HIGH FREE FATTY ACID REDUCTION FROM JATROPHA CURCAS OIL VIA ACID TRANSESTERIFICATION

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BACHELOR OF MECHANICAL ENGINEERING TECHNOLOGY (MAINTENANCE TECHNOLOGY) WITH HONOURS

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Faculty of Mechanical and Manufacturing Engineering Technology

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in fulfilment of the requirements for the degree of
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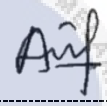
DECLARATION

I declare that this Choose an item. entitled “High Free Fatty Acid Reduction From Jatropha curcas Oil Via Acid Transesterification” is the result of my own research except as cited in the references. The Choose an item. has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : 

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APPROVAL

I hereby declare that I have checked this thesis and, in my opinion, this thesis is adequate in terms of scope and quality for the award of the Bachelor of Mechanical Engineering Technology (Maintenance Technology) with Honours.

Signature :

Supervisor Name : Mahanum Binti Mohd Zaaberi

Date : 18 JANUARY 2022

DEDICATION

This research is dedicated to my dear parents who have served as a source of inspiration and strength when me have felt like giving up.

To my dear supervisor, teammates, classmates, and brothers who encouraged me to finish this study with their words of advice and encouragement.

Finally, I want to express my gratitude to the almighty god for his guidance, strength, mental, power, and protection.

ABSTRACT

Biodiesel has earned a remarkable of attention as a renewable, biodegradable, and non-toxic alternative to fossil fuels. The multipurpose plant known as *Jatropha curcas* which contains a lot of oil and can be consider as non-edible oil. The main objective of the current research work is to study the effects of acid esterification of this highly Free Fatty Acid (FFA) content of oil in order to reduce acid content during transesterification process. Acid esterification process would be introduce using sulphuric acid (H_2SO_4) to reduce the high fatty acid of the feedstock. The best molar ratio alcohol to oil is 12:1 with 1% v/v acid sulfuric (H_2SO_4), which is value FFA is 0.18 mg KOH/g. Reduction percentage of FFA will be analysed according to ASTM D6751 and EN 14214.

Keywords: Biodiesel; *Jatropha curcas*; acid esterification

ABSTRAK

Biodiesel menarik perhatian luar biasa sebagai salah satu sumber alternatif yang boleh diperbaharui, biodegradasi, dan tidak beracun sebagai bahan bakar fosil. Tumbuhan serbaguna yang dikenali sebagai minyak biji pokok jarak yang memiliki kandungan minyak yang banyak dan boleh dianggap sebagai minyak yang tidak boleh dimakan. Objektif utama penyelidikan ini adalah untuk mengkaji kesan pengesteran asid kandungan Asid Lemak Bebas minyak yang tinggi dengan tujuan mengurangkan kandungan acid semasa proses transesterifikasi. Proses pengesteran asid diperkenalkan menggunakan asid sulfurik (H_2SO_4) untuk mengurangkan asid lemak tinggi bahan mentah. Nisbah molar terbaik alkohol kepada minyak ialah 12:1 dengan 1% isipadu asid sulfurik (H_2SO_4), iaitu nilai FFA ialah 0.18 mg KOH/g. Peratusan pengurangan FFA akan dianalisis mengikut ASTM D6751 dan EN 14214.

Kata kunci: *Biodiesel; Minyak biji pokok jarak; Pengesteran asid*

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LIST OF SYMBOLS AND ABBREVIATIONS

w/w	-	Weight per weight
N	-	Normality
ASTM D6751	-	American Society for Testing and Material
EN 14214	-	European Nation
FAME	-	Fatty Acid Methyl Ester
FFA	-	Free Fatty Acid
KOH	-	Potassium hydroxide
H_2SO_4	-	Sulphuric acid
v/v	-	Volume per volume
GCMS	-	Gas Chromatography-Mass Spectrometry (GCMS)

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CHAPTER 1

INTRODUCTION

1.1 Background

Biodiesel is a renewable fuel made primarily from domestic feedstock derived from agricultural or nutrition products, as well as the recycling of products such as cooking and vegetable oils (both edible and non-edible oil) and algae. Biodiesel had recently gained popularity due to its greenhouse advantages and the concept of making something out of renewable resources and to be more cost-effective than fossil fuel production. Soybean, sunflower, palm kernel, rapeseed, cotton seed, and jatropha oils are the most widely used oils for biodiesel processing (S. P. Singh & Singh, 2010).

Biodiesel production is thought to be more cost-effective than production of fossil fuels. Biodiesel made from energy crops is environmentally friendly because it is biodegradable, reduces the amount of acid rain, and reduces the environment impact brought by combustion process. It also reduces the amount of sulfur dioxide (SO_2) and hydrocarbons that have not been burned released at the process of combustion (Agarwal, 2007). More than 95% of biodiesel is currently made from vegetable oil as a feedstock (soya bean oil, sunflower oil, rapeseed oil, palm oil, and sesame oil), resulting in a significant out of balance in the human nutrition chain versus diesel (Muhammada et al., 2018).

As a matter of fact, an extensive variety of non-edible oil producing plants are considered for biodiesel production. Non-edible seed oil, such as that from *Jatropha curcas* seed can be used for commercial biodiesel production to prevent these situations and it is a possible feedstock for biodiesel extraction. Biodiesel that meets international fuel standards such as ASTM D6751 (American Society for Testing and Material) specified standards and requirements for blended biodiesel with medium petroleum fuels and EN 14214 (European Nation) that specifies the specification and test methodologies for fatty acid methyl ester has been acknowledge as a substitute for fossil diesel. This international standard detailed for B100 (biodiesel 100%).

One of most common method of making biodiesel is transesterification. Transesterification occurs when a lipid reacts with an alcohol in existence of potassium hydroxide (KOH) as catalyst to produce esters and glycerol as a by-product. Before that acid treatment was proposed firstly because of high content free fatty acid in crude *Jatropha curcas* oil. Alcoholysis is described as the action of one alcohol displacing another from an ester in principle (cleavage by an alcohol) (Anitha & Dawn, 2010). Several factors influence this reaction, including the molar ratio alcohol to oil, reaction time, catalyst concentration, reaction temperature, and stirring influence, and among others. One among the most popular raw materials used in the manufacturing of biodiesel is alcohol. The most frequently used alcohols in biodiesel production are methanol and ethanol. Methanol, on the other hand, is selected due to its physical and chemical properties. It also has a rapid reaction with triglycerides and is quickly dissolved in KOH. In addition, methanol is used in the manufacture of biodiesel because cheap and reactive. Biodiesel fuels that were made from methanol and ethanol have minor differences in terms of their characteristics as fuels. As a comparison purposes, biodiesel made from methanol have slightly higher pour and cloud

points and slightly lower viscosities compared with those made from ethanol (Yusuf et al., 2011).

In this study, the high FFA of *Jatropha curcas* seed oil will be fully utilized as the feedstock in producing a green and quality biodiesel. An acid transesterification will be used to perform the reduction of FFA. The value FFA will be set to meet the requirement determined by the ASTM D6751 and EN 14214.

1.2 Problem Statement

The relationship between current issues in biodiesel production and this study is demonstrated through problems statement. The study of objectives and scope are intended to address such various challenges in reduction of Free Fatty Acid of feedstocks. There are rarely of detailed study especially on the use of *Jatropha curcas* oil in acid transesterification method has been reported. Furthermore, *Jatropha curcas* produces a large amount of oil despite being an inedible fruit. If this benefit is not utilized or disregarded, it will be a loss. Amongst the most important problem should be highlight is the greenhouse impact caused by combustion process such as gas emission, sulfur dioxide and unburned hydrocarbons released during the combustion phase.

1.3 Research Objective

The main aim of this research from *Jatropha curcas* seed oil having a high free fatty acid are as follows:

a) To reduce Free Fatty Acid of *Jatropha curcas* oil using an acid transesterification process according ASTM D6751 and EN 14214.

b) To perform acid sulfuric (H_2SO_4) as acid catalyst in acid transesterifcation process.

c) To study the influences of variable including alcohol to oil molar ratio, catalyst loading, effect of temperature, and reaction time on the reduction of Free Fatty Acid.

1.4 Scope of Research

The scopes of this study consist of three important elements. They are: -

a) Develop an overall overview of the current construct of FFA reduction with the conventional method, including its process, variable parameters, and raw material that involved.

b) Performed acid-treatment process with an acid catalyst, which is sulfuric acid (H_2SO_4).

c) Acid value reduced are subjected to a thorough chemical and physical analysis, which was carried out in accordance with ASTM D6751 and EN 14214 standards.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In recent years, several studies have focused on biodiesel as alternative fuel made from animal fat, vegetable oil (edible or non-edible oil), and recycled cooking oil. Biofuels are seen as a part of the option to issues such as sustainable development, energy, and carbon reduction. The methods used, the type of oil, production process, sort of alcohol, the type of catalyst, the stirring effect, the reaction time, the reaction temperature, a molar ratio of alcohol to oil and acid value were all the factors that need to be considered in the production based on the criteria and factors. *Jatropha curcas* has been identified as one of the possible commercial sources of renewable energy that have a lot of benefit especially on the production output.

Free fatty acids (FFA), phospholipids, water, and other impurities are present in crude oil obtained by pressing natural vegetable oils. Even with these components, oil cannot be used as a fuel directly. Chemical adjustments to the oils are required to resolve the issues raised so that can meet those properties of biodiesel. Performed acid-treatment process with an acid catalyst, which is sulfuric acid (H_2SO_4) to reduced FFA of feedstock before Fatty acid methyl ester (FAME) was produced from reaction alcohol with triglyceride of raw *Jatropha curcas* oil (JCO) via 2-step pretreatment process and base-transesterification process. Acid value reduced were subjected to a thorough chemical and physical analysis, which was carried out in compliance with ASTM D6751 and EN 14214 standards.

2.2 Ishikawa Diagram

An Ishikawa diagram is used to represent the primary elements that influence a final outcome, which is frequently related to a production or design issue. These charts are commonly referred to as ‘Fishikawa’ diagrams since are shaped like a fish. Branch bones are mean variables in this study that influence an output, and the result was reduction in FFA (refer Figure 2.1).

There are six parameters to reduce free fatty acids of *Jatropha curcas* oil (JCO). First, effect of production, where acid transesterification was proposed first before base transesterification process because high free fatty acid content in JCO would cause separation issue and formation of soap. Effect of alcohol, where methanol was chosen to react with JCO in acid transesterification process. In addition, effect of catalyst was one of the most important influences, such as percentage concentration of acid sulfuric give high impact to the resultant JCO. Furthermore, effect of temperature means that reaction temperature must below and not exceed boiling point of methanol, where the range is 60℃ to 70℃. Next, effect of molar ratio alcohol to oil, where stoichiometric ratio for acid transesterification process. For example, molar ratios are 3:1, 6:1, 9:1, and 12:1. Effect of time means that the time needed for acid transesterification until reaction completed.

