

**THE STUDY OF TRANSESTERIFICATION OF
PALM OIL WITH EXCESSIVE
AMOUNT OF ETHANOL**

AHMAD FAKHRUDDIN BIN AHMAD FAUDZI

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

**Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG**

27 JANUARY 2014

© AHMAD FAKHRUDDIN AHMAD FAUDZI (2014)

ABSTRACT

Since past decades, most of the world energy demand is fulfilled through petroleum sources, coal, natural gas, hydroelectricity, and nuclear power. As a consequence, natural resources are diminishing and thereby become a global concern and the cause of rising price. The competition to create an alternative fuel underway as well as to reduce the cost, get high profitability and less pollution to human and environment. To overcome these problems, biodiesel is introduced by the researches to substitute the fossil fuels. Biodiesel is the monoalkyl esters of fatty acids produced from renewable feedstock, such as vegetable oils, with glycerin being the primary by product. Biodiesel being studied because of its unique properties and renewable fuels. The production of biodiesel in industrial scale involved triglyceride substance that present in fatty acid ethyl ester (FAEE) that affect the biodiesel production quality. Thus, this research is to minimize the presence of triglyceride substances in fatty acid ethyl ester (FAEE) for the alternative of energy sources. In this study, the biodiesel produced in 250 mL three-neck round-bottom flask by using ethanol and palm cooking oil as medium component. Three parameters are studied like ratio of cooking oil-ethanol, rate of reaction, and catalyst activation activity. The best condition of parameters determine by the fastest completed transesterification reaction in the optimal yield produced. Three-neck round-bottom integrated with condenser to generate transesterification process in 250 mL Three-neck round-bottom containing medium chemical reaction. The flasks boiled up by rotamantle in one hour that involved the Potassium Hydroxide (KOH) as catalyst accelerator, 7404 hours for sample experimental without catalyst. The products are analyzed using Gas Chromatography Flame Ionized Detector (GC-FID) for triglyceride concentration performance detection. Then, the research continued with the manipulated ratio with 1:6, 1:12 and 1:24. As a result, the best condition in transesterification of biodiesel are in ratio 1:6, 1200 rpm, 65 °C and 100% volume percentage of fatty acid ethyl ester (FAEE) concentration.

ABSTRAK

Sejak beberapa dekad yang lalu , kebanyakan permintaan tenaga dunia dipenuhi melalui sumber petroleum , arang batu , gas asli, hidroelektrik, dan kuasa nuklear. Akibatnya, sumber asli semakin berkurangan dan dengan itu menjadi kebimbangan global dan menyebabkan harga meningkat. Pertandingan untuk mewujudkan dijalankan bahan api alternatif serta untuk mengurangkan kos, mendapatkan keuntungan yang tinggi dan pencemaran yang kurang kepada alam sekitar dan manusia . Untuk mengatasi masalah ini , biodiesel diperkenalkan oleh kajian untuk menggantikan bahan api fosil. Biodiesel adalah ester monoalkyl asid lemak yang dihasilkan daripada bahan mentah yang boleh diperbaharui, seperti minyak sayuran , dengan gliserin yang utama oleh produk. Biodiesel sedang dikaji kerana sifat-sifat yang unik dan bahan api boleh diperbaharui . Pengeluaran biodiesel dalam skala industri yang terlibat bahan trigliserida yang hadir dalam asid lemak etil ester (FAEE) yang memberi kesan kepada kualiti pengeluaran biodiesel. Oleh itu, kajian ini adalah untuk mengurangkan kehadiran bahan-bahan trigliserida dalam asid lemak etil ester (FAEE) untuk alternatif sumber tenaga. Dalam kajian ini , biodiesel yang dihasilkan dalam 250 mL tiga leher kelalang bulat -bawah dengan menggunakan etanol dan minyak masak sawit sebagai komponen sederhana. Tiga parameter dikaji seperti nisbah minyak masak - etanol, kadar tindak balas , dan aktiviti pengaktifan pemangkin. Keadaan terbaik parameter ditentukan oleh tindak balas transesterification cepat siap dalam hasil yang optimum dihasilkan. Tiga leher bulat - bawah disepadukan dengan kondenser untuk menjana proses transesterification dalam 250 mL tiga leher bulat bahagian bawah yang mengandungi tindak balas kimia sederhana. Termos direbus oleh rotamantle dalam satu jam yang terlibat Hidroksida Kalium (KOH) sebagai pemangkin pemecut, 7404 jam untuk eksperimen sampel tanpa pemangkin. Produk ini dianalisis menggunakan Gas Chromatography Flame Detector terion (GC- FID) untuk trigliserida pengesanan prestasi penumpuan. Kemudian , penyelidikan terus dengan nisbah dimanipulasi dengan 1:06 , 1:12 dan 1:24 . Akibatnya , keadaan yang terbaik dalam transesterification biodiesel adalah dalam nisbah 1:6 , 1200 rpm , 65 oC dan 100% jumlah peratusan asid lemak etil ester (FAEE) penumpuan.

