PRODUCTION OF BIODIESEL FROM JATROPHA C. OIL USING KOH AND *LIPASE CANDIDA R.* IN AN AIRLIFT REACTOR

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DEGREE OF CHEMICAL ENGINEERING

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JUDUL   **PRODUCTION OF BIODIESEL FROM JATROPHA C. OIL USING**

         KOH AND LIPASE C.R IN AIRLIFT REACTOR

SESI PENGAJIAN   :   __2010/2011__

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PRODUCTION OF BIODIESEL FROM JATROPHA C. OIL USING KOH AND *LIPASE CANDIDA R.* IN AN AIRLIFT REACTOR

LIYANA BT AMER SHAH

**A thesis submitted in fulfillment
of the requirements for the award of the Degree of
Bachelor of Chemical Engineering (Biotechnology)**

**Faculty of Chemical & Natural Resources Engineering
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DECEMBER 2010

I declare that this thesis entitled "Production of Biodiesel from *Jatropha C*. oil using KOH and *Lipase Candida R*. in an Airlift Reactor" is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree."

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DEDICATION

Special dedication to all my friends,

My supervisor, Dr. Ir Said Nurdin, other lecturer,

FKKSA staffs and my beloved family.

For all your support, care, motivation and believe in me

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ABSTRACT

Biodiesel was one of the alternatives fuels to fuel the vehicle since world petroleum depleted. Production of biodiesel from jatropha oil was attractive option compared to other edible oil such canola oil because it has no competed with food consumption issue. This research objective was to produce biodiesel from *Jatropha Curcas L.* using KOH and *Lipase Candida Rugosa* catalyst and to investigate the effect of reaction time, reaction temperature and methanol/oil ratio to biodiesel production. Two-stage transesterification method was used for KOH catalyst reaction while one-stage transesterification for biocatalyst reaction. Two-stage transesterfication method was the suitable method used to reduce high free fatty acid content in jatropha oil and increase the biodiesel yield. Without acid treatment in two-stage transesterification process, triglycerides tend to go through saponification reaction which produce soap rather than biodiesel. Methanol was used as solvent in both methods due to it short chain characteristic that can produce higher result than other type of alcohol. As a conclusion, biodiesel has been successfully produced from jatropha oil using KOH and Lipase Candida Rugosa enzyme and resulted 98% and 4% biodiesel yield respectively. The highest biodiesel production was obtained at 65°C at 1 hour of reaction and 6:1 methanol/oil ratio.

ABSTRAK

Biodiesel adalah salah satu alternatif sumber bahan bakar untuk kenderaan semenjak simpanan petroleum dunia berkurangan.Penghasilan biodiesel daripada minyak buah jarak merupakan pilihan yang menarik dibandingkan dengan minyak sayuran yang lain seperti minyak jagung kerana ia tidak mengalami persaingan dengan isu sumber makanan. Kajian ini dilakukan untuk menghasilkan biodiesel daripada minyak buah jarak jenis Curcas Lineus dengan mengunakan Kalium hyrodsida dan Lipase sebagai pemangkin. Dua peringkat transester proses digunalkan untuk tindak balas pemangkin Kalium hydrosida, manakala satu peringkat transester process untuk tindak balas pemangkin Lipase. Dua peringkat transester process penting untuk mengurangkan jumlah lemak tepu yang terdapat di dalam minyak buah jarak sekaligus meningkatkan penghasilan biodiesel. Tanpa penggunaan acid dalam transester proses dua peringkat, minyak buah jarak akan menghasilkan lebih banyak sabun berbanding biodiesel. Methanol digunakan sebagai pelarut di dalam kajian ini kerana rangkain karbonny yang pendek mampu meningkatkan penghasilan biodiesel berbanding jenis alcohol yang lain. Kesimpulannya, biodiesel telah berjaya dihasilkan daripada minyak buah jarak dengan mengunakan Kalium hydrosida dan Lipase sebagai pemangkin. Dengan menggunakan Kalium hydrosida 98% biodiesel telah terhasil manakala hanya 4% biodiesel terhasil hasil daripada penggunaan pemangkin Lipase. Jumlah biodiesel yang paling banyak dihasilkan pada suhu 65°C dalam masa 1 jam dan jumlah methanol kepada minyak buah jarak ialah 6:1.

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LIST OF SYMBOLS/ABBREVIATIONS

KOH	Potassium Hydroxide
°C	Degree celcius
FKKSA	Fakulti Kejuruteraan Kimia & Sumber Asli
µm	Micrometer
Wt%	Weight percent
GC	Gas Chromatography
MJ/m3	Mega joule per meter cube
Kg/m3	Kilogram per meter cube
ppm	Part per million
Et al	All other
LCR	*Lipase Candida Rugosa*
PBR	Packed Bed Reactor
MP	Methly Palmitate
MS	Methyl Stearate
H_2SO_4	Sulphuric Acid

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Biodiesel was one of the alternatives fuels to fuel the vehicle. Biodiesel was introduced to the world by Rudolph Diesel, a Germany Engineer on 1895which transform peanut oil to biodiesel (Demirbas, 2006) but, at that time the petroleum diesel based fuel still abundant thus make biodiesel fact hidden. After a few years later in 1970s, the world petroleum reserves depleted (Canakci, 2005) and the earth start fighting with the environmental problems. This make biodiesel was taken into consideration as one of the efficient alternatives fuel. Biodiesel was chosen as the alternative because it properties differ a bit from conventional diesel depended on the oil feedstock and alcohol used but very close to diesel fuel (Mittelbach et. al., 1992) Besides, biodiesel promising better advantages from petroleum based diesel in several aspects because it was renewable and environment friendly characteristics.

Currently, biodiesel is produced commercially in Europe and USA to reduce air pollution and the emission of greenhouse gas (Huofang, 2008). The global production of biodiesel had increased from 0.5 billion liters in a997 to 1.8 billion liters in 2003 (Demirbas, 2006).

Biodiesel was produced by the transesterification process of vegetable oil or animal fats with alcohol such methanol and ethanol (Knothe et. al., 2006). Biodiesel production process is sensitive to the quality of the feedstock requiring vegetable oil or animal fats with very low amount of FFA. The used of high quality feedstock contributed 80-88% of the overall production cost (Zhang., 2003). The most common feedstock for biodiesel is edible oil such as soybean, rapeseed, canola, sunflower, palm, coconut and even corn oil (Mondala, 2008).

Most of biodiesel was produced from edible oil but, the food competing issues with edible oil make non-edible oil was attractive. Jatropha oil is one of the non-edible oil. Jatropha was suitable raw material for biodiesel production since it can be used in cooking besides, have similar free fatty acid composition with other edible oil (Shah, 2004).