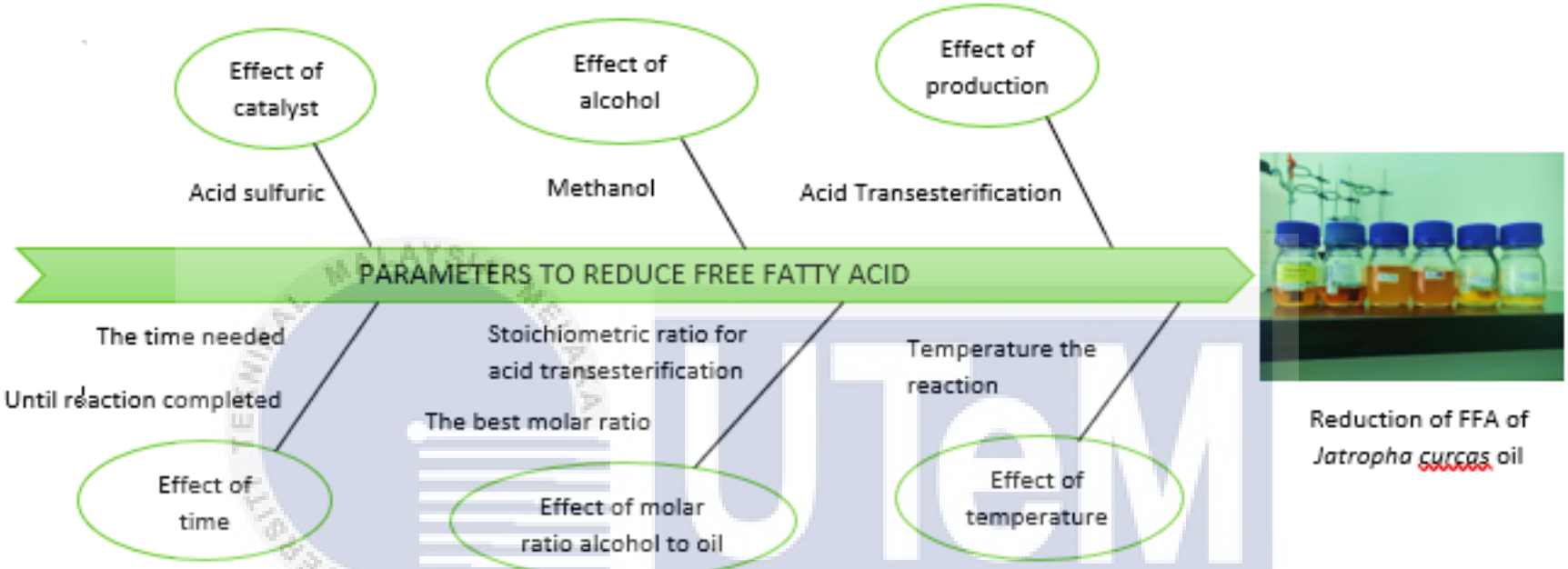

Figure 2.1 Parameters to reduce Free Fatty Acid

2.3 Raw Jatropha curcas

The tropical tree *Jatropha curcas* that originated in Mexico and has now spread over Asia and Africa. Since *Jatropha curcas* belongs to the *Euphorbiaceae* family, it has traditionally been used for medicinal purposes. *Jatropha curcas* is distinguished by the presence of 3±0 seeds in each fruit, which are black in colour. Figure 2.2 shows *Jatropha curcas* fruit and seeds. The average seed length is 18 mm (Abdulla et al., 2011). Mechanical pressing is one of the most popular methods for extracting oil. Crude oil is obtained by pressing vegetable oil, which include free fatty acids, moisture and other impurities (Abdulla et al., 2011). *Jatropha curcas* is non-edible oil, it does not pose a threat to food supplies once used to make biodiesel, and it also produces a lot of oil. The leaves and seeds of *Jatropha curcas* are harmful and animals, among other things.

Table 2.1 shows a properties specification of *Jatropha curcas* oil and *Jatropha curcas* biodiesel. Properties specification that has been highlighted are density at 15 ℃, cloud point, flash point, pour point, viscosity at 40 ℃, cetane number, iodine number, and acid value.

Figure 2.2 *Jatropha curcas* fruit and seeds (Tuttosemi, 2021)

Table 2.1 Properties of *Jatropha curcas* oil and *Jatropha curcas* biodiesel (D. Singh et al., 2019).

Properties specification	***Jatropha curcas* oil**	***Jatropha* biodiesel**
Density at 15 ℃	916	865
Cloud point (℃)	-	5.66
Flash point (℃)	211.7	175.5
Pour point (℃)	-	6
Viscosity at 40 ℃ (mm²/s)	37.28	4.52
Cetane number	21	55.43
Iodine number	97.9	96.75
Acid value (mg/g)	-	0.24

2.4 Effect of Production Process

Free fatty acids (FFA), phospholipids, water, and other impurities are present in crude oil obtained by pressing natural vegetable oils. Even with these components, oil cannot be used as a fuel directly. Chemical adjustments to the oils are required to resolve the issues raised so that can meet those properties of biodiesel. Transesterification is a method that involved reaction of oil with an alcohol in the presence of catalyst to produce fatty acid methyl ester, to produce a good biodiesel and glycerol (Abdulla et al., 2011). Acid transesterification process was used to reduce FFA and eliminate other impurities were present in crude oil before start transesterification for production of biodiesel. So other impurities did not to disturb a process production of biodiesel.

In another study, Rajalingam et al., (2016) examined the process of thermal cracking to convert a hydrocarbon's complex structure into its simplest structure, either with or without the use of a catalyst. Oil density and viscosity will be reduced as a result of this process. Another study by Rajalingam et al., (2016) were direct use to engine and blending. In direct injection engines, animal fat or vegetable oil can be utilized as a fuel because it has

a high heating value and can produce enough power. However, it cannot be used in the engine without modification if it has undesirable properties. To avoid such problems, biodiesels are mixed directly with conventional fossil fuels. According to Sankumgon et al., (2018), microemulsion fuels have been considered as an alternative method to produce biofuels with acceptable qualities while avoiding waste disposal issues. This approach requires nanionic surfactants as an emulsifier to avoid phase separation between three compositions, diesel, *Jatropha curcas* oil and ethanol (Sankumgon et al., 2018).

2.5 Gas Chromatography-Mass Spectrometry (GCMS)

Free fatty acid in *Jatropha curcas* oil is one of the most critical factors influencing the conversion to methyl esters. As indicated in Table 2.2, crude jatropha oil contains a wide range of FFA concentrations with varying composition ranges. The type of carbon-to-carbon bonds determines whether fatty acids are saturated (SFAs) or unsaturated (USFAs). SFAs are carboxylic acids having 12 to 24 single carbon-to-carbon bonds that are less reactive chemically. At room temperature, capric, lauric, myristic, palmitic, margaric, stearic, arachidic, and behenic acids, for example, are solids. USFAs, on the other hand, have one or more carbon-to-carbon double bonds.

Monounsaturated (MUFA) and polyunsaturated (PUFA) are the two types of USFAs. The number of double bonds in a compound improves its chemical reactivity. The most naturally occurring MUFA is oleic acid. Caproleic, lauroleic, elaidic, myristoleic, and palmitoleic acids are other MUFAs. Linoleic acids, two double bonds, linolenic acids, three double bonds, arachidic acids, four double bonds, eicosapentaenoic acids, five double bonds,

docosahexaenoic acids, and six double bonds are examples of PUFA with the number of double bonds.

According by Olaoluwa R. & Sanni Muideen, (2017) reported that vegetable oil should be strong in monounsaturated fatty acids and have low saturation and polyunsaturation. High polyunsaturated fats produce methyl ester fuels that are prone to oxidation and have a high freezing point. The research study by Akbar et al., (2009) also found that The major fatty acids were determined to be oleic acid (44.7%) and linoleic acid (32.8%), while the saturated fatty acids discovered in Jatropha oil were palmitic acid and stearic acid (Table 2.3). In addition, according reported by Berchmans & Hirata, (2008) that the greatest fatty acids in *Jatropha curcas* oil are oleic and linoleic, which consist for 34.3% and 29%, respectively (Table 2.4)

Table 2.2 Fatty acid composition crude *Jatropha curcas* oil (Farouk et al., 2014)

Fatty acid	Composition (%)					
	Range a	Range b	Range c	Range d	Range e	Range f
Lauric (C12:0)	-	-	-	0.1	0.14	-
Myristic (C14:0)	-	-	0-0.1	0.1	0.17	0-0.1
Palmitic acid (C16:0)	14.2	11.3	14.1-15.3	13	14.82	14.1-15.3
Palmitoleic (C16:1)	1.4	-	0-1.3	0.7	0.81	0-1.3
Stearic acid (C18:0)	6.9	17	3.7-9.8	5.8	4.15	3.7-9.8
Oleic acid (C18:1)	43.1	12.8	34.3-45.8	44.5	40.98	34.3-45.8
Linoleic (C18:2)	34.4	47.3	29-44.2	35.4	38.61	29-44.2
Linolenic acid (18:3)	-	-	0-0.3	0.3	0.27	0-0.3
Arachidic (C20:0)	-	4.7	0-0.3	0.2	0.06	0-0.3
Behenic (C22:0)	-	-	0-0.2	-	-	0-0.2
Saturates (%)	21.1	-	-	-	-	>22.3
Unsaturates (%)	78.9	-	-	-	-	>42-43.1

a, b, c, d, e, f, Data obtained from (Koh et al., 2011),(Tiwari et al., 2007), (Silitonga et al., 2013) respectively.

Table 2.3 Fatty acid composition (%) (Akbar et al., 2009)

Fatty Acid	Jatropha curcas oil seed
Oleic 18:1	44.7
Linoleic 18:2	32.8
Palmitic 16:0	14.2
Stearic 18:0	7.0
Palmitoliec 16:1	0.7
Linolenic 18:3	0.2
Arachidic 20:0	0.2
Margaric 17:0	0.1
Myristic 14:0	0.1
Caproic 6:0	-
Caprylic 8:0	-
Lauric 12:0	-
Capric 10:0	-
Saturated	21.6
Monounsaturated	45.4
Polyunsaturated	33

Table 2.4 Fatty acid composition of crude *Jatropha curcas* oil (Berchmans & Hirata, 2008)

Fatty acid	Structure	Wt%
Myristic	14:0	0–0.1
Palmitic	16:0	14.1– 15.3
Palmitoleic	16:1	0–1.3
Stearic	18:0	3.7–9.8
Oleic	18:1	34.3– 45.8
Linoleic	18:2	29.0– 44.2
Linolenic	18:3	0–0.3
Arachidic	20:0	0–0.3
Behenic	22:0	0–0.2

2.6 Effect of Alcohol

Methanol, ethanol, propanol and other alcohols can all be used in the transesterification process. Even though both methanol and ethanol are widely utilized, methanol is preferred due to its physical and chemical qualities (Yusuf et al., 2011). Biodiesel made from methanol and ethanol exhibit modest differences in terms of fuel properties. As an example, biodiesel made from methanol have slightly higher pour and cloud points and slightly lower viscosities than those made from ethanol. In addition, methyl esters provided much more energy and torque than ethyl esters that observed by engine testing (Bozbas, 2008). Significantly lower smoke opacity, lower exhaust temperature, and lower pour point are also some of the advantages of ethyl esters compared methyl esters (Bozbas, 2008).