TABLE OF CONTENTS

SUPERVISOR'S DECLARATION	IV
STUDENT'S DECLARATION	V
<i>Dedication</i>	VI
ACKNOWLEDGEMENT	VII
ABSTRACT.....	VIII
ABSTRAK.....	IX
TABLE OF CONTENTS.....	IX
LIST OF FIGURES	XII
LIST OF TABLES.....	XIVI
LIST OF ABBREVIATIONS.....	XV
1 INTRODUCTION	1
1.1 Motivation and statement of problem.....	1
1.2 Objectives	3
1.3 Scope of this research	4
1.4 Main contribution of this work.....	4
1.5 Organisation of this thesis	5
2 LITERATURE REVIEW	6
2.1 Overview	6
2.2 Introduction	6
2.2.1 Properties of biodiesel	7
2.2.2 Biodiesel production process.....	8
2.2.3 Process of transesterification	10
2.2.3.1Mechanism of transesterification	11
2.2.3.2Principle of kinetics.....	12
2.2.3.3Reactor optimization	14
2.2.3.4Batch and continuous type of reactor.....	15
2.2.4 The liquid-liquid extractive	16
2.2.5 Current technologies of producing biodiesel	18
2.2.5.1Biodiesel production with batch processing	19
2.2.5.2Biodiesel production with continuous process.....	19
2.2.5.3Biodiesel production with BIOX process	19
2.2.5.4Biodiesel production with supercritical	20
2.3 Summary.....	20
3 MATERIALS AND METHODS.....	21
3.1 Overview	21
3.2 Chemicals	21
3.2.1 Apparatus.....	22
3.2.2 Equipment.....	23
3.3 Experimental procedure.....	23
3.3.1 Standard solution preparation.....	23
3.3.2 Standard curve preparation	23
3.3.3 Biodiesel production with catalyst	24
3.3.3.1Preparation	24
3.3.3.2Heating and stirring process.....	24
3.3.3.3Transesterification process.....	25
3.3.3.4Settling process	25

3.3.3.5	Washing process.....	25
3.3.4	Biodiesel production without catalyst	25
3.4	Gas Chromatography Flame Ionized Detector (GC-FID) analysis procedure .	26
3.4.1	Procedure	27
3.4.1.1	Column.....	27
3.4.1.2	Chromatograph conditions	27
3.4.1.3	C-R8A recorder.....	28
3.4.1.4	Sample injection.....	28
3.4.1.5	Sequence of measurement-summary.....	28
3.5	Safety aspects	30
3.6	Precaution	31
3.7	Summary.....	32
4	RESULT AND DISCUSSION	33
4.1	Overview	33
4.2	Data collection	33
4.2.1	Sample analysis	33
4.2.2	Gas Chromatography Flame Ionized Detector (GC-FID) analysis	33
4.2.3	Result analysis	34
4.3	Standard curve	36
4.4	Transesterification process without catalyst.....	37
4.4.1	Rate of reaction for transesterification process without catalyst (1 st & 2 nd order).....	38
4.5	Transesterification process with catalyst.....	40
4.5.1	Rate of reaction for transesterification process with catalyst (1 st order).....	45
4.5.2	Rate of reaction for transesterification process with catalyst (2 nd order).....	47
4.6	Summary.....	50
5	CONCLUSION AND RECOMMENDATION.....	51
6.1	Conclusion	51
6.2	Recommendation	51
	REFERENCES	53
	APPENDICES	56
	Calculation.....	516
	Technical report.....	70
	Gas Chromatography Flame Ionized Detector (GC-FID) result	79

LIST OF FIGURES

Figure 2-1: Process flow schematic for biodiesel production.....	8
Figure 2-2: Reactor design for transesterification process.....	10
Figure 2-3: Simplified transesterification reaction	11
Figure 2-4: Summarization the mechanism of transesterification.....	12
Figure 2-5: The detail mechanism of transesterification	12
Figure 2-6: Flowsheet configuration for biodiesel production from oil palm and ethanol. Conventional configuration. b. Integrated configuration involving reactive extraction. (1): biodiesel-enriched stream, (2): glycerol-enriched stream...	17
Figure 2-7: Simplified flow diagram of base-catalysed biodiesel processing	18
Figure 3-1: The standard solution in 500ml volumetric flask	23
Figure 3-2: Test tube for standard solution preparation	24
Figure 3-3: Simplified experimental procedures for production of biodiesel.....	26
Figure 3-4: Gas Chromatography Flame Ionized Detector (GC-FID).....	29
Figure 3-5: Front view of gas chromatography.....	29
Figure 3-6: Rear view of gas chromatography.....	30
Figure 4-1: Identification of monoglycerides, diglycerides and triglycerides	35
Figure 4-2: Normalized concentration of triglyceride from palm oil based on normalizes area analyzed by GC-FID	36
Figure 4-3: Biodiesel profile for transesterification based on troglyceride removal concentration without catalyst	37
Figure 4-4: 1 st order reaction for transesterification based on triglyceride removal concentration without catalyst	38
Figure 4-5: 2 nd order reaction for transesterification based on triglyceride removal concentration without catalyst	39
Figure 4-6: Biodiesel profile for transesterification based on triglyceride removal concentration with catalyst and ratio, 1:6.....	41
Figure 4-7: Biodiesel profile for transesterification based on triglyceride removal concentration with catalyst and ratio, 1:12	41
Figure 4-8: Biodiesel profile for transesterification based on triglyceride removal concentration with catalyst and ratio, 1:24	42
Figure 4-9: 1 st order reaction for transesterification based on triglyceride removal concentration with catalyst and ratio, 1:6.....	46
Figure 4-10: 1 st order reaction for transesterification based on triglyceride removal concentration with catalyst and ratio, 1:12	46
Figure 4-11: 1 st order reaction for transesterification based on triglyceride removal concentration with catalyst and ratio, 1:24	47