In biodiesel production there is several transesterification methods to converted vegetable oil into biodiesel. Since jatropha oil content high free fatty acids, two-step methanolysis method is more suitable which can reduced free fatty acid content before esterification process (Tiwari, 2007).

1.2   Problem Statement

In this study, jatropha curcas L. was selected as raw material for biodiesel production because the poison characteristic of jatropha oil which makes it have no competing issue compared to other edible oil. Besides, it was easy to grow in tropical and sub-tropical climate such Malaysia.

Most of biodiesel production used batch reactor with mechanical stirrer. But the suitable reactor for biodiesel production still has been searching in order to obtain the maximum product yield and reduce the biodiesel production cost.

The world demands for biodiesel keep increasing year by year this make researcher still searching the optimum parameter to obtain high yield, high quality and comparable biodiesel fuel with petroleum-based diesel.

Generally, the percentage of biodiesel yield from jatropha oil is still low due to the high free fatty acid content in jatropha oil.

1.3   Objectives

1. To produce biodiesel from Jatropha Curcas L. using KOH and Lipase Candida R.
2. To investigate the effect of temperature, reaction time, methanol-oil ratio on the biodiesel yield.

1.4   Scope of Research

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

1. Producing biodiesel from *Jatropha Curcas L.* using KOH and *Lipase Candida R.* in airlift reactor.
2. Evaluating the selected parameter for both KOH and Lipase catalyst (methanol/oil ratio, reaction temperature and reaction time).
3. Analyze the biodiesel produce using Gas Chromatography equipment.

CHAPTER 2

LITERATURE REVIEW

2.1   Biodiesel

Biodiesel refers to a vegetable oil- or animal fat-based diesel fuel consisting of long-chain alkyl (methyl, propyl or ethyl) esters. It produced from transesterification of vegetable oil or animal fats with alcohol. Biodiesel can be used alone or mixed with petroleum-based diesel as an alternative efficient fuel (Gerpen, 2005) and can be used in any diesel engine without modification (Progress and recent trends in biodiesel fuels., 2009). Biodiesel can be used as pure fuel or blended at any level with petroleum-based diesel for use by diesel engines. The most common biodiesel blends are B2 (2% biodiesel and 98% petroleum diesel), B5 (5% biodiesel and 95% petroleum diesel), and B20 (20% biodiesel and 80% petroleum diesel) (Balat, 2010).

Biodiesel have attractive characteristics compared to petroleum-based diesel because it is biodegradable, non-toxic, renewable and has reduced emission of CO, SO2, particulate matter, volatile organic compound and unburned hydrocarbons as compared to conventional diesel (Benjamin, 2008). But biodiesel also have several disadvantages such have high viscosity of vegetable oils as compared to petroleum-based diesel at 40°C leads to unfavorable pumping and spray characteristics (Sinha, 2008). As the result, it cause poor fuel atomization incomplete combustion, and carbon deposition on the injector and valve seats which give serious engine fouling (Kumar, 2010). Biodiesel offer safety benefits over diesel fuel because it is much less combustible, with a flash

point greater than 423 K compared to 350 K for petroleum-based diesel fuel (Balat, 2008).

2.1.1 Biodiesel Characteristics

Biodiesel is a light to dark yellow liquid. It is immiscible with water, has a high boiling point and low vapor pressure. Typical methyl ester has flash point around 150°C making it non-flammable. Selected properties of biodiesel compared to biodiesel fuels are shown in table below

Table: Specification of diesel and biodiesel fuel

Fuel property	Diesel	Biodiesel
Fuel standard	ASTM D975	ASTM PS 121
Fuel composition	C10-C21 HC	C12-C22 FAME
Lower heating value (MJ/m^3)	36.6 x 10^3	32.6 x 10^3
Kinematic Viscosity at 40°C (mm^2/s)	1.3-4.1	1.9-6.0
Specific gravity at 15.5°C	0.85	0.88
Density at 15°C (kg/m^3)	848	878
Water (ppm by wt)	161	0.05 % max
Carbon (wt %)	87	77
Hydrogen (wt %)	13	12
Oxygen (wt %)	0	11
Sulfur (wt %)	0.05 max	0.0-0.0024
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	40-55	48-65
Stoichiometric air/fuel ratio (wt/wt)	15	13.8

2.1.2 Biodiesel Standard

Biodiesel must meet American Society of Testing and Materials (ASTM) specifications. Standard specification for biodiesel fuel (B100) blend stock for distillate fuel is shown in Table 2.1. The purpose of this standard is to have biodiesel meet the performance requirement of engines without specifying the actual composition of the fuel. This will allow biodiesel to be produce from any feedstock as long as it meets the standard.

Table 1.1: ASTM standards of maximum allowed quantities in diesel and biodiesel (ASTM D6751-02).

Property	ASTM method	Limits	Units
Flash Point	D 93	130 min	°C
Water and sediment	D 2709	0.050 max	Vol %
Kinematic Viscosity, 40°C	D 445	1.9-6.0	Mm^2/s
Sulfated ash	D 874	0.020 max	Mass %
Sulfur	D 5453	0.05 max	Mass %
Copper strip corrosion	D 130	No. 3 max	-
Cetane number	D 613	47 min	-
Cloud point	D 2500	Report	°C
Carbon residue, 100% sample	D 4530	0.05 max	Mass %
Acid number	D 664	0.80 max	Mg KOH/g
Free glycerin	D 6584	0.02 max	Mass %
Total glycerin	D 6584	0.240 max	Mass %
Phosphorus content	D 4951	0.001 max	Mass %
Distillation temperature, 1 atm	D 1160	360 max	°C

Source: http://www.astm.org

2.2   Raw Material

The most common feedstock for biodiesel is edible oil such as soybean, rapeseed, canola, sunflower, palm, coconut and even corn oil (Mondala, 2008). The efforts to find alternative vegetable oil for biodiesel production with the aim to lowering the feedstock cost often suggested the utilization of waste cooking oil or non-edible vegetable oil which containing high amount of free fatty acid (FFA) (Nestor et. al., 2008).

Transesterification of rapeseed oil with candida rugosa lipase showed more than 99% of conversion (Wu, 1996). Biodiesel produced from soybean oil using rhizopus oryzae lipase resulted in 80-90% of conversion (Kaieda, 1999) and of sunflower oil with pseudomonas fluorescens lipase led to almost complete conversion of oil into biodiesel and glycerol (Iso, 2001).

2.2.1   Edible Oil

Biodiesel has been mainly produced from edible vegetable oils all over the world. More than 95% of global biodiesel production is made from edible vegetable oils (Demirbas, 2008).