The above finding is compatible with Erdiwansyah et al, (2019) studied, which found that thermal energy of evaporation and carbon concertation in alcohols are crucial characteristics. Ethanol and methanol are more suitable than other alcohols such as butanol and propanol since the resulting emissions are significantly lower and more cost-effective (Erdiwansyah et al., 2019). Table 2.5 shows a comparison of the properties of alcohol and gasoline.

Table 2.5 Comparison properties of gasoline and alcohol-based (Erdiwansyah et al., 2019)

Properties	Methanol	Ethanol	Butanol	Propanol	Gasoline
Chemical formula	CH_3OH	C_2H_5OH	C_4H_9OH	C_3H_7OH	C_8H_{15}
Cetane number	2	8	17	12	10 to 15
Molecular weight (g/mol)	32.04	46.07	-	60.1	96.5
Density (kg/m^3)	791.3	789.4	-	803.7	746
Boiling point (°C)	65	79	117	97	25-125
Lower heating value (MJ/kg)	20.01	26.08	32.01	29.82	42.7
Vaporization latent heat (kJ/kg)	1162.64	918.42	-	727.88	-
Self-ignition temperature (°C)	385	363	-	350	-
Oxygen (%) (wt.)	49.93	34.73	21.6	26.62	-
Latent heating (kJ/kg) 25 °C	1162	904	585	728	380-500
Viscosity (mm^2/s) 40 °C	0.59	1.13	2.22	1.74	0.4-0.8[3]

2.7 Effect of Catalyst

Alkali, acid, heterogeneous, and lipase catalysts being the most successful have been discovered from previous study. Furthermore, a purpose catalyst on biodiesel production to increase the reaction rate and percentage of yield.

2.7.1 Alkali Catalyst

Agarwal, (2007) reported that transesterification catalysed by alkali is faster than transesterification catalysed by acid and it is most commonly employed in commercial industries. In addition, potassium hydroxide, KOH is utilized as a fundamental catalyst with methanol and ethanol. Furthermore, KOH is less expensive and is commonly employed in large scale production. Most vegetable oils are converted form esters at a rate of 94% to 99%

when using an alkali catalyst concentration of 0.5% to 1% by weight (Agarwal, 2007). Due to the obvious potential of contamination by free acid or water, the soap will be made separation become difficult.

This is supported by Lu et al. which revealed that formation of soaps will be appeared due to high FFA in raw *Jatropha curcas* reacted with alkali catalyst and causing in significant emulsification and separation issues (Lu et al., 2009). Base catalysts were compared for the synthesis of biodiesel from *Jatropha curcas* such as KOH and calcium oxide (CaO). The result found with the KOH catalyst were promising, as the values were within ASTM guidelines. KOH has been found to be an ideal catalyst that is both cost-effective and scalable to provide maximum yield (Reddy et al., 2020).

2.7.2 Acid Catalyst

In another study by Abdulla et al. (2011), acid catalyst includes sulphuric acid (H_2SO_4), sulfonic acids, and hydrochloric acids (HCl). If the triglyceride has a higher level of free fatty acid (FFA) and water, acid catalyst is used in experiment (Abdulla et al., 2011).

For example, if the FFA content of *Jatropha curcas* seed oil is high, a pre-treatment phase is required to lower the FFA content of the feedstock in the presence of H_2SO_4. According to an investigation by Baldwin et al. even though yields may be large, the corrosiveness of acids may produce failure to equipment, and the reaction rate possibly slow, take up all day to complete (Baldwin et al., 2017). By using acid in the production process will end up with sluggish, and need higher temperature which is over 100℃ and in excess of 3 hours to complete (Meher et al., 2006).

Most FFA esterification in various vegetable oils was completed at a reaction temperature of 50 ℃ (Berchmans & Hirata, 2008). The procedures were established to reduce the FFA concentration of *Jatropha curcas* oil (JCO) to fewer than 2% by using H_2SO_4 (1% w/w). Additionally, (Azhari et al., 2008) reported that using H_2SO_4 (1% w/w), molar ratio methanol to JCO is 6:1, and 180 minutes of reaction time, the FFA concentration of JCO was effectively reduced to 0.5% at 60℃ under atmospheric pressure.

Table 2.6 Comparison of the different catalyst to produce biodiesel (Abdulla et al., 2011).

Variable	Alkali catalysis	Acid catalysis
Reaction temperature (℃)	60-70	55-80
Free fatty acid in raw materials	Saponification products	Esters
Water in raw materials	Interference with reaction	Interference with reaction
Yields of methyl esters	Normal	Normal
Recovery of glycerol	Difficult	Difficult
Purification of methyl esters	Repeated washing	Repeated washing
Production cost of catalyst	Cheap	Cheap

2.8 Effect of Reaction Time

Freedman et al., (1986) have studied that under a molar ratio methanol to oil of 6:1, 0.5% catalyst concentration and reaction time 60℃, the conversion rate is crucial in the transesterification process of peanut, cotton-seed, sun flower and soybean oils. After 1 minutes, roughly 80% yield was reported for soybean and sun flower oil. After one hour, yields from four different oil are in ranged 93% between 98% (Freedman et al., 1986). This

is supported by Ma et al., (1998) studied which reveal that affect of reaction time on beef tallow transesterification including methanol. Containing a mixture and dispersion of methanol into beef tallow, the reaction was relatively low for the first minute. The reaction time increased rapidly from 1 to 5 minutes. In around 15 minutes, the maximum amount of beef tallow methyl ester was produced.

2.9 Effect of Reaction Temperature

Baldwin et al., (2017) discovered that temperature obviously affected the reaction time and yield of esters by conducted transesterification process of soybean oil with molar ratio methanol to oil (6:1) was tested at 32℃, 45℃ and 60℃. Depending on the oil used, the transesterification process can take place at various temperatures. The reaction is usually carried out at methanol is boiling point, which is in ranged between 60℃ to 70℃ at atmospheric pressure. The influence of reaction temperature on yield for *Jatropha curcas* oil at atmospheric pressure was tested in temperature range of 40℃ to 100℃ (Patil & Deng, 2009). The highest yield was obtained at a temperature of 60 ℃. However, when the reaction temperatures were higher than 60℃, the yield decreased. Furthermore, alkali transesterification at temperature above 60 ℃ leads in significant methanol evaporation, greatly decreasing the overall biodiesel output (Patil & Deng, 2009).

2.10 Effect of Molar Ratio Alcohol to Oil

The molar ratio of alcohol to oil is one the most critical factors impacting ester yield. The most common used stoichiometric ratio for transesterifications are 3:1, 6:1, 9:1, 12:1, and 15:1. However, transesterification is an equilibrium process that require a significant amount of alcohol to force the reaction to the right. Abdulla et al. (2011) have studied the effect of molar ratio and summarized that a molar ratio of 6:1 with alkali as catalyst is commonly selected to produce yields of methyl esters more than 98% by weight. Molar ratio greater than 6:1 ratio does not enhance yield but rather issue glycerol separation due to higher in glycerol solubility (Abdulla et al., 2011).

The result was contradicted by the reported of Meher et al. (2006) where molar ratio of 9:1 and 12:1 produced the best outcomes. The reaction was incomplete at molar ratios less than 6:1. Separation of glycerin is difficult at a molar ratio of 15:1, and the appears yield of esters is reduced because some glycerol remained in biodiesel phase (Meher et al., 2006). As a result, the molar ratio of 9:1 considered to be the most suited. The acid, saponification, and iodine value of methyl esters are affected by the molar ratio (Tomasevic & Siler-Marinkovic, 2003).

2.11 Biodiesel Standard

The qualities of biodiesel are influenced by various of factors, including refining methods, feedstock composition, biodiesel synthesis methodology, and oil distillation method. Biodiesel standards are made to enhance properties of significant biodiesel. Biodiesel specifications are provided by ASTM (American Society for Testing and Material) and EN (European Nation). These requirements must be meet by all biodiesel fuels. These guidelines establish a working principle for testing biodiesel fuels and provide values for various chemical and physical qualities of oil that should be used in the engine in a correct sequence.

ASTM D6751 standard for biodiesel (B100) and ASTM D7467 standards for biodiesel fuel blends (B6 to B20) with petroleum diesel were produced by ASTM (D. Singh et al., 2019). ASTM D975 standards are preferred for 5% of biodiesel (B5) and lower levels. In EN 14214, EN defined criteria for biodiesel fuel (B100), although these criteria do not apply to a medium blend like B20. EN 590 criteria for diesel fuel blends were develop by the EN and provide for mixture of B7 and below. The ASTM and EN requirements for biodiesel (B100) are listed in Table 2.7.

2.12 Properties of Biodiesel

There are also plenty of criteria that are strongly linked to fatty acid methyl ester (FAME) composition profile such as acid number, boiling point, cetane number, density, flash point, pour point, saponification value, kinematic viscosity and many more. Table 2.7 shows ASTM and EN requirement for biodiesel (B100).