Figure 4-12: 2 nd order reaction for transesterification based on triglyceride removal concentration with catalyst and ratio, 1:6.....	48
Figure 4-13: 2 nd order reaction for transesterification based on triglyceride removal concentration with catalyst and ratio, 1:12	48
Figure 4-14: 2 nd order reaction for transesterification based on triglyceride removal concentration with catalyst and ratio, 1:24	49

LIST OF TABLES

Table 2-1: The properties of several fuels versus biodiesel	6
Table 4-1: Result form Gas Chromatography Flame Ionized Detector (GC-FID)	35
Table 4-2: Physical characteristics for biodiesel	36
Table 4-3: Standard curve for triglyceride content in palm oil.....	37
Table 4-4: Effect of triglyceride concentration on transesterification process over time	38
Table 4-5: Effect of triglyceride concentration on transesterification process over time (continue).....	39
Table 4-6: Effect of triglyceride concentration on transesterification process with presence of potassium hydroxide (KOH) as catalyst with molar ratio,palm oil:ethanol, 1:6.....	42
Table 4-7: Effect of triglyceride concentration on transesterification process with presence of potassium hydroxide (KOH) as catalyst with molar ratio,palm oil:ethanol, 1:12.....	43
Table 4-8: Effect of triglyceride concentration on transesterification process with presence of potassium hydroxide (KOH) as catalyst with molar ratio,palm oil:ethanol, 1:24.....	43
Table 4-9: Effect of triglyceride concentration on transesterification process with presence of potassium hydroxide (KOH) as catalyst with molar ratio,palm oil:ethanol, 1:6(continue)	44
Table 4-10: Effect of triglyceride concentration on transesterification process with presence of potassium hydroxide (KOH) as catalyst with molar ratio,palm oil:ethanol, 1:12(continue)	44
Table 4-11: Effect of triglyceride concentration on transesterification process with presence of potassium hydroxide (KOH) as catalyst with molar ratio,palm oil:ethanol, 1:24(continue)	45

LIST OF ABBREVIATIONS

$^{\circ}F$	Fahrenheit
$^{\circ}C$	Degrees
<i>RPM</i>	Revolutions per minute
<i>min</i>	minutes
<i>wt%</i>	Weight percent
$\%$	Percentages
μ	Micro (1×10^{-9})
<i>L</i>	Liter
<i>mL</i>	Mililiter (1×10^{-3} liter)
<i>ppm</i>	Part per million
<i>g</i>	gram

Subscripts

<i>FAEE</i>	Fatty Acid Ethyl Ester
<i>GC-FID</i>	Gas Chromatography Flame Ionized Detector
<i>KOH</i>	Potassium Hydroxide
<i>CSTR</i>	Continuous stirred tank reactor

1 INTRODUCTION

1.1 Motivation and statement of problem

Nowadays, alternatives fuels are very important things due to environmental concerns and sources reduction (Scholl and Sonrenson, 1993; Zhang and Van Gerpen, 1996; Cardone et al., 2001, 2005). Since past decades, most of the world energy demand is fulfilled through petrochemical sources, coal, natural gas, hydroelectricity, and nuclear power. As a result, natural resources are diminishing and thereby become a global concern and the cause of rising price. The competition to create an alternative fuel are underway as well as to reduce the cost, get high profitability and less pollution to human and environment. Also the aggressive action to use sources like petrochemical sources and natural gas has caused the drastic depletion in natural energy resources thereby making those energy resources becomes limited day by day. This situation makes the world becomes worst and some alternatives method should be implemented to reduce the burden of problems. Using petroleum diesel will contribute to air pollution due to high greenhouse gas emissions like CO₂, carbon monoxide, hydrocarbon and also contain no aromatics compound like sulphur content. Importantly, the alternatives fuel must be technically feasible, economically competitive, environmentally acceptable and readily available.