2.2.1.1 Cottonseed Oil

Cottonseed oil was converted to biodiesel by alkali-catalyzed transesterification reaction at 0.75% catalyst concentration, 65°C reaction temperature, 6:1 methanol to oil molar ratio and 600 rpm of agitation speed. This optimum condition produced 96.9% of methyl ester.

2.2.2   Non-Edible Oil

The continuous and large-scale production of biodiesel from edible oils has recently been of great concern because they compete with food materials – the food versus fuel dispute. There are concerns that biodiesel feedstock may compete with food supply in the long-term (Refaat, 2009). Hence, use of non-edible vegetable oils when compared with edible oils is very significant in developing countries because of the tremendous demand for edible oils as food, and they are far too expensive to be used as fuel at present (Pramanik, 2003)

2.2.2.1   Cooking Waste Oil

Due to the high cost of the fresh vegetable oil, waste cooking oil attracted researcher to produce biodiesel from waste cooking oil because it is available with relatively cheap price (Nisworo, 2006: Zhang et. al., 2003). Although, the use of waste oils can lower the feedstock cost significantly, complicated procedures are needed to remove impurities, resulting in high operating costs (Al-Widyan, Bioresource Technology)

2.2.2.2   Jatropha Oil

Jatropha oil was extracted from jatropha plant. Jatropha Curcas Lineus was a natural wild plant, can grow without irrigation under a broad spectrum of rainfall (Foidl, 1996). Jatropha curcas is a genus comprising 70 species growing in tropical and sub-tropical country. It grows rapidly, takes approximately 2-3 years to reach maturity and it has lifespan in excess of 30 years. Jatropha contain high –seed yield and high oil content (Wood, 2005). The FFA composition in jatropha oil is similar to other edible oils but the presence of some anti-nutritional factors such as toxic phorbol ester makes this oil unsuitable for cooking purposes (Shah, 2004).

Jatropha pressed cake can be used as fertilizer and its organic waste products can be digested to produce biogas methane (Staubmann, 1997).

2.3   Catalyst

In conventional processes, biodiesel was produced by the transesterification of oils with alcohol in the presence of catalysts such as alkalis (KOH, NaOH) or their corresponding alkoxides (Jitputti, 2006).

Chemical catalysts including alkalis have been employed most widely since they give a high conversion of triglycerides to methyl esters in a short reaction time. However, chemical catalyst used in biodiesel production have several drawbacks including the difficulty of recycling glycerol, the need to eliminate the catalyst and salt leading to development of alternative pathways (Zhang, 2003). To overcome these problems an enzymatic process using extracellular or intracellular lipase catalyst has been developed (Kaieda, 1999). Biocatalyst is expensive than chemical catalyst but, reduced chemical consumption and waste water treatment cost in biodiesel production.

Biocatalyst is critically influenced by some parameters in biodiesel production such enzyme concentration, oil to alcohol ratio, water concentration, reaction temperature, reaction time and PH (Salis, 2005). Also, the enzymatic methylation do not present consistent conversions (Chen, 2010).

2.3.1 Biocatalyst

Lipases (acylglycerol acylhydrolases) are enzyme that hydrolyzes the ester bonds in tri-, di-, and monoacylglcerols (Pizarro et. al., 2003). Lipases are versatile catalysts and reaction can be carried out with or without organic solvent. Recently, lipase catalyzed production of biodiesel from sunflower (Lipase catalyzed alcoholysis of sunflower oil., 1990), soybean oil

Several have reported that the commercially available Novozym 435 (Candida Antartica Lipase B immobilized on acrylic resin) was the most effective catalyst among tested lipases for the production of biodiesel (Noda, 1999). Later, the other researcher found that the whole cell of lipase producing Rhizopus Oryzae (ROL) immobilized onto biomass support particles made of reticulated polyurethane foam can catalyst the aoholysis of jatropha oil more effectively than novozym 435 (Akihiko, 2007).

Of the four lipases that were tested inclusing Novozym 435, lipase candida rugosa (CR) resulted in the highest yield of mono alkyl ester. (Pirajan, 2010)

2.3.2 Chemical Catalyst

Cvengro and Povaz have used 4% of NaOH as a catalyst to produce biodiesel by using two-stage low temperature trans-esterification of cold pressed rapeseed oil with methanol at temperature up to 70°C (Kaieda, 1999).

Table: Comparison between alkali catalysis and lipase-catalysis methods for biodiesel fuel production (Fukuda, 2001)

	Alkali-catalysis	Lipase-catalysis
Reaction Temperature (K)	333-338	303-313
FFA in raw materials	Saponified products	Methyl esters
Water in raw materials	Interference in reaction	No Interference
Yield of methyl esters	Normal	Higher
Recovery of glycerol	Difficult	Easy
Purification of methyl ester	Washing	None
Production of catalyst	Cheap	Expensive

2.4   Reactor

A packed-bed reactor (PBR) system using fungus whole-cell biocatalyst was developed for biodiesel fuel production by plant oil methanolysis A high methyl ester content of over 90% was achieved at a flow rate of 25 l/h in the first cycle of repeated batch methanolysis and a high value of around 80% was maintained even after the tenth cycle (Shinji, 2006).

Most of the biodiesel production was done in batch reactor. Airlift reactors are used in many chemical and biochemical industries due to their simple construction, low power requirements and low shear (Cristi and Moo-Young, 1987). Airlift reactor used pressure different to force the fluid from the bottom of downcomer towards the riser which create liquid mixing (Merchuk, 1997). Other alternative was ultrasonic radiation which can effectively promote transesterification reaction of crude oil and enormously reduce the reaction times (Zeng, 2008).

2.5   Transesterification

Transesterification ia a most common and well established chemical reaction in which a primary alcohol reacts with the triglycerides in presence of a catalyst to form glycderol and methyl ester (Lotero, 2006). Transesterification process was shown below

Triglycerides + methanol (alcohol) → biodiesel (methyl ester) + glycerol
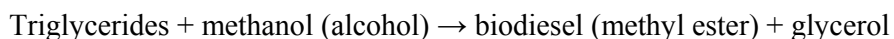
Transesterification reaction process can be initiate using several of catalyst such alkali, acid and enzyme (Li, 2010). The transesterification process in industry is usually carried out by heating an excess of the alcohol with vegetable oils under different reaction conditions in the presence of an inorganic catalyst (Mittelbach, 1990)

2.5.1 Acid/Alkali-Catalyzed Transesterification

Acid or alkali catalyzed transesterification process is the conventional method to produced biodiesel from vegetable oil or animal fats. The acid catalyst transesterification of soybean conversion reached 98.4% at the methanol to oil ratio of 30:1 with sulphuric acid as catalyst at 60°C (Freedman, 1984). For FFA jatropha oil transesterification process foam saponication reaction and the separation of the products will be exceedingly difficult, and as a result it has low yield of biodiesel product (Berchmans, 2008). Saponification reaction was shown below

Vegetable oils or fats + NaOH -----→ RCOONa + Glycerin

The acid-catalyzed esterification of the oil is an alternative (Crabbe at al., 2001), but it is much slower than the base-catalyzed transesterification reaction. Therefore, two-step transesterification process was investigated for feedstock which having the high FFA content (Ghadge, 2005).