Table 2.7 ASTM and EN requirement for biodiesel (B100) (D. Singh et al., 2019)

Properties specification	**Unit**	**Biodiesel**			
		ASTM D6751		**EN 14214**	
		Test method	**Limits**	**Test method**	**Limits**
Acid number	mg KOH/g	ASTM D664	0.5 maximum	EN 14104	0.5 maximum
Boiling point	℃	ASTM D7398	100 - 615	-	-
Carbon	wt%	ASTM PS121	77	-	-
Cetane number	-	ASTM D613	47 minimum	EN ISO 5165	51 minimum
Cloud point	℃	ASTM D2500	-3 to 12	-	-
Copper corrosion	-	ASTM D 130	No. 3 maximum	EN ISO 2160	Class 1
Density at 15 ℃	Kg/m^3	ASTM D 1298	880	EN ISO 3675/ 12185	860 - 900
Flash point	℃	ASTM D 93	130 minimum	EN ISO 3679	101 minimum
Iodine number	g I_2/100 g	-	-	EN 14111	120 maximum
Kinematic viscosity at 40 ℃	mm^2/s	ASTM D445	1.9 - 6.0	EN ISO 3104	3.5 - 5.0
Pour point	℃	ASTM D97	-15 to `16	-	-
Saponification value	mg KOH/g	ASTM D5558-95	370 maximum	-	-

2.12.1 Acid Number

Acid number is determined by amount of free fatty acids contained in the sample of fuel. The acid number is measured in mg KOH/g. A high acid number causes corrosion in the engine fuel delivery channel, and this high acid value is caused by a high free fatty acid level (Atabani et al., 2012). The acid value can also be used to indicate how much lubrication is there in the fuel. ASTM D664 and EN 14104 biodiesel fuel are required to evaluate the acid number (Atabani et al., 2013; S. P. Singh & Singh, 2010). The highest allowed value of acid number, according to these standards is 0.5 mg KOH/g (refer in Table 2.7). Equation 2.1 shows the calculation of determining the acid value. Equation 2.2 shows the calculation of determining the percentage free fatty acid (FFA).

$$Acid\ value = \frac{ml\ of\ KOH \times N \times 56}{W} \quad (2.1)$$

$$\%\ Free\ Fatty\ Acid\ (FFA) = Acid\ value \times 0.53 \quad (2.2)$$

Where, ml of KOH is titrated value, *N* is normality of KOH the value is 0.1 *N*, 56 g is molecular weight of KOH and *W* is the weight of sample or oil.

2.12.2 Boiling Point

The boiling point is the temperature at which point the vapor pressure of the substance matches the ambient pressure. The normal boiling point can be used to calculate an overall volatility of substance. If a substance has a greater boiling point, it indicates that the substance is less volatile, whereas a low boiling point indicates that the substance is more volatile. The type of interaction that exists between the molecules of an element determines its boiling point. According to ASTM D7398 standard, boiling point range from 100 to 615 ℃ reported by (D. Singh et al., 2019).

2.12.3 Density

One of the most important fuel characteristics is density, which is utilized to determine the roughly amount of fuel given injection systems for efficient combustion (Sakthivel et al., 2018). When compared to low density fuel, high density fuel has more mass. As a result, the density of the fuel has an impact on the amount of energy in the combustion chamber. The methyl ester profile, feedstock type, and biodiesel production technique directly influence the density of biodiesel fuel and also give impacts the engine thermal efficiency (Pratas et al., 2011). The ASTM D1298 and EN ISO 3675/12185 test methods can be determine biodiesel density. Equation 2.3 shows the calculation of determining the density of oil.

$$\rho\ oil = \frac{mass\ oil}{mass\ water} \times \rho\ water \tag{2.3}$$

Where, ρ oil is the sample density, ρ water is the density of the distilled water, mass oil is mass of the sample, and mass water is mass of the distilled water.

2.13 Summary of The Literature Review

A review matrix allows to compare and contrast articles quickly in order to evaluate the scope of study throughout time. A review matrix can assist in identifying differences and similarities among academic journals on a certain research topic about Jatropha biodiesel production. Table 2.8 shows free fatty acid reduction from *Jatropha curcas* oil.

Based on Table 2.8, there are many molar ratio alcohol to oil, such as 3:1, 6:1, 8:1 and 9:1. All this differences molar ratio give influence to the resultant free fatty acid reduction. In addition, according to Prafulla et al. (2009) reported that molar ratio alcohol to oil 3:1 can reduced free fatty acid to 0.61%. Furthermore, different finding from Eugenio et al. (2015) reported that 9:1 molar ratio alcohol to oil can reduced 0.4% content of free fatty acid in *Jatropha curcas* oil.

Another parameter gives a high influence is reaction time of acid transesterification process. It can be said there are many reactions time have been reported for acid transesterification process. According by Supriya et al. (2015) reported that reaction time was take about 1.3 hours. Different findings from Eugenio et al. (2015) reported that reaction time was take about 24 hours for acid transesterification completed. From this parameter, it can conclude that the conversion rates increased as the reaction time increased.

Reaction temperature is the one of main part for reduction of free fatty acid. Based on Table 2.8, the common range reaction temperature is 60°C to 65°C. This is because to ensure that the alcohol is not lost through vaporization during acid transesterification process. Furthermore, if exceed the optimal temperature, the resultant oil will drop.

Table 2.8 Free fatty acid reduction from *Jatropha curcas* oil

Researcher	Title	Apparatus Model	Input Material			Process		FFA %
			Alcohol	Catalyst	Oil	Time	Temperature	
Houfang Lu; Yingying Liu; Hui Zhou; Ying Yang; Mingyan Chen; Bin Liang (2009)	Production of biodiesel from *Jatropha curcas* L.oil	250 ml three-neck flask, mechanical agigator, reflux condenser, thermometer, and water bath	Methanol (20:1)	Calcining metatitanic acid (4 wt%)	*Jatropha curcas* oil	2 h	90 ℃	0.1%
Okullo, Aldo, Temu, A. K. Ntalikwa, J. W, Ogwok, P (2010)	Optimization of base catalyst for biodiesel production from *Jatropha curcas* oil	250 ml flask, thermometer, stirrer, weigh balancing, 100 ml beaker	Methanol (10 ml)	CaO (0.5 g)	*Jatropha curcas* oil (100 ml)	24 h	60 ℃	1.73
Prafulla D. Patil; Shuguang Deng (2009)	Optimization of biodiesel production from edible and non-edible vegetable oils	flask, thermometer, stirrer, weigh balancing	Methanol (3:1)	H_2SO_4 (0.5 wt%)	*Jatropha curcas*	2 h	45 ℃	0.61
Hanny Johanes Berchmans; Shizuko Hirata (2008)	Biodiesel production from crude *Jatropha curcas L*. seed oil with a high content of free fatty acids	15 cm^3 special reaction glass tube, water bath, magnetic stirrer, electric heater, control temperature	Methanol (24% w/w)	H_2SO_4 (1% w/w)	*Jatropha curcas*	2h	50 ℃	<1
Azhari; M. Faiz; R. Yunus; T.I Mohd. Ghazi; T.C.S Yaw (2008)	Reduction of free fatty acids in crude *Jatropha curcas* oil via an esterification process	Three neck flask reactor, control temperature, burette, conical flask, dropper	Methanol (60% w/w)	H_2SO_4 (1% w/w)	*Jatropha curcas* oil	2h	60℃	0.5
Dena A. Kamel; Hassan A. Farag; Nevine K. Amin; Ahmed A. Zatout; Rehab M. Ali (2018)	Smart utilization of jatropha (*Jatropha curcas* Linnaeus) seeds for biodiesel production: Optimization and mechanism	Three neck round bottom flask reactor, dropper, water cooled reflux condenser	Methanol 6:1	H_2SO_4 (1% w/w)	*Jatropha curcas*	120 min	60℃	0.91
S. Dharma; H.H. Masjuk; Hwai Chyuan Ong; A.H. Sebayang; A.S. Silitonga; F. Kusumo; T.M.I. Mahlia (2016)	Optimization of biodiesel production process for mixed Jatropha curcas–Ceiba pentandra biodiesel using response surface methodology	Bottom flask, mechanical stirrer, filter paper, heater	Methanol 3:1	H_2SO_4 (1% w/w)	*Jatropha curcas*	3 h	60 ℃	0.025
Supriya B. Chavan; Rajendra R. Kumbhar; D. Madhu; Bhaskar Singh; Yogesh C. Sharma (2015)	Synthesis of biodiesel from Jatropha curcas oil using waste eggshell and study of its fuel properties	Necked batch reactor of 2 L capacity, oven, rotavapor	Methanol 8:1	H_2SO_4 (1.7 % w/w)	*Jatropha curcas*	1.3 h	60 ℃	0.94
Eugenio Sanchez-Arreola; Gerardo Martin-Torres; Jose D. Lozada-Ramírez; Luis R. Hernandez; Erick R. Bandala-Gonzalez; Horacio Bach (2015)	Biodiesel production and de-oiled seed cake nutritional values of a Mexican edible Jatropha curcas	a Soxhlet apparatus, rotator evaporator, 50 ml round bottom flask connected to a reflux condenser and magnetic stirrer	Methanol 9:1	H_2SO_4 (1.3 % w/w)	*Jatropha curcas*	24 h	62 ℃	0.4

Arridina Susan Silitonga; Masjuki Haji Hassan; Hwai Chyuan Ong; Fitranto Kusumo (2017)	Analysis of the performance, emission and combustion characteristics of a turbocharged diesel engine fuelled with Jatropha curcas biodiesel-diesel blends using kernel-based extreme learning machine	Mechanical stirrer, A double-jacketed reactor, rotary evaporator	Methanol 9:1	H_2SO_4 (1 % w/w)	*Jatropha curcas*	2.5 h	55 °C	0.391
Jain, Siddharth; Sharma, M.P. (2010)	Biodiesel production from Jatropha curcas oil	1.5 L capacity equipped with condenser, stirrer, inlet and outlet ports and thermometer	Methanol 30% (v/v)	H_2SO_4 (1 wt%)	*Jatropha curcas oil (JCO)*	3 h	65 °C	0.5
Bhupendra Singh Chauhan a*, Naveen Kumar a , Haeng Muk Cho b (2012)	A study on the performance and emission of a diesel engine fueled with Jatropha biodiesel oil and its blends	cylinder gas pressure, single cylinder, air cooled, direct injection, burette, dropper, conical flask, hot plate.	Methanol 3:1	H_2SO_4 (1 wt%)	*Jatropha curcas*	3 h	65 °C	0.09

CHAPTER 3

METHODOLOGY

3.1 Introduction

In general, *Jatropha curcas* seed has a large rate of oil. Biodiesel is produced in conventional methods by transesterifying oils with methanol in the existence of catalysts such like KOH. However, because high free fatty acids (FFA) react with alkaline catalyzed to generate soaps, *Jatropha curcas* seed oil unable to be utilized directly in an alkaline catalyzed transesterification process, causing major emulsification and separation issues. Pre-treatment with sulfuric acid (H_2SO_4) is a common and effective way for lowering FFA levels, since it can make raw oils transesterifiable by an alkaline catalyst and transform FFA to desirable fatty acids methyl esters (FAME).