Renewable energy is a promising alternative solution because it is clean and environmentally safe and produce lower or negligible levels of greenhouse gases and other pollutants as compared with the fossil energy sources. Approximately half of the global energy supply will come from renewables in 2040, according to the European Renewable Energy Council (2006). World energy demand continues to rise day by day. One possible alternative to fossil fuel is biodiesel. Biodiesel is briefly defined as the monoalkyl esters of of fatty acids produced from renewable feedstock, such as vegetable oils, with glycerin being the primary by product. On the other hand, the benefits of biodiesel is it could help to reduce global warming gas emissions such as carbon dioxide as well as it is renewable in nature and safer to handle, has no aromatic compounds, practically no sulfur content, and an oxygen atoms in the molecule of fuel which may reduce the emissions of carbon monoxide, hydrocarbon and particulate matter (Lapuerta et al., 2005, 2002; Freedman et al., 1984; Ballesteros, 2002). However, biodiesel fuel also may cause several

problems than petroleum diesel fuel such as poorer low temperature properties (Dunn et al., 1996; Ballesteros, 2002) and higher production expenses (Mittelbach et al., 1992).

Basically during the process of biodiesel production, the raw materials from vegetable oils or animal fat are reacted with alcohol using basic or homogeneous catalysts. Vegetable oil contains negligible level of sulphur and reduces emissions of sulphur dioxide responsible for acid rain. Vegetable oils are also more environmentally friendly in the case of a spill out to environment. A recent study (Ayhan Demirbas, 2007) highlighted that the transesterification process (alcoholysis) was chosen compared other methods with the aid of controllable parameter such as type of catalyst, type of solvent, reactor system, condition of reaction temperature, concentration, molar ratio, mixing intensity, water content, free fatty acid content, reaction time and technology used that potentially to be upgraded. It uses alcohols in the presence of catalyst (e.g., base, acid or enzyme depending on the free fatty acid content of the raw material) that chemically breaks the molecules of triglycerides into alkyl esters as biodiesel fuels and glycerol as a by-product. The chemical conversion of the oil into its corresponding fatty ester is called transesterification (Bala, 2005).

Then, the process of transesterification reduces the high viscosity of vegetable oil, resulting in a higher-quality fuel. The commonly used alcohols for the transesterification include methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol and ethanol are espoused most frequently, particularly the former due to its low cost. Although ethanol reacts at a slower rate than methanol, but it is preferred for the enzymatic process since it is non-toxic and safer to handle and store. In the transesterification process of triglyceride, vegetable oil reacts with ethanol (ethanolysis) in the presence of a homogeneous or enzyme catalyst to make ethyl esters of straight-chain fatty acids. The presence of some homogeneous catalyst or alkaline catalyst that will be used such as sodium methoxide, sodium hydroxide and potassium hydroxide can accelerate considerably the adjustment of the equilibrium and the rate of the reaction that can be significantly improved by provides the satisfactory conversion within a short time period. Since transesterification is a reversible reaction, alcohols are usually charged in excess to assist in rapid triglyceride conversion and ensure a complete conversion.

A Common problem that had been faced by industrial players in the production of biodiesel is how to achieve the most efficiency or internal effectiveness factor of transesterification reaction. Normally, the problem take places with the phase change transformation after the reaction between palm oil and ethanol in the reaction exclusive zone through counter-current contact movement to achieve high conversion target of reaction. The product will be separated between two phase layers of the product (Fatty Acid Ethyl Ester-Ethanol) in the top side and (glycerol-Ethanol) in the bottom side of the reactor-extractor column. This problem may affect the production target, increases costing, the efficiency of the production and the quality of the product. So, this research is important to define the potential of both techniques and make the comparison between them. The Triglyceride substance present in FAEE affect the biodiesel production quality. Hence, it is desirable to minimize the presence of triglyceride substances in FAEE for the alternative of energy sources.

1.2 Objectives

The following are the objectives of this research:

- To obtain the optimum condition on the production of biodiesel and its effects on the triglyceride removal performance. (Temperature, RPM and ratios).
- To study the transesterification reaction on the production of biodiesel in the presence of catalyst and without catalyst and its effects on triglyceride concentration removal performance.

1.3 Scope of this research

The following are the scope of this research:

- Experimental analysis of biodiesel production and performance in transesterification reaction.

1.4 Main contribution of this work

The research of production of biodiesel fuel from the palm oil have been made in order to reduce the high cost of raw material used. Ethanol as the main solvent and reactant in this research. Thus, it is in order to reduce the cost of producing biodiesel with controlling the amount of the

excess ethanol (as reactant and solvent) in the ethanol recovery process. Then, using the biodiesel as new potential source that will help to reduce the CO₂, carbon monoxide, hydrocarbon and particulate matter with aid of oxygen content in molecule and also contain no aromatics compound like sulphur content that emission to atmosphere. From that, it will give positive impacts like reduce the air pollution, can reduce health disease, renewable source and environmentally product.