Table : Summary of several studies on acid catalyst

Catalyst	Oil	Catalyst (wt %)	Temperature (°C)	Reaction Time (h)	Yield (%)	Refferences
H_2SO_4	Soybean	1	65	69	90	(Freedman, 1984)
HCl	Soybean	10	70	45	65	(Rachmaniah, 2004)
AL_2O_3	Jatropha	6	70	6	84	(Amish, 2008)

2.5.2 Two-Stage Transesterification

A pre-esterification operation was applied to eliminate FFAs by reacting the oil with methanol in the presence of an acid catalyst. The process can be describes as below,

Pre-esterificatin → purification → transesterification → phase separation

Pre-esterification catalyzed by homogeneous acids, such as sulfuric acid, phosphorous acid, or sulfonic acid, is a conventional and useful method to reduce the content of FFAs, which can turn the raw oils transesterificable by an alkali catalyst and convert FFAs to valuable fatty acidmethyl esters (FAME) (Ghadge, 2005). The two-stage transesterification process reduced FFA content from 14% to less than 1% at 60°C with H2SO4 for 88 min reaction time at the first step, and produced more than 99% biodiesel yield at 60°C with KOH for 24 min. (Tiwari, 2007)

2.5.3 Supercritical Transesterification

For transesterification in supercritical methanol or ethanol, no catalyst is required and nearly complete conversions can be achieved in very short periods (Madras, 2004). Supercritical method produced biodiesel from vegetable oil under high temperature and pressure. It was investigated that the critical temperature and the critical pressure of ethanol were 516.2 K and 6.4 MPa, respectively (Balat, 2008). It was observed that increasing reaction temperature, especially for supercritical temperature had an influence on ester conversion.

2.6 Alcohol

Alcohol played an important role in biodiesel production. The transesterification process is reversible reaction thus; excess alcohol was required to shift the equilibrium to product side and raise the product yield and allow the phase separation from the glycerol to be formed (Srivastava, 2000). The minimum alcohol to oil ratio must be 2:1 which excess alcohol from oil. Frequently used alcohol is methanol and ethanol because of their low cost, physical and chemical advantages shortest chain alcohol.

The molar ratio of methanol to oil at 6:1 or higher generally gives the maximum yield (higher than 98 wt %) . Lower molar ratios required a longer time to complete the reaction. With higher molar ratio, production is increased but the recovery of biodiesel is decreased due to poor separation of glycerol (Balat, 2010).

Generally, short chain alcohols such as methanol, ethanol, propanol and butanol can be used in the transesterification reaction to obtain high methyl ester yields. Using t-butanol as a solvent in the enzymatic process improves the solubility of methanol in oil and reduces the inhibitory effect of glycerol (Royon, 2007).

Excess alcohol levels may inhibit the enzyme activity and thereby decrease it catalytic activity toward the transesterification reaction (Moreno, 2010). Among alcohol tested, methanol is most active for production of biodiesel from jatropha oil and the activities of lipase decrease with the increase in alcohol chain length (Akihiko et. al., 2007).

CHAPTER 3

METHODOLOGY

3.1   Raw Material & Equipment

The raw material in this research is Jatropha Curcas L.oil. The extracted oil was bought from Bionass office at Kampung Baru, Kuala Lumpur.

3.1.1   Chemical

3.1.1.1 Sulphuric Acid (H_2SO_4)

H_2SO_4 was used as acid-catalyzed in first step of transesterification process to reduce the free fatty acid content in jatropha oil. The concentration of H_2SO_4 used in this research was constant at 3% (wt %) from jatropha oil used in every experiment. Industrial grade of H_2SO_4 was used in order to make sure the product is high quality. The H_2SO_4 was supplied by R & M chemical Malaysia to FKKSA laboratory.

3.1.1.2 Potassium Hydroxide (KOH)

KOH was used as base-catalyzed in second step transesterification process that produced biodiesel and glycerol. KOH concentration in this research was also constant at 3% (wt %) from jatropha oil used. The KOH was supplied by R & M chemical Malaysia to FKKSA laboratory.

3.1.1.3 *Lipase Candida Rugosa*

Lipase Candida Rugosa (LCR) was used as biocatalyst at constant weight which is 1 gram for each experiment.

3.1.1.4 Methanol

Methanol was functioning as solvent in methanolysis reaction of jatropha oil. The volume of methanol used was different depend on methanol to oil ratio. Methanol was supplied by Fisher, Germany to FKKSA laboratory.

3.1.1.5 Hexane

Hexane used as solvent in preparation of Gas Chromatography (GC) samples. HPLC grade of hexane was used in order to prevent GC failure. Biodeisel was diluted to 1% in hexane before analyzed with GC. Hexane was supplied by fisher, Germany to FKKSA laboratory.

3.1.2 Apparatus

There are list of the apparatus was used in order to done this research:

    I.   Beaker (25, 100, 500 & 1000 ml)

    II.   Spatula

    III.   Glass rod

    IV.   Thermometer

    V.   Separatory Funel

    VI.   Retort Stand

    VII. Syringe

  VIII. Filter, 0.2 μm

    IX.   Dropper

    X.   Measuring Cylinder (10 & 100 ml)

    XI.   Silicon Tube

3.1.3 Equipment

There are list of equipment that was used in this experiment:

    I.   Balance

    II.   Water Bath

    III.   Air Pump

    IV.   Hot Plate

    V.   Centrifuge

    VI.   Gas Chromatography

3.1.3.1 Centrifuge Working Principle

Centrifuge machine used acceleration against gravity force by rotates the camber at the axial axis. The rotor moved by electric motor. The centrifuge works using the sedimentation principle, where the centripetal acceleration causes more dense substances to separate out along the radial direction (the bottom of the tube). By the same principle, lighter objects will move to the top (of the tube; in the rotating picture, move to the centre).
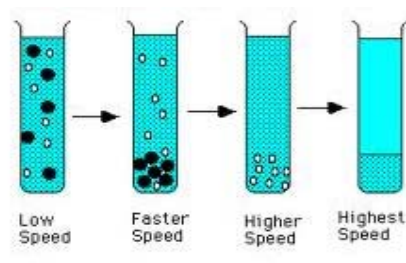

Figure 3.1: Centrifuge

Figure 3.2: Sedimentation Principle

(Source: www.wikipedia.com)

3.1.3.2 Gas Chromatography Working Principle

      Gas Chromatography (GC) is one of the common types of chromatography used in analytical chemistry for separating and analysis. GC used specially to detect the compound that can be vaporized without decomposition. Inert gas was used as moving phase such helium or an unreactive gases such nitrogen. The stationary phase is a microscopic layer of liquid or polymer on an inert solid support, inside tubing called a column. The column through which the gas phase passes is located in the oven where the temperature of the gas can be controlled.