3.2 Research Design

This thesis presents a new and integrated analytical approach to production of biodiesel from *Jatropha curcas* seed oil. The essence of the approach used in this project is centered on the concept of ASTM D6751 establishes specifications for a biodiesel. The selected approach is based on experimental type, which approach to reduce and analyse the acid value from raw *Jatropha curcas* seed oil. Figure 3.1 shows flow chart of Free Fatty Acid reduction from *Jatropha curcas.*

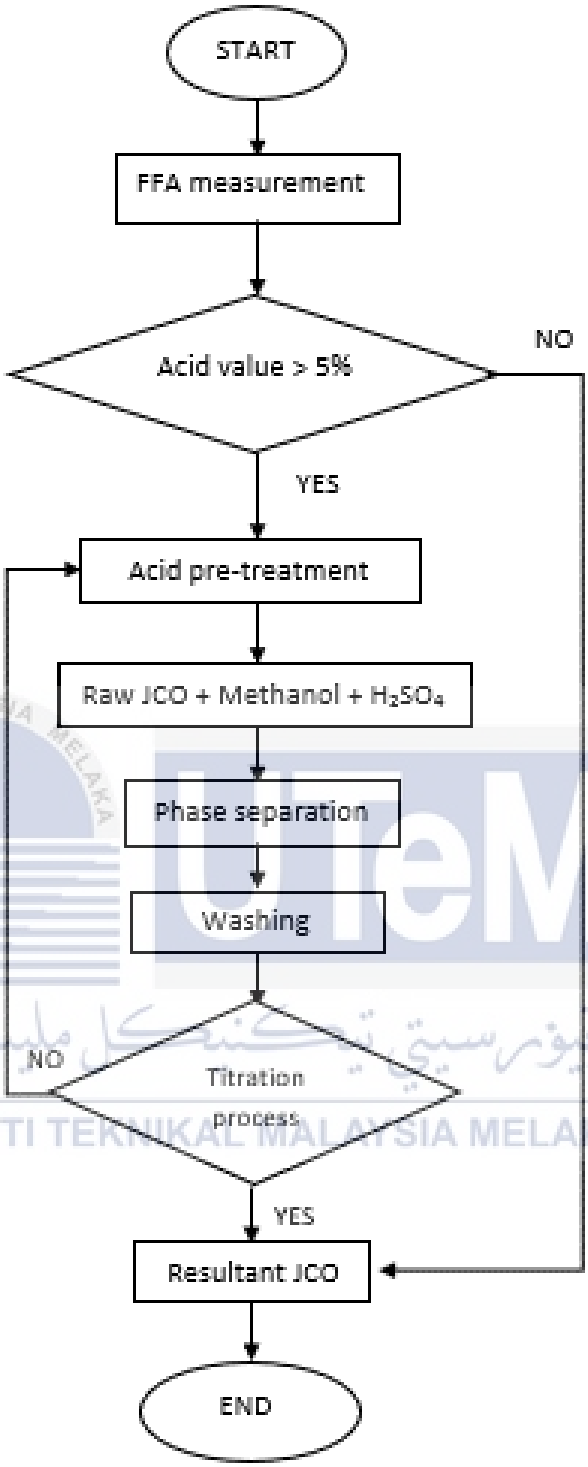

Figure 3.1 Flow chart of Free Fatty Acid reduction from raw *Jatropha curcas.*

3.3 Proposed Methodology

An Acid pre-treatment was proposed to reduce acid value of raw *Jatropha curcas* for optimal biodiesel production from raw *Jatropha curcas*. By responding the oil with methanol in the involvement of an acid sulfuric (H_2SO_4) was used to reduce level acid value. Pre-esterification, phase separation, and purification are all terms used to described the process. Resultant *Jatropha curcas* oil was split from glycerol by product during phase separation.

3.3.1 Experimental Setup

The *Jatropha curcas* oil (JCO) was purchase from BIONAS Sdn Bhd, Setapak, Kuala Lumpur. Oil was then being filtered to remove all the contaminants moisture and unwanted products. The filtered oil was then heated up. In order to determine the value of FFA in raw JCO, titration process was introduced before transesterification. If level of free fatty acids in *Jatropha curcas* seed oil is over than 1%, an acid catalysed esterification was employed to decrease FFA to less than 1% by using H_2SO_4 as catalyst at quite an appropriate temperature.

3.3.1.1 Acid Transesterification

The acid pre-treatment method was carried out with heating 50 ml of crude JCO up 110 ℃ to 120℃ to remove water content in oil. The ideal value for reducing acid value concentration are 0.5% and 1% v/v sulphuric acid (H_2SO_4) in reference to the volume of oil and molar ratio methanol to oil are 6:1, 9:1 and 12:1. Figure 3.2 shows a mixture of methanol and acid sulfuric. Then, the put crude oil and solution of methanol and acid sulfuric in a beaker for 60 minutes at 60℃ to 65℃ shows in Figure 3.3. After 60 minutes, put the mixture in the separation funnel for 24 hours.

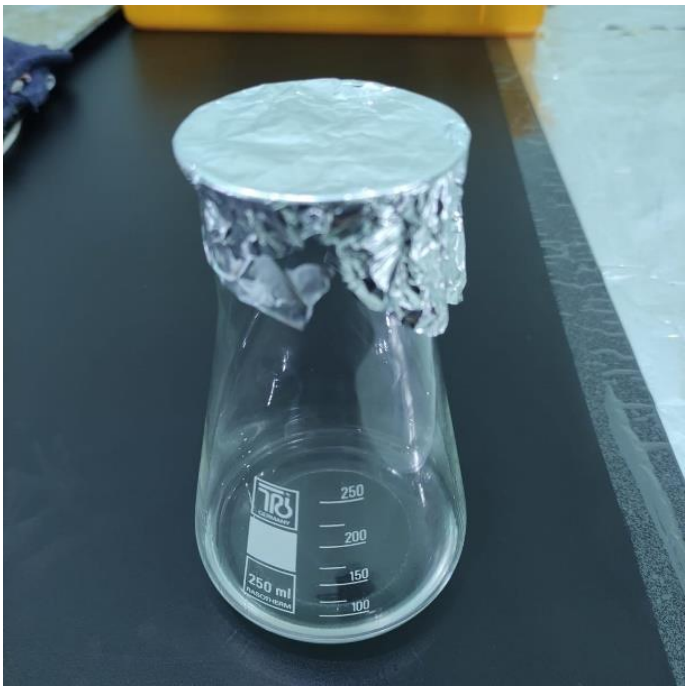

Figure 3.2 Mixture of methanol and acid sulfuric.

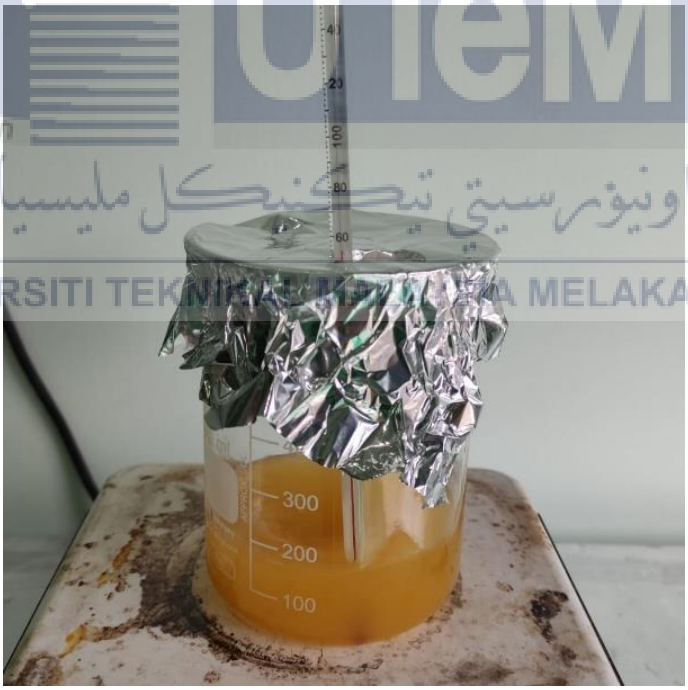

Figure 3.3 Heating both crude oil and mixture.

3.3.1.2 Washing process

Glycerol will be entirely isolated from the resultant JCO oil after 24 hours at room temperature. Only the oil remained after the glycerol and methanol were removed from the separating funnel. Then, heated resultant *Jatropha curcas* oil for 100℃ to 110℃ to remove contaminants.

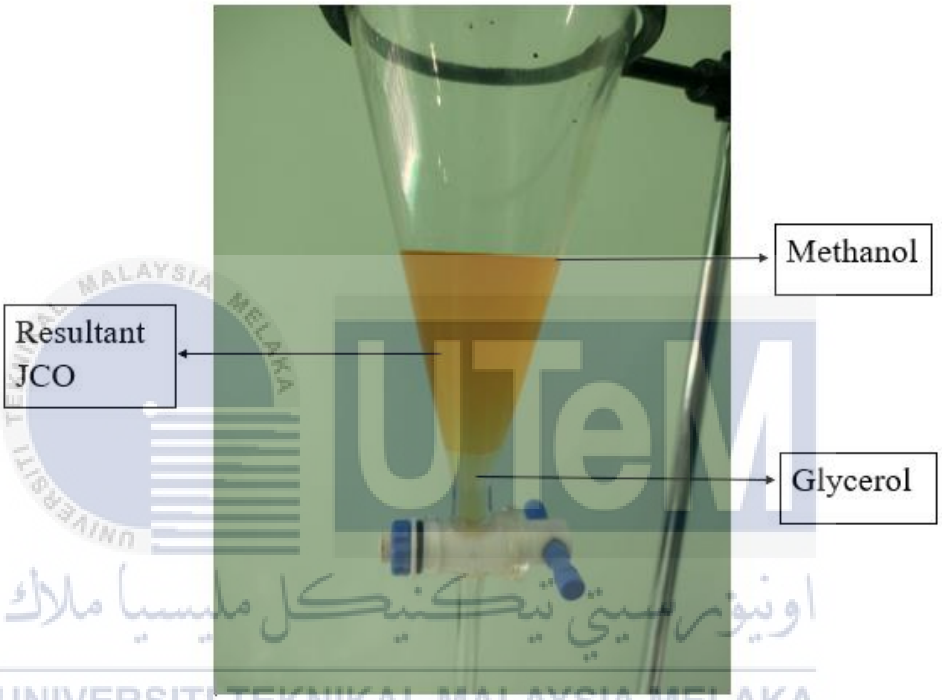

Figure 3.4 Eliminate glycerol and methanol.

3.3.1.3 Titration process

5 g of oil was initially added to a dried conical flask, followed by 25 ml pure alcohol (isopropyl alcohol). Three drops of phenolphthalein were added to the mixture. The mixture was then heated on a hot plate for 5 minutes while gently shaking. The titration process began by titrating the solutions against 0.1 N KOH until a pink colour exists that shows in Figure 3.5. Pink colour indicating titrations is endpoint. The volume of reactant consumed was measured and used to calculate value of acid and free fatty acid using equations 3.1 and 3.2, and the results are compared following to the ASTM D664 standard.

Figure 3.5 Titration process.