For the industrial player, this research will give alternative solutions to generate the efficient method in selectivity of the yield during the chemical reaction process when handling the heterogeneous or difference phase of product. It will give positive result in increasing of the quality of the production and perform the most effective rate of the production. When the reaction occurs, it will involve some phases and difficulty to separate the phase between each other. Alternatively, the separation technique between two phases of the product (Fatty Acid Ethyl Ester-Ethanol) and (glycerol-Ethanol) is also one of main issue. So, it is significance to conduct the biodiesel research from palm oil as raw material and ethanol as reactant via transesterification process through liquid-liquid extractive to achieve an accurate concentration of yield (Fatty Acid Ethyl Ester-Ethanol or biodiesel). Based on that statement, the increasing of the reaction yield will be achieved.

1.5 Organisation of this thesis

The structure of the thesis is outlined as follow:

Chapter 2 provides a description of the biodiesel, transesterification reaction and liquid-liquid extractive technology. A general description of oil palm, the reaction of transesterification that involve in batch and continuous reaction method.

Chapter 3 gives a review of the experimental design of the research, beginning from the standard curve preparation, followed by transesterification reaction that contained the manipulated variable.

Chapter 4 is devoted to an optimum condition of biodiesel production based on parameter setting. The peak area of the sample recorded from Gas Chromatography Flame Ionized Detector (GC-FID) converted into the product concentration via standard curve of biodiesel prepared.

Chapter 5 draws together a summary of the thesis and outlines the future work which might be derived from the potential of biodiesel production.

2 LITERATURE REVIEW

2.1 Overview

This paper presents the experimental studies of biodiesel in industrial scale involved Triglyceride substance that presents in FAEE affect the biodiesel production quality. Thus, this research is to minimize the presence of triglyceride substances in FAEE for the alternative of energy sources. The results for the best condition in transesterification of biodiesel are in ratio 1:6, rpm 1200, 65 °C and 100% volume percentage of fatty acid ethyl ester concentration.

2.2 Introduction

Biodiesel is one of the results of the increasing search for fuels from renewable sources, It is can be produced from vegetable oil, animal oil/fats, tallow and waste cooking oil. Then, it is also contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend and can be used in diesel engines with little or no modifications. Biodiesel is simple to use, nontoxic, biodegradable and essentially free of sulphur and aromatics. The advantages of biodiesel as diesel fuel are its portability, ready availability, renewability, higher combustion efficiency, and lower sulphur and aromatic content (Ma and Hanna, 1999; Knothe et al., 2006). Table 2.1 below shows the properties of several fuels versus biodiesel.

Table 2-1: The properties of several fuels versus biodiesel

Parameter	FUELS				
	DME	BIODIESEL	Propane	Methanol	Diesel
Chemical formula	CH ₃ OCH ₃	R-COCO ₂ H	C ₃ H ₈	CH ₃ OH	-
Boiling point (°C)	-25,1	188-343	-42	64,5	180~360
Liquid density (gr/cm ³ , 20°C)	0,67	0,875	0,49	0,79	0,84
Specific gravity of Gas	1,59	-	1,52	-	-
FLASH POINT	6,1	160 MIN	9,3	-	100 MIN
Ignition point (°C)	235	-	470	450	250
Explosion limit (%)	3,4 ~ 17	-	2,1 ~ 9,4	5,5 ~ 36	0,6~7,5
Cetane number	55 ~ 60	52	5	5	40~55
Net calorific value (kcal/kg)	6.900	41 (MJ/KG)	11.100	4.800	10.200
Net calorific value (kcal/Nm ³)	14.200	-	21.800	-	-

Biodiesel is one of the results of the increasing search for fuels from renewable sources, it contributes no net carbon dioxide or sulphur to the atmosphere and emits less gaseous pollutants than “fossil” diesel. Carbon monoxide, aromatics, polycyclic aromatic hydrocarbons (PAHs) and partially burned or unburned hydrocarbon emissions are all reduced in vehicles operating on biodiesel. The term “biodiesel” has a specific, technical definition that has been agreed to through a painstaking process by members of industry and government which has received full approval by the American Society of Testing and Materials (ASTM), the premier standard setting organization for fuels and fuel additives. That definition is used for purposes such as alternative fuel designation, EPA registration, or other regulatory purposes. Biodiesel can be used as a pure form (B100) or blended with diesel in any percentage. Much of the world uses a system known as the “B” factor to state the amount of biodiesel in any fuel mix .As type of B20 which means a blend of 20 percent by volume biodiesel with 80 percent by volume petroleum diesel has present significant environmental benefits with a minimum increase in cost for operations and other consumers.

2.2.1 Properties of biodiesels

The properties of biodiesel are similar to those of diesel fuels. Viscosity is the most important property of biodiesels. Since, it may affect the operation of fuel injection equipment, particularly at low temperatures when an increase in viscosity affects the fluidity of the fuel. High viscosity leads to poorer atomization of the fuel spray and less accurate operation of the fuel injectors. The lower the viscosity of the biodiesel, the easier it is to pump and atomize and achieve finer droplets (Islam et al., 2004). The conversion of triglycerides into methyl or ethyl esters through the transesterification process reduces the molecular weight to one third that of the triglyceride and reduces the viscosity by a factor of about eight.