      The function of stationary phase is to separate different components, causing each one to exit the column at a different time (retention time). As the chemicals exit the end of the column, they are detected and identified electronically. The gas chromatography separate the components of the mixture primarily based on the boiling point differences.
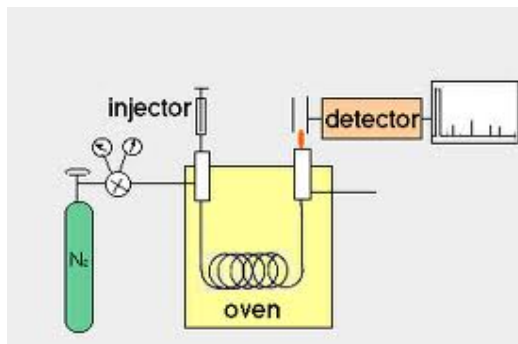

Figure 3.3: Gas Chromatography Principle

(Source: www.wikipedia.com)

3.2   Methodology

3.2.1   Two-Step Transesterification

3.2.1.1 Acid-Catalysis

Biodiesel production was started by weigh 50 gram of jatropha oil, 150 gram of methanol and 1.5 gram (3 wt %) of H_2SO_4 into three separate clean beakers. The H_2SO_4 then been poured into methanol at room temperature to avoid spark. The jatropha oil together with mix solution of methanol and H_2SO_4 then being heated up to required temperature using water bath. When all material reached the required temperature, the jatropha oil was poured into mix solution of methanol and H2SO4 and the reaction time start to be counted. The reaction was stopped at specific required time by switch off the air pump and removes the beaker from water bath. Tryglycerides then being separated from excess methanol using separator funnel and leaved for at least 24 hours. After 24 hours the two layers were formed indicated the triglycerides at bottom and excess methanol at upper layer. The triglyceride was used in the second step to produce biodiesel.

3.2.1.2 Base-Catalysis

Tryglycerides was weighted into clean beaker and heat up in the water bath at the similar temperature for the first step. Methanol was weighted according to the triglycerides also using the similar methanol to oil ratio used in the first step. In the second step, aicd-catalyst was replaced by base-catalyst which is potassium hydroxide (KOH). 3 (wt %) of KOH concentration was used. Generally, all the parameters were being kept constant as the first step. Only the parameters of the first step were changed then the second step will also change equivalently. The product from second step then was being heat-up to 110°C using hot plate to remove excess methanol and water and separate using separator funnel for 24 hours. The upper layer was the biodiesel while the bottom was glycerol. Biodiesel then being analyzed using Gas Chromatography to check the methyl ester content.

3.2.1.3 Biodiesel Analysis

Biodiesel was diluted to 1 (wt %) of concentration in hexane solvent and filtered using 0.2 µm filter before analyzed using Gas Chromatography. This procedure implemented to prevent the GC column to be block by impurities and failure.

Figure 3.4: The weighing process

Figure 3.5: Adding of H_2SO_4 into methanol in fume cupboard

Figure 3.6: Heating process in Water Bath

Figure 3.7: First step separation process

Figure 3.8: Removal of excess methanol and water process using hot plate

Figure 3.9: Second step separation process

Figure 3.10: Preparation of Gas Chromatography analysis sample

Figure 3.11: Gas Chromatography N 6890

3.2.2 Biocatalyst Transesterification

Biocatalyst transesterification process required only one step to produce biodiesel from jatropha oil. Using the similar jatropha oil and methanol weight which is 50 gram and 150 gram respectively the lipase enzyme was weighted at 1 gram. Both jatropha oil and methanol and lipase mix solution was heated up to required temperature using water bath. When they reached the temperature, jatropha oil was poured into methanol and lipase mix solution. The reaction times start to be counted. The air pump was stopped at the specific reaction time. The oil was then been put in the centrifuge to separate the catalyst from product. The oil and methanol mixture then being heated up to 110°C using hot plate to remove excess methanol and water. Biodiesel then ready to being analyzed using Gas Chromatography.

Figure 3.12: Methanol weighing Process

Figure 3.13: Lipase enzyme weighing process.

Figure 3.14: Methanol was added into heated jatropha oil process

Figure 3.15: Removal of excess methanol and water process using hot plate

Figure 3.16: Preparation of Gas Chromatography analysis sample

Figure 3.17: Gas Chromatography N 6890

CHAPTER 4

RESULT & DISCUSSION

4.1 Biodiesel Production Using KOH

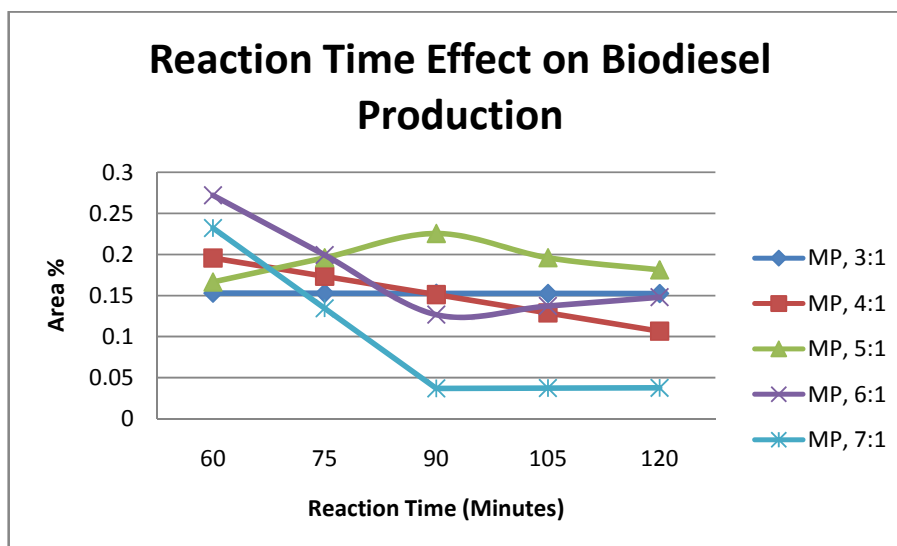### 4.1.1 The Effect of Reaction Time on Biodiesel Production Using KOH Catalyst

Figure 4.1: The reaction time effect on biodiesel yield (methyl palmitate)

The reaction time effect on biodiesel production using KOH catalyst was different due to methanol/oil ratio. Figure 4.1 show that only methanol/oil ratio 5:1 increase after 1 hour reaction while other decrease and the 6:1 ratio seem to increase

pattern at 2 hours of reaction time. The graph pattern was similar to both methyl palmitate and methyl stearate. The longer reaction times reduce the biodiesel yield because the oil was burned due to the temperature.