3.4 Crude *Jatropha curcas* Properties Testing

Property testing will be carried out in this experiment in order to achieve the desired requirements for all characteristics that follow the ASTM D6751 standard. In addition, properties that have been measured were acid value and free fatty acid content in resultant *Jatropha curcas* oil, density, and gas chromatography-mass spectrometry

3.4.1 Acid Value and Free Fatty Acid

Acid value is determined by amount of free fatty acids contained in the sample of *Jatropha curcas* oil. To measure the acid value, 5g of *Jatropha curcas* oil pre-treated was weighed and put it in a conical flask using a dropper. 25 ml of propanol and three drops of phenolphthalein were mixed together with the oil. After that, the solution was titrated with 0.1 N potassium hydroxide drop by drop for the titration process. Then, end a process until pink colour appeared. By using the Equation (3.1) and (3.2) to calculate acid value and free fatty acid.

$$Acid\ value = \frac{ml\ of\ KOH \times N \times 56}{W} \quad (3.1)$$

$$\%\ Free\ Fatty\ Acid\ (FFA) = Acid\ value \times 0.53 \quad (3.2)$$

Where, ml of KOH is titrated value, *N* is normality of KOH the value is 0.1 *N*, 56 g is molecular weight of KOH and *W* is the weight of sample or oil.

3.4.2 Density

By using a pycnometer, the density of *Jatropha curcas* oil can be determined. Then, estimated the weight of *Jatropha curcas* oil and distilled water. The density of oil was calculated using Equation (3.3).

$$\rho\ oil = \frac{mass\ oil}{mass\ water} \times \rho\ water \tag{3.3}$$

3.4.3 Gas Chromatography-Mass Spectrometry (GCMS)

The GCMS process were examined at Process Control Laboratory, Faculty of Engineering Universiti Putra Malaysia. The GCMS data will identified the structure composition free fatty acid (FFA) of *Jatropha curcas* oil. GCMS analysis primarily determined the amount FFA composition in product sample. The model of GCMS is GC-MS Headspace.

The sample of *Jatropha curcas* oil put in injection port. Then, the sample oil would vaporise through the coil column with the help of inert carrier gas. The coil column would provide a surface for the compound to interact to allow the component to slow down for separation would occur. When the vaporised sample oil pass through the coil column, the oven temperature will increase. Moreover, the compound reach end of column, will hit the detector. The peaks of each chemical component would record on the chromatogram. After the molecules pass through the column coil, electron volt was hit which can cause the molecules to break. The break molecules would form positive cations. Besides, the ion will travel through electromagnetic field that will filtered into mass. Furthermore, the detector would amplify and counted each number of ions associated with specific mass. The

information would be sent to computer where mass spectrum created. The spectrum will show every component on sample.

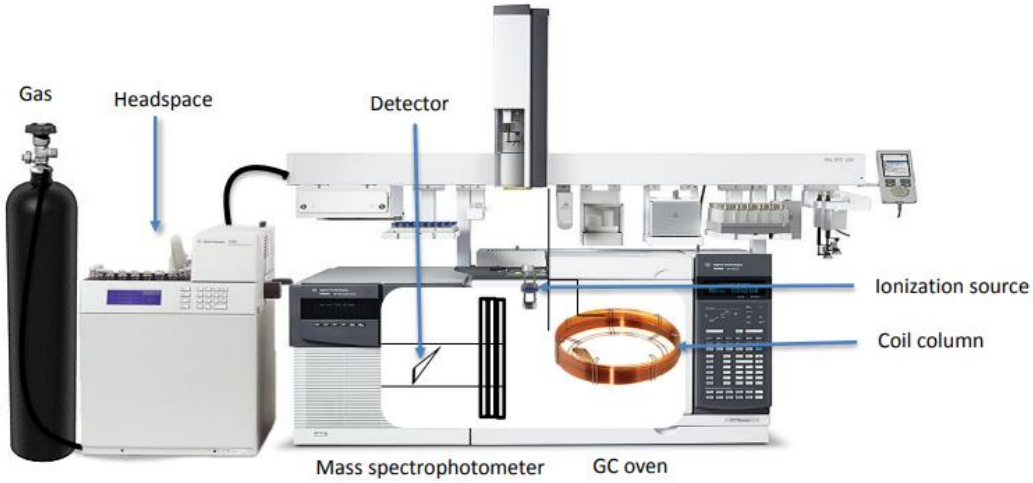

Figure 3.6 GC-MS Headspace (Universiti Putra Malaysia, (2004).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

The results were achieved based on the several tests that has being conducted in the project. The results were included properties of crude *Jatropha curcas*, and acid pre-treatment. An acid transesterification process was needed to reduce free fatty acid value of *Jatropha curcas* oil before used for biodiesel production.

Following the completion of an acid transesterification, many tests were performed to analyse the qualities of the oil in order to establish whether it was qualified as biodiesel according to ASTM D6751. Gas chromatography mass spectrometry (GCMS), density measurement, acid value, and free fatty acid were among the tests performed.

In this free fatty acid reduction, there are some variables that have been included to study the effects of the variables to the acid value. The variables are the methanol to oil ratio, the concentration of acid catalyst, and reaction time. The results of the tests will be discussed in details in this chapter.

4.2 Characteristic of Crude *Jatropha curcas*

The physical properties of crude JCO were investigated, and the results are presented in Table 4.1.

Table 4.1 Properties of crude *Jatropha curcas*

Properties	Unit	Method	Results
Acid Value	mg KOH/g	ASTM D664	32.47
Free Fatty Acid	%	N/A	17.21
Kinematic viscosity at 40℃	mm^2/s	ASTM D445	36.83
Density at 15℃	kg/m^3	ASTM D4052	0.9002
Colour	N/A	N/A	Golden Yellow

Before the experiment began, the qualities of selected crude *Jatropha curcas* were examined. It is crucial to understand the characteristics of the crude oil before moving on to the other steps of the biodiesel production process, so that the finished product's properties can be contrasted. All of the tests were carried out in accordance with ASTM D6751 and EN 14214.

4.3 Acid Transesterification

The first stage of two-step transesterification is acid transesterification. The objective of acid transesterification as a pre-treatment process is to decrease the Free Fatty Acid (FFA) content of crude *Jatropha curcas* at under 5%, lowering the acid value of the oil as well. This would be due to the need to avoid soap formation. The creation of soap can complicate the separation of methyl ester and fats, lowering the percentage of biodiesel yield. To obtain the optimal value of FFA in the oil, a variety of parameters were used. The methanol to oil molar ratio and the acid concentration utilised during the acid esterification process were the most important factors in the pre-treatment process.

The stoichiometric ratio for the transesterification reaction involves 3 mol of methanol and 1 mol of *Jatropha curcas* oil to produce 3 mol of fatty acid ester and 1 mol of glycerol. According by Koh et al. (2011) reported that excess alcohol is used during transesterification to ensure that the oils will be completely converted to ester due to the forward reaction being more favorable. Furthermore, a higher alcohol to triglyceride ratio can result in a greater ester conversion in a shorter time. The molar ratio is starting from 3:1, 6:1, 9:1, 12:1 and so on. For acid transesterification where the free fatty acids are higher than 1%, a molar ratio of methanol to oil of 9:1 or 12:1 is sufficient to reduce free fatty acid of Jatropha oil.

Six samples of crude JCO were used in the experiments, two different acid sulfuric concentration (v/v%) which were 0.5% and 1.0%. In addition, there were three proposed methanol to oil molar ratios: 6:1, 9:1, and 12:1. The FFA value of the oil samples was determined after the acid esterification and filtering processes were completed. Table 4.2 shows the results of acid esterification process. Figure 4.1 shows effect variables of methanol to oil molar ratio and acid sulfuric concentration to the free fatty acid.

Based on the Figure 4.1, it can be seen that the value of FFA mostly the lowest at 1.0% of acid sulfuric concentration. The best and lowest FFA value shown at 1.0% of acid sulfuric concentration and the methanol to oil molar ratio was 12:1. The FFA value was successfully decreased to 0.18% and can be used for transesterification process because the condition of FFA for the oil used for transesterification are below 1%. Therefore, the other molar ratio that still can be applied for transesterification in according to ASTM D6751 and EN 14214 were 9:1 and 12:1 with a presence of 0.5% and 1% of acid sulfuric concentration. In addition, the others samples that failed to meet the requirement such as 6:1 molar ratio were not used because above 0.5% of FFA value as the requirement.

Table 4.2 The results of acid esterification process.

Methanol to oil molar ratio	Jatropha curcas oil (ml)	Acid sulfuric concentration (v/v%)	Methanol (ml)	Acid value (mg KOH/g)	Free Fatty Acid (%)
6:1	50	0.5	12.92	1.008	0.534
6:1		1	12.92	1.120	0.593
9:1		0.5	19.38	0.672	0.356
9:1		1	19.38	0.400	0.212
12:1		0.5	25.77	0.56	0.297
12:1		1	25.77	0.336	0.178

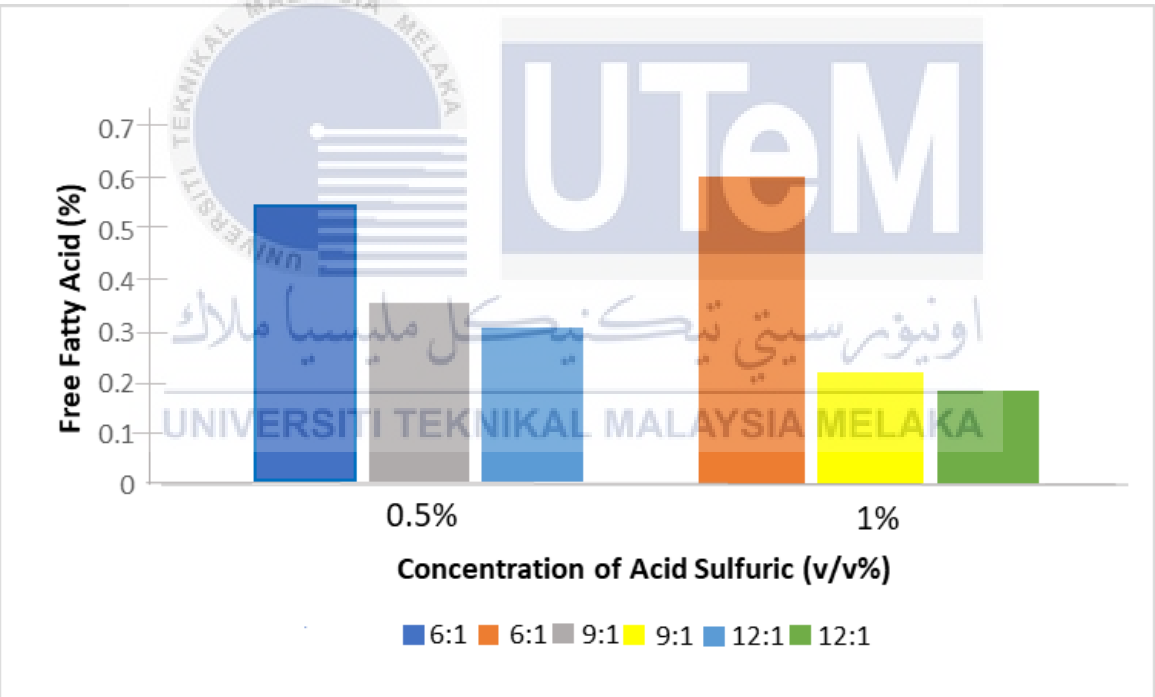

Figure 4.1 Effect variables of methanol to oil molar ratio and acid sulfuric concentration to the free fatty acid.