Biodiesel has better properties and much higher certain ratings than today's lower sulphur diesel fuels. Biodiesel addition reduces fuel system wear, and in low levels in high pressure systems increases the life of the fuel injection equipment that relies on the fuel for its lubrication. Depending on the engine, this might include high pressure injection pumps, pump injectors (also called unit injectors) and fuel injectors.

water washing. Acid is added to the biodiesel to neutralize any residual catalyst and to split any soap that may have formed during the reaction. Soaps will react with the acid to form water soluble and the free fatty acids. The salts will be removed during the water washing step, and the free fatty acids will stay in the biodiesel. The water washing step is intended to remove any remaining catalyst, soap, salts, ethanol, or free glycerol from the biodiesel. Neutralization before washing reduces the water required and minimizes the potential for emulsions to form when the wash water is added to the biodiesel. Following the wash process, any remaining water is removed from the biodiesel by a vacuum flash process.

The glycerol stream leaving the separator is only about 50% glycerol. It contains some of the excess ethanol and most of the catalyst and soap. In this form, the glycerol has little value and disposal may be difficult. The ethanol content requires the glycerol to be treated as hazardous waste. The first step in refining the glycerol is usually to add acid to split the soaps into free fatty acids and salts. The free fatty acids are not soluble in the glycerol and will rise to the top where they can be removed and recycled. The salts remain with the glycerol although depending on the chemical compounds present, some may precipitate out. One frequently touted option is to use potassium hydroxide as the reaction catalyst and phosphoric acid for neutralization so that the salt formed is potassium phosphate, which can be used for fertilizer. After acidulation and separation of the free fatty acids, the methanol in the glycerol is removed by a vacuum flash process or another type of evaporator.

The ethanol that is removed from the ethyl ester and glycerol streams will tend to collect any water that may have entered the process. This water should be removed in a distillation column before the ethanol is returned to the process. This step is more difficult if an alcohol such as ethanol or isopropanol is used that forms an azeotrope with water. Then a molecular sieve or pervaporation is used to remove the water.

2.2.3 Process of transesterification

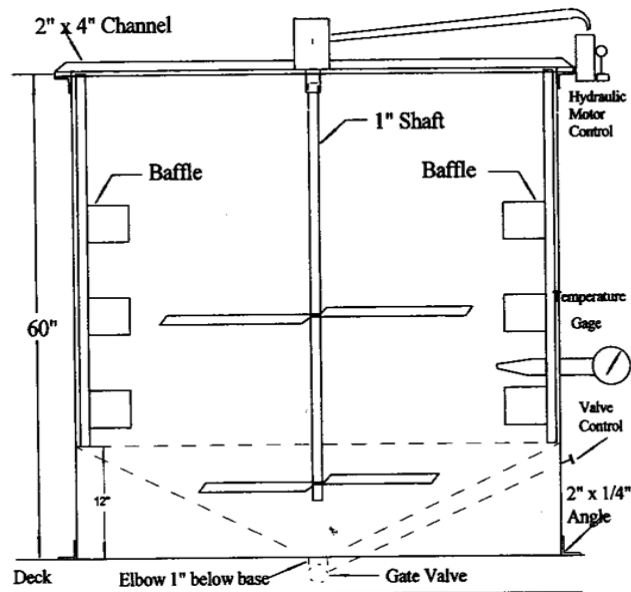


Figure 2-2: Reactor design for transesterification process

Some feedstocks must be pretreated before they can go through the transesterification process. Feedstocks with more than 4% free fatty acids, which include inedible animal fats and recycled greases, must be pretreated in an acid esterification process. In this step, the feedstock is reacted with an alcohol (like ethanol) in the presence of a strong acid catalyst (sulfuric acid), converting the free fatty acids into biodiesel. The remaining triglycerides are converted to biodiesel in the transesterification reaction. Through this reaction, the oil is contacted with an excess of ethanol forming the ethyl esters of the fatty acids of palm oil (biodiesel).

Generally, the main reaction for converting oil to biodiesel is called transesterification.. The transesterification process of reaction an alcohol (like ethanol) with the triglyceride oils contained in vegetable oils, animal fats, or recycled greases, forming fatty acid alkyl esters (biodiesel) and glycerin. The reaction requires heat and a strong base catalyst. It is in principle, the action of one alcohol displacing another from an ester, referred to as alcoholysis (cleavage by an alcohol). Through this reaction, the oil is contacted with an excess of ethanol forming the ethyl esters of the fatty acids of palm oil (biodiesel). An excess of ethanol is required to favour the direct reaction leading to an increased conversion. Thus, an oil: ethanol molar ratio of 1:6

were recommended by Marchetti, Miguel and Errazu (2007); Van Gerpen (2005). The simplified transesterification reaction is shown in figure 2.3 below.