Reaction Time Effect on Biodiesel Production
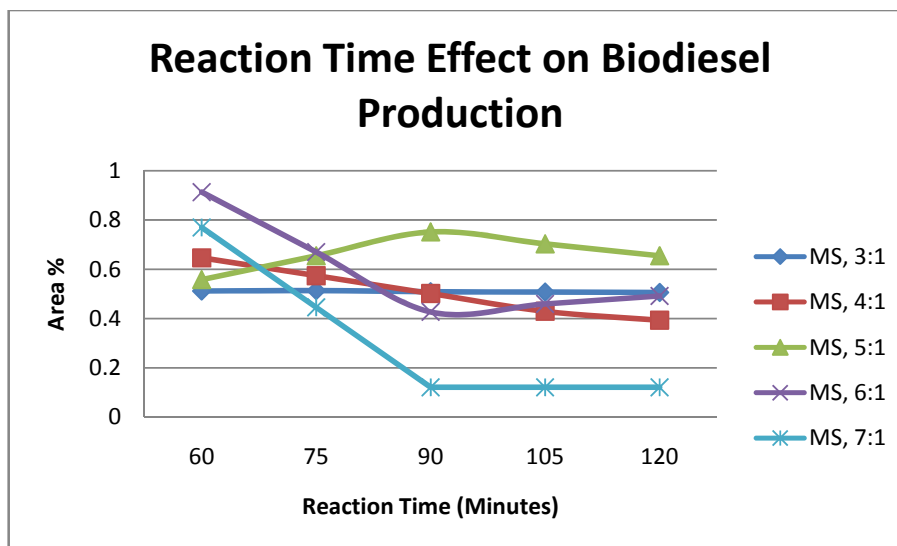
Figure 4.2: The reaction time effect on biodiesel yield (methyl stearate)

Figure 4.2 show the similar pattern with figure 4.1, only 5:1 methanol/oil ratio increase the yield while the other decrease. After minute 90, all the ratio show constant line because the longer reaction time burn the oil since the concentration of sulphuric acid in this experiment was about 3% which higher than optimum. If the concentration of sulphuric acid increases the reaction time to complete the reaction time decrease thus, longer reaction time did not help to increase the yield.

4.1.2   The Reaction Temperature Effect on Biodiesel Production Using KOH Catalyst

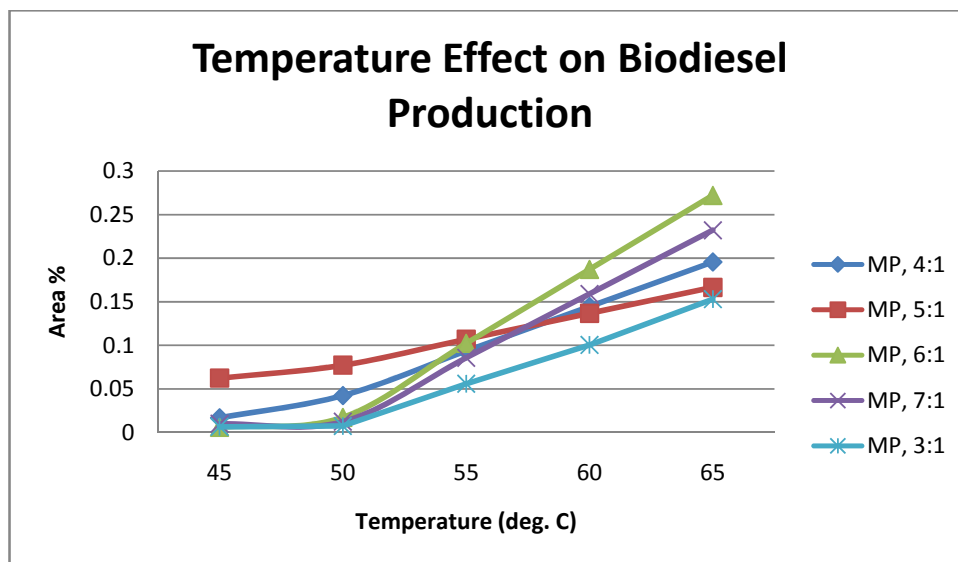Figure 4.3: The reaction temperature effect on biodiesel yield (methyl palmitate)
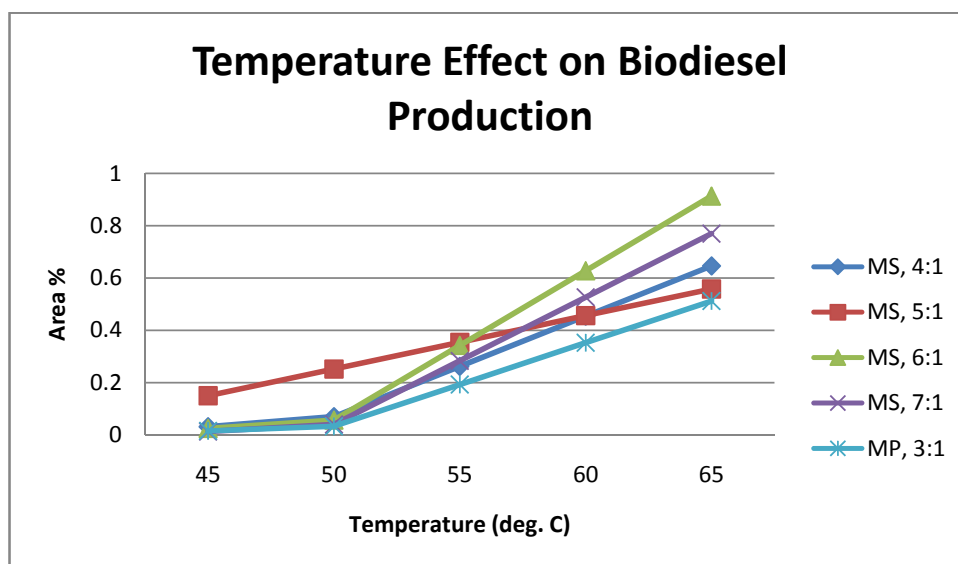

Figure 4.4: The effect of reaction temperature on biodiesel yield (methyl stearate)

Both figure 4.3 and figure 4.4 show the similar pattern of yields. Temperatures keep increase after 50 deg. Celsius. Optimum temperature for production of biodiesel using KOH is 65 deg. Celsius (Balat, 2010).