4.4 Effect of Reaction Temperature

The temperature of the reaction has a significant impact on the efficiency of the reaction. As more energy is supplied for the reaction to proceed, a higher reaction temperature can reduce the viscosities of oils, leading to an increase in reaction rate. As a result, the *Jatropha curcas* oil (JCO) obtained maximises. To ensure that the alcohol is not lost through vaporisation, the reaction temperature must be lower than the boiling point of the alcohol, which is 60–70 ℃ at atmospheric pressure for methanol. Also, if the reaction temperature exceeds its optimal level, the yield of the resulting oil will drop since a higher reaction temperature will help accelerate the saponification reaction, resulting in a lower output. The greatest resulting oil is achieved at temperatures ranging from 60 to 65 ℃, depending on the type of oil. Figure 4.2 (a) shows that *Jatropha curcas* oil were burned. Based on Figure 4.2 (a), happened when JCO was heated over a boiling point of methanol that cause evaporated of methanol. Furthermore, Figure 4.2 (b) shows that *Jatropha curcas* oil in optimum temperature (60 to 65 ℃), the colour is golden yellow.

The similar finding by Freedman et al. (1984) reported that the temperature obviously affected the reaction rate and yield of ester with methanol to oil molar ratio is 6:1 at different temperature 32℃, 45℃, and 60℃. Another similar finding by Farouk et al. (2014) reported that transesterification must be conducted at optimum temperature (60℃) and increases in temperature exceed this scale would result in a reduction in yield.

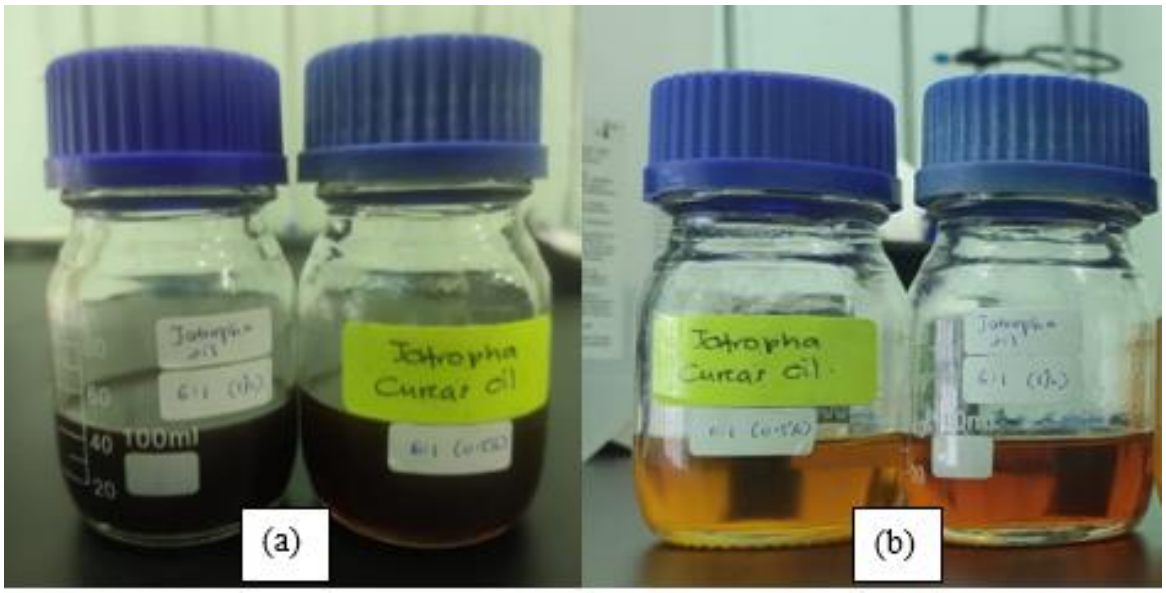

Figure 4.2 (a) Burned JCO, (b) JCO in optimum temperature.

4.5 Effect of Reaction Time

The conversion rates increased as the reaction time increased. Due to the mixing and dispersion of alcohol into the oil, the reaction was initially sluggish. After 10 minutes, the reaction speeds up until the maximum amount of resulting oil is attained, which takes about 60 minutes shows in Figure 4.4. According to the experiment, the reaction time required to convert *Jatropha curcas* oil to the resulting oil after separation process was around 24 hours shows in Figure 4.5. Furthermore, according to Leung et al., (2010) reported that excess reaction time will result in a lower product yield entirely due to the reverse reaction of transesterification, causes more fatty acids to produce soaps.

Similar finding by according to Farouk et al. (2014) stated that for acid transesterification process can go up to 180 minutes but if over reaction time, it will cause backward reaction of transesterification.

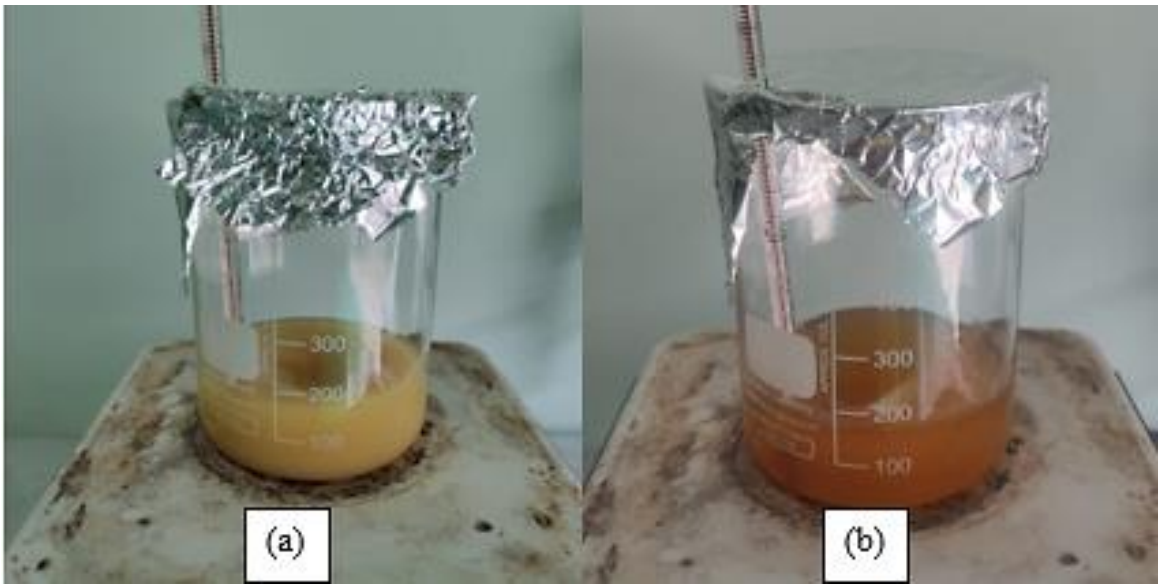

Figure 4.3 (a) The mixing and dispersion methanol into JCO, (b) After 10 minutes methanol reacts with JCO.

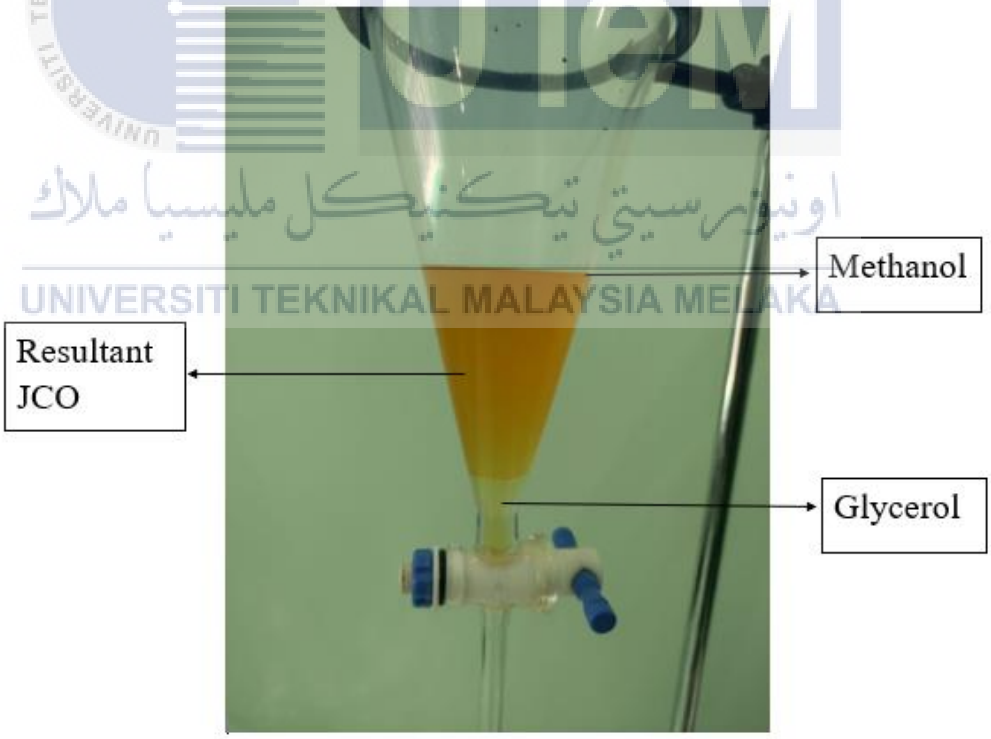

Figure 4.4 Resultant oil after 24 hours for separation process.

4.6 Gas Chromatography-Mass Spectrometry (GCMS)

Free fatty acid in *Jatropha curcas* oil is one of the most critical factors influencing the conversion to methyl esters. Indicated Table 4.3, crude jatropha oil contains a wide range of FFA concentrations with varying composition ranges. Saturated fatty acid (SFA) has a value of 21.91 %. Monounsaturated (MUFA) and polyunsaturated (PUFA) are the two types of unsaturated fatty acid. Monounsaturated fatty acids (MUFA) contributed for 40.15 %, The most naturally occurring MUFA is oleic acid. In addition, polyunsaturated fatty acids (PUFA) contributed for 37.94 %. Figure 4.5 shows that composition *Jatropha curcas* oil in graph form. Therefore, this studied has similar findings with Olaoluwa R., (2017) that vegetable oil has strong in monounsaturated fatty acids and have low saturated and polyunsaturated. The number of double bonds in a compound improves its chemical reactivity.

