1	phenol	34.416
2	Butanoic acid, butyl ester	17.783
3	Carbonic acid,isoheptyl methyl ester	1.373
4	Azidoacetic acid, cyclobutyl heptadecyl ester	6.543
5	Oxalic acid,cyclobutyl heptadecyl ester	1.446
6	1-dodecene	1.982
7	1-dodecene	1.219
8	1,2-Benzenedicarboxylic acid,butyl 2-methylpropyl ester	4.557
9	1,2-benzenedicarboxylic acid,mono(2-ethylhexyl)ester	30.681

Butyl ester was one of the components in ester rich phase that validate the biodiesel production during the experiment conducted. Besides, that, there were many alkyl esters that can also called as biodiesel that has been produced by the reaction of bio-oil with alcohol with presence of Cao as catalyst. The percentages of each ester were shown in the table above.

4.5.3 Component Analysis of Water Rich Phase

Table 4.5: Component of Water Rich Phase

No of Peak	Composition	Concentration (%)
1	Phenol	10.71
2	Cyclopropane,1-ethyl-2-heptyl	3.162
3	Cyclopentane,1,1,3-trimethyl	4.034
4	Dodecanol	2.679
5	1,2 - Benzenedicarboxylic acid, (2-methylpropyl)	10.125
6	1,2-Benzenedicarboxylic acid,mono (2-ethylhexyl)ester	69.288

In water rich phase by product, 1,2-Benzenedicarboxylic acid,mono (2-ethylhexyl)ester see to have the highest percentage. It should be further analyzed to know the reason of this behaviour.

4.5.4 Component Analysis of Conventional Petroleum Diesel

Table 4.6: Component of Conventional Petroleum Diesel

No of Peak	Composition	Concentration (%)
1	Decane	0.56
2	Undecane	1.308
3	Dodecane	2.016
4	Decane, 2-methyl	1.1
5	Tridecane	2.998
6	Cyclohexanone,2,3-dimethyl	0.547
7	Dodecane,2,6,10-trimethyl	1.004
8	Decahydro-4,4,8,9,10-pentamethylnaphthalene	0.601
9	Tetradecane	5.81
10	Fluorene,2,2 a-dihydro-	0.666
11	Naphthalene,1,6-dimethyl	1.123
12	Naphthalene,1,6-dimethyl	0.94
13	Dodecane,2,6,10-trimethyl	0.58
14	Benzene,1-(1,5-dimethylhexyl)-4-methyl	0.91
15	Pentadecane,7-methyl	2.533
16	3,5-Dimethyldodecane	0.697
17	Pentadecane,7-methyl	7.256
18	Naphthalene,1,6,7-trimethyl	1.199

19	n-Nonylcyclohexane	0.922
20	Pentadecane,2-methyl	1.266
21	Tridecane,2-methyl	0.888
22	Hexadecane	7.08
23	Napthalene,2,3,4-trimethyl	0.874
24	Pentadecane,2,6,10-trimethyl	2.808
25	Decane,3,8-dimethyl	0.799
26	Tridecane,5-propyl	12.706
27	methoxyaceticacid,2-pentadecyl ester	0.603
28	Heptadecane,3-methyl	0.564
29	Octadecane	5.027
30	Tetradecane	0.588
31	Nonadecane	6.222
32	Eicosane	6.112
33	Hexadecane	0.647
34	Hexadecane,2,6,10,14-tetramethyl-	5.723
35	Hexadecane	4.694
36	Hexadecane	3.903
37	Tetracosane	2.941
38	Heptadecane	2.024
39	Hexacosane	1.167
40	Octacosane	0.592

For the conventional petroleum diesel, most of the component was alkenes groups like decane, hexadecane and heptadecane.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

Since Malaysia was large producer of biomass, it has a high potential to produce bio-oil. So, the conversion of biodiesel from bio-oil can be one of the alternatives as renewable energy produced by Malaysia to encounter future energy shortage. Biodiesel was a type of upgraded bio-oil that can be used as an alternative for petroleum diesel. By upgrading the bio-oil, bio-oil applicability is no longer limited due to its properties but can be used in a wide range of possible applications.

Base on the objectives of the experiment, biodiesel or butyl ester can be produced by reacting the bio-oil and butanol with presence of metal oxides as heterogeneous catalyst. Besides, the optimum condition for biodiesel production base on Taguchi L9 Orthogonal Array were at temperature 90°C, 3: 1 ratio of butanol to bio-oil and with presence of 2wt% CaO. Type of catalyst used for biodiesel production affects the conversion, selectivity and yield. Higher yield production was shown by acid catalyst, but at the optimum trial number, the yield produced by base catalyst was higher.

Base on the analysis conducted on properties of biodiesel, it was shown that the value of biodiesel was similar to the conventional petroleum diesel for its density and specific gravity. For the other properties like calorific value and pour point, petroleum diesel was shown to have better properties compared to biodiesel produced. These properties should be studied to improve the properties of biodiesel produced. pH for petroleum diesel was acidic but biodiesel produced with presence of CaO was alkali. So, the pH must be purified until the pH nearly to neutral.

Other than that, type of biomass used should be varies as it affect biodiesel properties especially for calorific value. The calorific value for biodiesel was low compared to conventional biodiesel, so study must be done in order to improve the heat of combustion of the bio-oil. Pour point of biodiesel produce was higher than petroleum diesel, it not a good sign for biodiesel user especially at cold country as the biodiesel might freeze at their surrounding temperature. This problem might be solved by adding additive towards it, and this must be studied for further details.

Reactive distillation method is a novel method to produce biodiesel. Since this experiment is using solid base heterogeneous catalyst (CaO), it recommended to repeat the experiment with solid acid heterogeneous catalyst to observe the conversion and yield. Then a comparative study between solid acid heterogeneous catalyst and solid base heterogeneous catalyst is analyzed. Besides, different types of catalyst for solid base heterogeneous catalyst can be the manipulated variables and the activity base on Lewis structure can be analyzed. Further analysis on the biodiesel properties like cetane number, boiling point, flash point cloud point should be done.

Another aspect that should be improved was the condition of variables. Temperature of reaction, alcohol to bio-oil ratio and catalyst wt% can be manipulated into other conditions that might give better yield of the production. Type of catalyst, whether it is base or acid, homogenous or heterogeneous, solid or liquid and amount of catalyst must be further studied. Analysis of catalyst should be done in terms of it surface area, strength, concentration, pore size and volume also can be further developed.

As a conclusion, biodiesel was world widely known as a green fuel for future energy demand. Besides, the usage of CaO as heterogencous catalyst also known as green technology as it requires neither catalyst recovery nor aqueous treatment steps and high yield of biodiesel obtained. It helps to reduce CO₂ emissions, as well as helps to improve the environment where biomass can be converted into valuable product. Production of biodiesel with novel method that can improve the conversion and yield

should be further studied in order to increase the efficiency. Yet, biodiesel is one of the important energy in the future that should have further research and development.

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