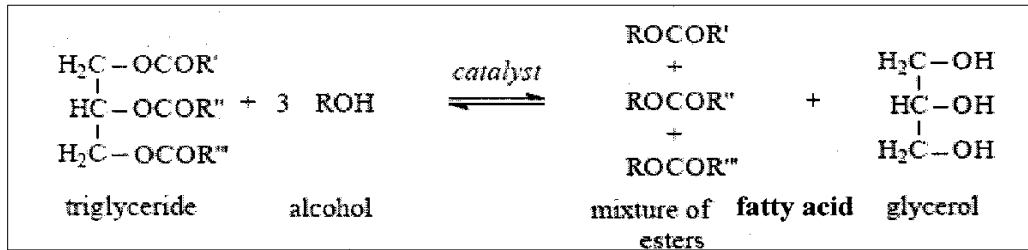


Figure 2-3: Simplified transesterification reaction

2.2.3.1 Mechanism of transesterification

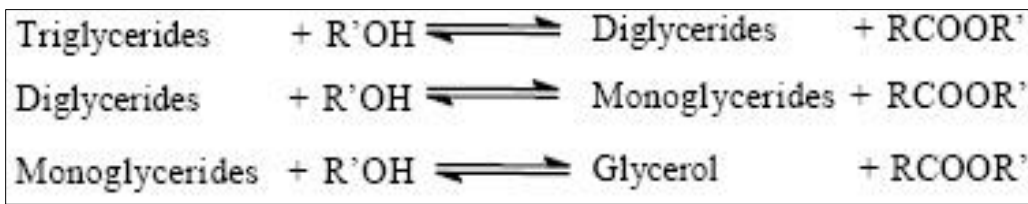


Figure 2-4: Summarization the mechanism of transesterification

Figure 2.3 summarized the mechanism of transesterification and figure 2.4 describe detail mechanism of the transesterification. Transesterification consists of a sequence of three consecutive reversible reactions. The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and finally monoglycerides into glycerol, yielding one ester molecule from each glyceride at each step. The reactions are reversible, although the equilibrium lies towards the production of fatty acid esters and glycerol (Ma F., Hanna M. A., 1999, Meher L.C. *et al.*, 2006).

The detail mechanism of transesterification is described as Figure 2.5

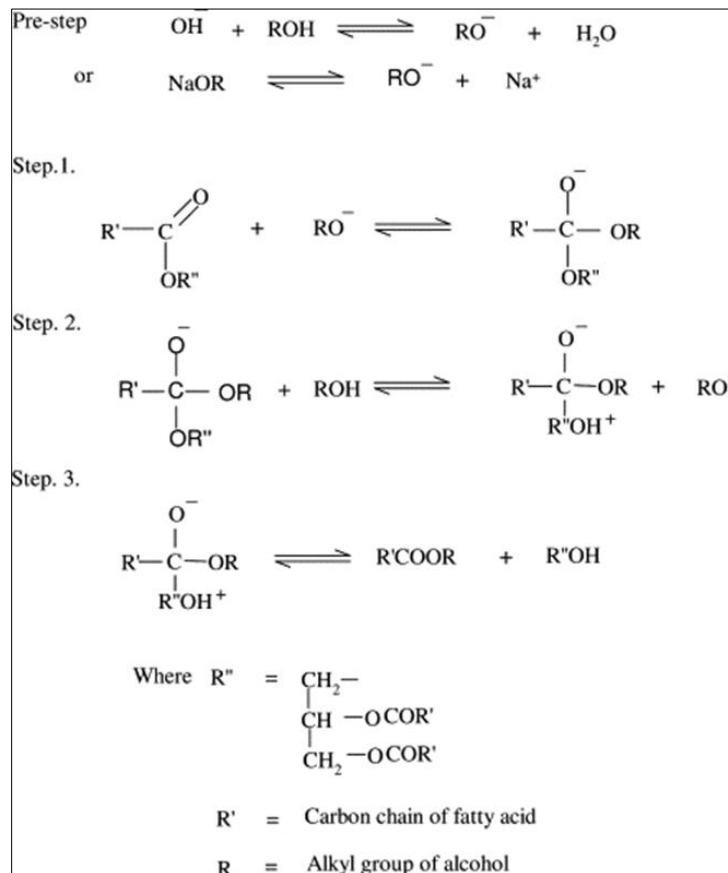


Figure 2-5: The detail mechanism of transesterification

2.2.3.2 Principle of kinetics

Derivation of the kinetics of a reaction is based upon a few generally accepted principles. The main ones are presented here, for use in the succeeding chapters. Chemical reactions are classified as either irreversible or reversible. An irreversible reaction proceeds in only one direction, which by convention is assigned to be from left to right: A reversible reaction can proceed in either direction:



This shows the conversion between an alcohol and the hydroxide base on the left, and alkoxide and water on the right. Alkoxide is formed when the hydroxide hydrogen of an alcohol is

removed by a base. This reaction can proceed in either direction. The forward rate is governed by the rate constant k_f , while the rate of the reverse reaction is governed by k_r . With reversible reactions, it is important to control the conditions of the reaction to favor the desired direction of conversion. Kinetics describes the rate of chemical reactions. Rate equations are typically written in terms of the concentrations of the reactants, like:

$$-d(TG)/dt = k [TG]^2 \quad (2.2)$$

In words, this equation says that the rate of disappearance of triglycerides is proportional to the square of the molar concentration of triglycerides. This rate expression appeared in a recent paper (Darnoko 2000), it is not the expression used in the model described here. Rate equations can be obtained by application of the law of mass action (LMA), which relates the rate of reaction to the concentrations of reactants. For example, LMA applied to Equation (2.2) produces the rate expression

$$dW/dt = k_{12} [FFA]_1 [OH^-]_1 \quad (2.3)$$

Under LMA, the rate of reaction in a given direction is proportional to the products of the reactant concentrations, each raised to the power of its coefficient in the reaction. The law of mass action only applies to elementary reactions, those which reflect the mechanism at the molecular level, and which occur as a single event. Even with simplicity tests, the order of reactions predicted by LMA should be verified by experiment. When a reversible reaction proceeds at the same rate in the forward and reverse directions, it is said to be in equilibrium. The relative proportions of the reactants are given by the equilibrium constant. The equilibrium condition for Equation (2.3) is given by

$$K = k_1/k_2 = [RO^-][H_2O]/[ROH][OH^-] \quad (2.4)$$

This reaction occurs in three steps:



Where TG means triglycerides, DG means diglycerides, MG means monoglycerides, G means glycerol, ROH means alcohol, and E means alkyl ester. The catalyst is usually either potassium hydroxide (KOH), or sodium hydroxide (NaOH). When the catalyst dissolves in the alcohol, it forms an ionic solution, in which the K^+ or Na^+ ions and the OH^- ions are not directly bound to each other. The active ingredient is the hydroxide ion, OH^- . When describing chemical reactions and rate equations, the K^+ or Na^+ ions are never written out explicitly.

2.2.3.3 Reactor optimization

The three main factors that drive the conversion of triglycerides into fatty acid methyl esters (FAEE) were studied according to a full factorial design at two levels. These factors were catalyst concentration, temperature and reaction time. Several parameters affect the transesterification: catalyst concentration, ethanol concentration, temperature, reaction time, pressure and the type of oil because of different content of triglycerides and phospholipids. In this study three of the most important parameters which affect the yield of the first transesterification reaction were tested, i.e. catalyst concentration, temperature and time of reaction. Moreover, these are the easiest factors which can be carefully controlled during the industrial production. All the tests were performed by using rapeseed oil at atmospheric pressure, since the transesterification proceeds very fast even at low pressure: this avoids the increase of costs both in terms of equipment and energy consumption. From a stoichiometric point of view three moles of ethanol are required for each mole of triglyceride: however, in order to maximize ester production, a greater molar ratio is employed, usually the double.

2.2.3.4 Batch and continuous type of reactor

A kinetic model was employed to represent biodiesel production via transesterification of vegetable oils. Reaction rate constants found in the open literature were used in order to compare the behaviour of batch and continuous processes. A single continuous stirred tank reactor (CSTR) under the usual operation conditions was not capable of achieving the same productivity as a batch process. However, when reactors in series were used, the continuous process presented a behaviour similar to batch processes. As a result, it was evidenced that a series of CSTRs can be an industrially feasible choice for replacing batch transesterification reactors in large scale biodiesel plants. Further, it was shown that the loss in

productivity caused by changing from batch to continuous process can be compensated by means of using higher catalyst concentrations. Nevertheless, it was the enlarging interest from governments, regulatory agencies and general public in the field of renewable fuels which made researchers from all over the world to look for better ways of understanding and optimizing the production of fuels derived from vegetable oils. The proposition of a representative kinetic model has been, and still is, a great part of this task.

The majority of studies in transesterification of vegetable oils available with batch processes. However, batch processes suffer several disadvantages compared to continuous processes: they require larger reactors volumes and hence higher capital investment; they are inherently less efficient due to their start-up and shut-down nature; there are batch to batch variations in the quality of the products; and labour costs are higher (Darnoko and Cheryan, 2000). Facing those problems and motivated by the needs to increase its production, the biodiesel industry was obliged to develop large scale continuous processes.

Higher molar ratios of alcohol to oil and higher catalyst concentrations both resulted in higher conversions. Higher mixing intensities likewise had favorable effects. According to the authors, however, excessive mixing created additional mass transfer resistances, decreasing the conversion. The effect of flow rate was also investigated and the overall conversion was not significantly affected

Darnoko and Cheryan (2000) studied the influence of residence time in a continuous stirred tank reactor (CSTR). For the data presented there, the optimal residence time was 60 min. The authors stated that higher residence times could shift the reaction equilibrium to the left thus reducing the overall conversion. Recently, researches on continuous biodiesel production have been focusing on novel reactors and new processing technologies.

In large scale plants, transesterification reactions are generally carried out in one or a series of CSTRs, either with or without intermediate removal of glycerine. Since operational parameters are most often selected based on batch experiments, they usually have to be adjusted for continuous operation. Due to this fact, the optimum operating conditions are not known when