In addition, saturated fatty acid are carboxylic acids having 12 to 24 single carbon-to-carbon bonds that are less reactive chemically. Furthermore, high polyunsaturated fats produce methyl ester fuels that are prone to oxidation and have a high freezing point. According by Akbar et al. (2009) stated that vegetable oil should low saturation fatty acid and also have low polyunsaturation. In addition, if oil rich polyunsaturated fatty acid such as linoleic and linolenic acid will cause oil tends to poor oxidation stability and high freezing point. High freezing point means that the oil has worse flow characteristic and maybe come to solid at low temperature.

Furthermore, according by Singh et al. (2019) reported that high acid value was cause by high free fatty content in oil, that can create the issue of corrosion to the engine part. In addition, the high unsaturated fatty acid will cause a low cetane number of oil. The low cetane number will cause higher emission from engine exhaust. This happened due to incomplete combustion process. Oil with a higher cetane number contains more oxygen and, as a result, has a higher combustion efficiency.

In addition, high polyunsaturated fatty acid will give impact to iodine number of oil. The amount of iodine absorbed by the double bonds of FAME molecules in a 100 g fuel quantity is indicated by the iodine number. It is used to determine how unsaturated an oil and how quickly it oxidises when it comes into interface with air.

Table 4.3 Fatty acid composition crude Jatropha curcas oil.

Fatty acid	Composition (%)
Myristic (C14:0)	0.10
Palmitic acid (C16:0)	15.30
Palmitoleic (C16:1)	1.30
Stearic acid (C18:0)	9.80
Oleic acid (C18:1)	45.80
Linoleic (C18:2)	44.20
Linolenic acid (18:3)	0.30
Arachidic (C20:0)	0.30
Behenic (C22:0)	0.20
Saturated fatty acid, SFA (%)	21.91
Monounsaturated fatty acid, MUFA (%)	40.15
Polyunsaturated fatty acid, PUFA (%)	37.94

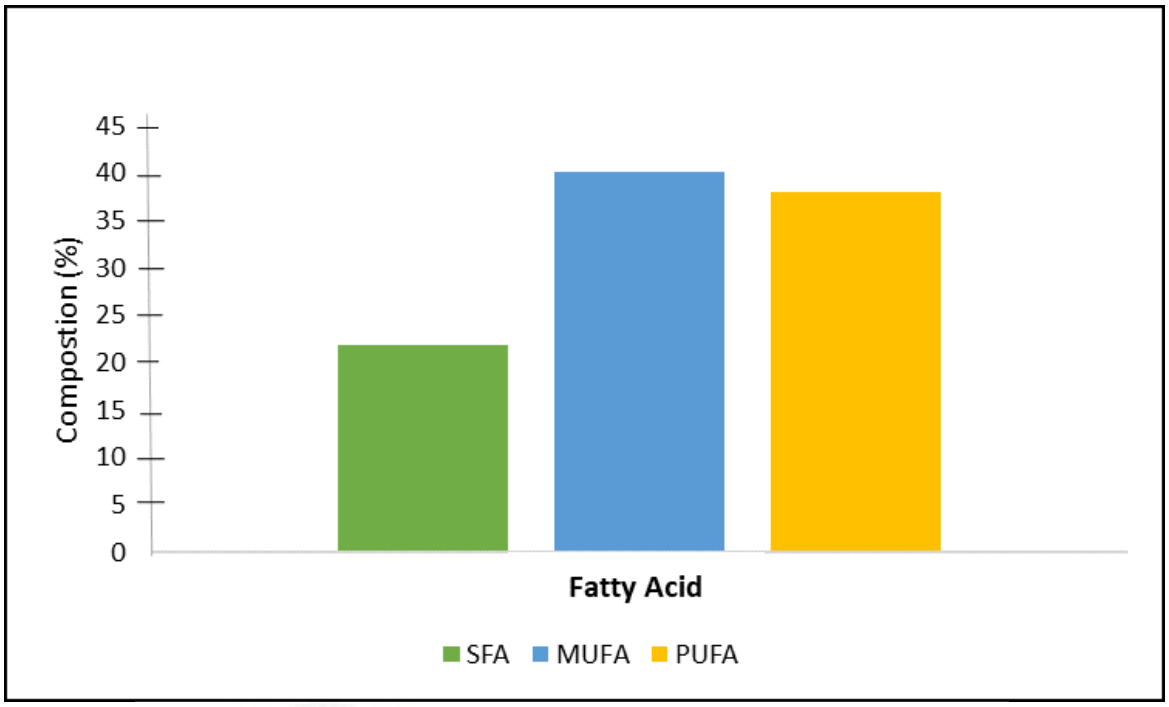

Figure 4.5 Composition of *Jatropha curcas* oil.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In conclusion, *Jatropha curcas* is a significant potential source of oil that can be processed into biodiesel, reducing greenhouse gas emissions, and providing a large source of renewable energy both local and international. The main objective of the current research work is achieved by to reduced free fatty acid from 17.21% to 0.178% of *Jatropha crucas* oil using an acid transesterification process with the best molar ratio alcohol to oil is 12:1 with a presence of 1% v/v acid sulfuric concentration according to ASTM D6751 and EN 14214. In general, high free fatty acids (FFA) react with alkaline catalysed to generate soaps, *Jatropha curcas* seed oil unable to be utilised directly in an alkaline catalyzed transesterification process, causing major separation issues. Furthermore, another aim of this study is to performed acid sulfuric (H_2SO_4) as acid catalyst in acid transesterification process. Pre-treatment with sulfuric acid (H_2SO_4) is a common and effective way for lowering FFA levels, since it can make raw oils transesterifiable by an alkaline catalyst and transform FFA to desirable fatty acids methyl esters (FAME).

In addition, another objective is to study the influences of variable including alcohol to oil molar ratio, catalyst loading, effect of temperature, and reaction time on the reduction of Free Fatty Acid. The methanol to oil molar ratio and the acid concentration utilised during the acid esterification process were the most important factors in the pre-treatment process. There were three proposed methanol to oil molar ratios: 6:1, 9:1, and 12:1. There are two different acids sulfuric (H_2SO_4) concentration (v/v%) which were 0.5% and 1.0%. Based on

data from table 4.2, it can be said 12:1 methanol to oil molar ratio in presence of 1% v/v H_2SO_4 was the best and lowest FFA value. where it successfully decreased to 0.18%. Another parameter in this study is effect of reaction temperature, which is give impact on the efficiency of the reaction. Reaction temperature cannot over a limit boiling point of a methanol (60 – 70 ℃). While if exceed it is limit temperature, a resultant product would be drop. In addition, reaction time also in parameter that effect to the production. Therefore, acid pre-treatment process required 24 hours for separation process to separate glycerol and resultant *Jatropha curcas* oil

All of properties were successfully meets the ASTM D6751, especially the total acid number and free fatty acid (FFA), which was reduced from 17.21% to 0.178% of FFA.

5.2 Recommendation

In this biodiesel production, the variables that have been used are alcohol to oil molar ratio, catalyst loading, effect of reaction temperature, and reaction time to reduce high free fatty acid in *Jatropha curcas* oil (JCO). In order to discover more about the factors that influence a resultant JCO, varying reaction temperature and reaction time can be additional idea for the future study of biodiesel. Furthermore, varying in alcohol to oil molar ratio such as 15:1, 17:1 and many more. Varying in this parameter can be analysed which the best to reduce free fatty acid and produce more resultant JCO.

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APPENDICES

APPENDIX A Calculation Density

No.	Details	Readings (g)
1.	Pycnometer	27.6 g
2.	Distilled water + Pycnometer	77.55 g
3.	Jatropha curca oil (JCO) + Pycnometer	72.70 g
4.	Distilled water	49.95 g
5.	Jatropha curcas oil (JCO)	45.10 g

$$\rho\ oil = \frac{mass\ oil}{mass\ water} \times \rho\ water$$

$$\rho\ oil = \frac{45.10\ g}{49.95\ g} \times 997 kg/\ m^3$$

$$\rho\ oil = 900.194\ kg/m^3$$

APPENDIX B Molar Ratio *Jatropha Curcas* Oil

Molecular Weight = 847.5 g/mol

Density = 900.194 kg/m^3

$$1\ mole\ JCO\ (847.5\ g/mol) \times \frac{1\ kg}{1000\ g} \times \frac{1\ kg}{900.194\ \text{kg}/m^3} = 941.46\ ml$$

1 mole JCO = 847.5 g = 941.46 ml

APPENDIX C Molar Ratio Methanol

Boiling point = 65 ℃

Molecular Weight = 32.042 kg/mol

Density = 791 kg/m^3 at 20 ℃

$$1\ mole\ Methanol\ (32.042\ g/mol) \times \frac{1\ kg}{1000\ g} \times \frac{1\ kg}{791 \text{kg}/m^3} = 40.508\ ml$$

1 mole Methanol = 32.042 g = 40.508 ml

APPENDIX D Volume

$$\frac{6}{1}\ molar\ ratio = \frac{6\ mole\ methanol}{1\ mole\ JCO}$$

$$= \frac{6 \times 40.508\ ml\ methanol}{1 \times 941.46\ ml} = 0.258$$

$$\frac{1}{0.258} = 3.874$$

When; JCO was used 50 ml.

$$\frac{50\ ml}{3.874} = 12.91\ ml\ of\ Methanol$$

It means when the molar ratio is 6:1, when JCO is 50 ml, volume for methanol is 12.91 ml.

APPENDIX E Acid Value and Free Fatty Acid

Molar ratio = 12:1

Acid sulfuric concentration = 1% v/v

Titrant consumed = 0.3 ml

$$\text{Acid value} = \frac{\text{ml of KOH} \times \text{N} \times 56}{\text{W}}$$

$$\text{Acid value} = \frac{0.3\ \text{ml} \times 0.1 \times 56.1}{5} = 0.336\ \text{mg KOH/g}$$

$$\%\ \text{Free Fatty Acid (FFA)} = \text{Acid value} \times 0.53$$

$$= 0.336 \times 0.53$$

$$= 0.178\ \%$$

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

BORANG PENGESAHAN STATUS LAPORAN PROJEK SARJANA

TAJUK: **HIGH FREE FATTY ACID REDUCTION FROM JATROPHA CURCAS OIL VIA ACID TRANSESTERIFICATION**

SESI PENGAJIAN: **2020/21 Semester 1**

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