4.1.3 The Effect of Methanol/Oil Ratio on Biodiesel Production Using KOH Catalyst
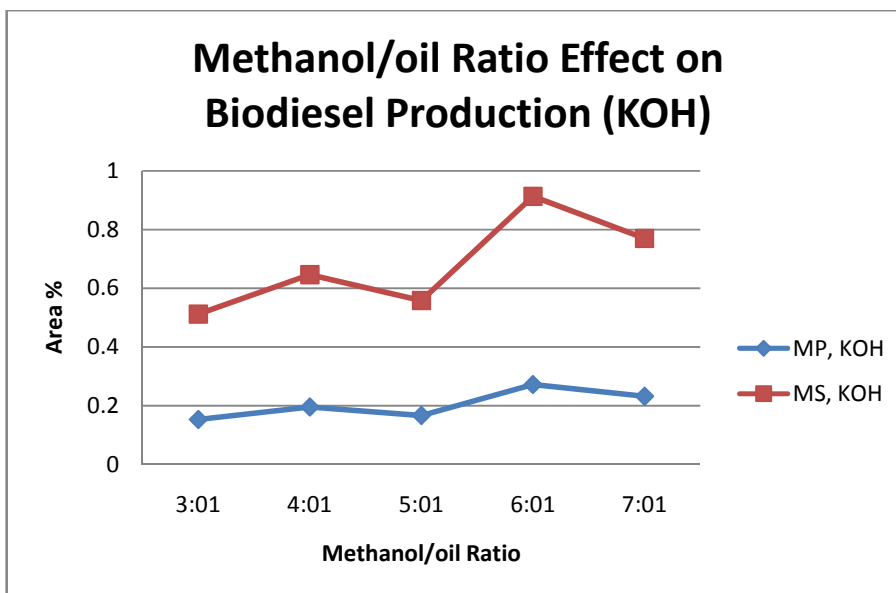
Figure 4.5: The effect of methanol/oil ratio on biodiesel yield

The methanol/oil ratio effect on biodiesel production using KOH catalyst gives inconsistent graph pattern. Even number of ratio always higher than before it odd number ratio. The transesterification process is reversible reaction thus; excess alcohol was required to shift the equilibrium to product side and raise the product yield and allow the phase separation from the glycerol to be formed (Srivastava, 2000).

The molar ratio of methanol to oil at 6:1 or higher generally gives the maximum yield (higher than 98 wt %) . Lower molar ratios required a longer time to complete the reaction. With higher molar ratio, production is increased but the recovery of biodiesel is decreased due to poor separation of glycerol (Balat, 2010).

4.2   Biodiesel Production Using Lipase Enzyme

4.2.1   The Effect of Methanol/Oil Ration on Biodiesel Production Using Lipase Enzyme
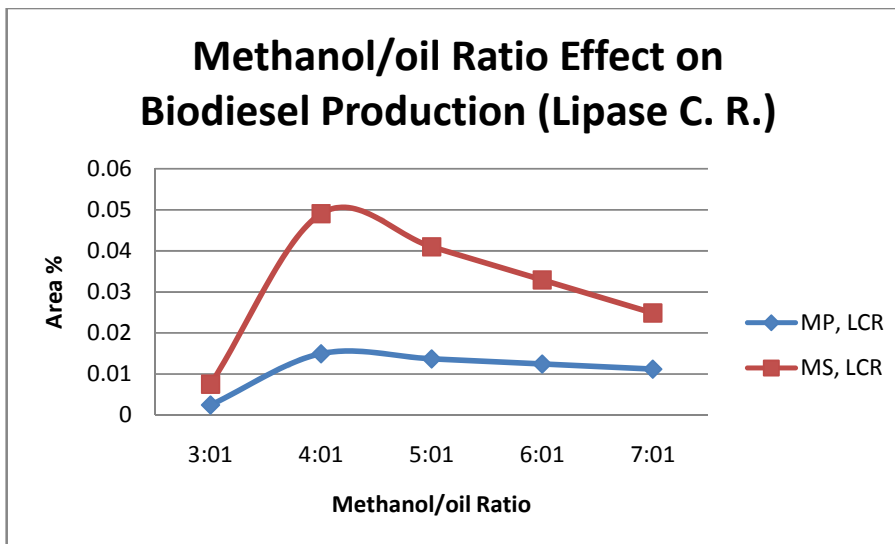
Figure 4.6: The effect of methanol/oil ratio on biodiesel yield

Methyl palmitate show higher yield than methyl stearate because the composition of methyl palmitate in biodiesel was higher than methyl stearate naturally (Balat, 2010). The 4:1 methanol/oil ratio has shown the highest yield in biodiesel production using *lipase candida rugosa.*Higher ratio than 4:1 show the decreasing pattern because the excess volume of methanol might prevent the optimum reaction for *lipase candida rugosa*

4.3 Comparison of Methanol/Oil Ratio Effect on Biodiesel Yield Produced Using KOH and Lipase Catalyst

4.3.1 Methyl Palmitate

Comparison of Methanol/oil Ratio Effect on Biodiesel Production
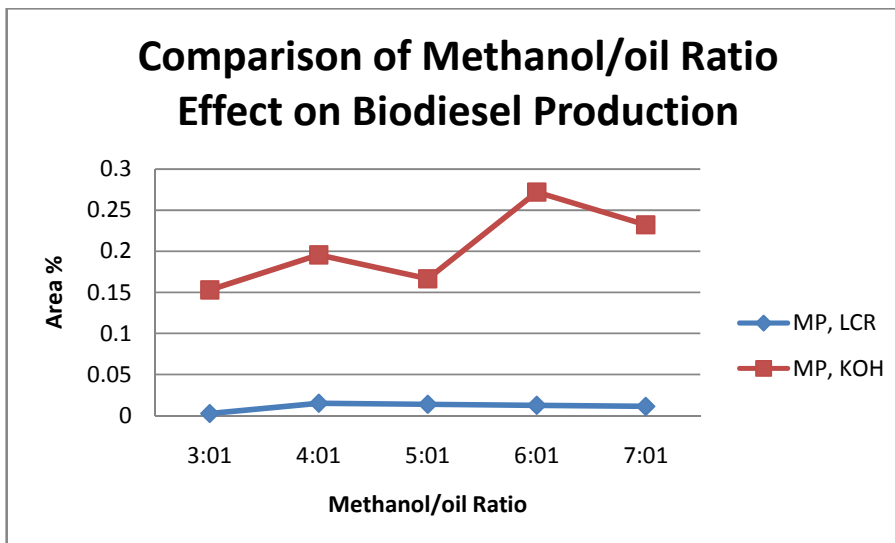
Figure 4.7: The effect of methanol/oil ratio on methyl palmitate production

4.3.2 Methly Stearate

Comparison of Methanol/oil Ratio Effect on Biodiesel Production
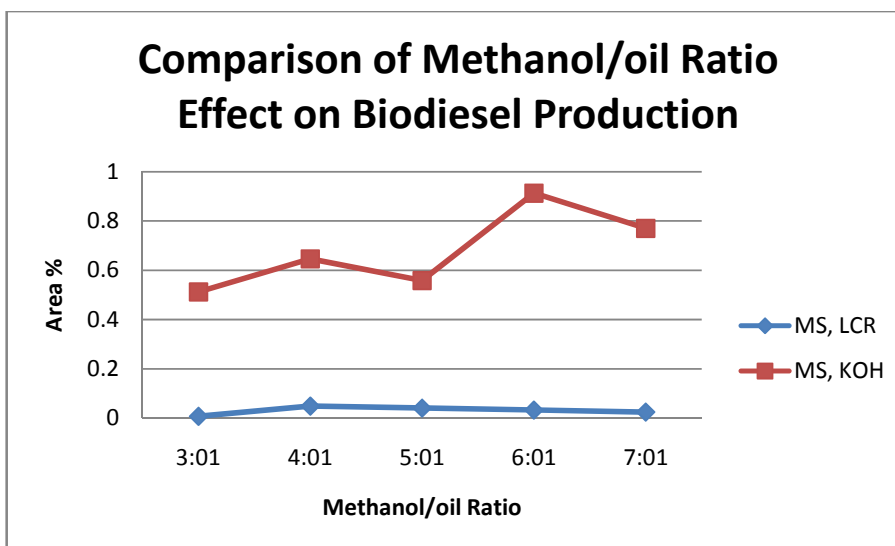
Figure 4.8: The effect of methanol/oil ratio on methyl stearate production

Both figure 4.7 and 4.8 show the different yield between methyl palmitate and methyl stearate in biodiesel using different catalysts. KOH show the faster reaction than *Lipase candida rugosa* Enzyme usually take longer reaction to give higher yield

compared than chemical catalyst. The optimum hour for *lipase candida rugosa* was reported at 86 hours to achieve higher yield which is 98% (Akihiko, 2007). KOH only take about 2 hours to complete the reaction at high yield which is about 99% (Houfang, 2009). Eventhough the chemical catalyst give faster and higher yield than enzyme but it consumed twice volume of methanol and produced hazardous waste which difficult to treat. (Balat, 2010). Enzyme used is environmental friendly thus, make enzyme still attractive to researcher.

CHAPTER 5

CONCLUSION & RECOMMENDATIONS

5.1 Conclusion

- Biodiesel has been successfully produced from Jatropha Curcas L. using KOH and Lipase Candida R. in an airlift reactor

- KOH and Lipase Candida R. catalyst resulted 98 % and 4 % biodiesel. These values shown KOH more effective than Lipase Candida R. catalyst

- Use of those catalyst and variation of reaction time, temperature and methanol/oil ratio played more roles in the biodiesel production.

- The highest biodiesel production was obtained at 65 deg C temperature, at 1 h reaction time and methanol/oil ratio 6:1

5.2   Recommendations

- Investigate on other type of reactor that result in better mixing

- Search the relationship between methanol/oil ratio and other parameters and it optimal conditions.

- Develop the research on how to reduce chemical consumption in biodiesel production and environmentally biodiesel waste.

- Find other economical, easy and time saving method to detect methyl ester content in biodiesel.

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APPENDICES

Gas Chromatography Result

Table A.1: Reaction Time Effect on Biodiesel Production (Methyl Palmitate)

Min	Ratio	3:01	4:01	5:01	6:01	7:01
60	MP	0.15289	0.1956	0.16648	0.27197	0.23209
75	MP	0.152765	0.17332	0.19599	0.19933	0.1345
90	MP	0.15264	0.15104	0.2255	0.12669	0.03692
105	MP	0.152515	0.12876	0.19599	0.1373	0.03727
120	MP	0.15239	0.10648	0.181235	0.1479	0.03761

Table A.2: Reaction Time Effect on Biodiesel Production (Methyl Stearate)

Min	Ratio	3:01	4:01	5:01	6:01	7:01
60	MS	0.51199	0.64623	0.55819	0.91306	0.76998
75	MS	0.5135	0.57398	0.6549	0.6701	0.4455
90	MS	0.50894	0.50172	0.75158	0.42723	0.12107
105	MS	0.50742	0.429465	0.70323	0.45966	0.12116
120	MS	0.50589	0.3933	0.6549	0.49208	0.12124

Table A.3: Temperature Effect on Biodiesel Production (Methyl Palmitate)

Temp	Ratio	3:01	4:01	5:01	6:01	7:01
45	MP	0.00653	0.01681	0.06235	0.00598	0.00987
50	MP	0.00748	0.04235	0.07722	0.01736	0.01236
55	MP	0.05595	0.09344	0.10698	0.10223	0.08561
60	MP	0.100442	0.14452	0.13673	0.1871	0.15885
65	MP	0.15289	0.1956	0.16648	0.27197	0.23209

Table A.4: Temperature Effect on Biodiesel Production (Methyl Stearate)

Temp	Ratio	3:01	4:01	5:01	6:01	7:01
45	MS	0.01553	0.03128	0.14986	0.02515	0.01306
50	MS	0.03326	0.06971	0.25194	0.05686	0.04009
55	MS	0.19283	0.26189	0.35403	0.34226	0.28338
60	MS	0.35241	0.45406	0.45611	0.62766	0.52668
65	MS	0.51199	0.64623	0.55819	0.91306	0.76998

Table A.5: Methanol/oil Ration Effect on Biodiesel Production (Enzyme) at 24h, 35C.

Ratio	MP	MS
3:01	0.00249	0.00753
4:01	0.01496	0.04904
5:01	0.01371	0.04098
6:01	0.01246	0.03293
7:01	0.01121	0.02487

Table A.6: Methanol/oil Ratio Effect on Biodiesel Production (KOH) at 1h, 65°C.

Ratio	MP	MS
3:01	0.15289	0.51199
4:01	0.1956	0.64623
5:01	0.16648	0.55819
6:01	0.27197	0.91306
7:01	0.23209	0.76998