THE NOVEL CONTINUES BIODIESEL USING ULTRASOUND CLAMP TUBULAR REACTOR

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ABSTRACT

Jatropha curcas oil (JCO), is used as the feedstock in this research work. The work starts with design a new continuous process for biodiesel using ultrasound clamp on tabular reactor for producing pure biodiesel from jatropha curcas oil (JCO). Form this design, we fabricate the rig and test the application of sonochemistry technique in biodiesel production through optimal and low cost production technique for enhancing their capabilities and effective process. Before run process of biodiesel the analysis of physical and chemical properties of the feedstock and the associated product to obtain the major fatty acid compositions of triglycerides applicable in the jatropha curcas oil. Based on testing the free fatty acid of jatropha curcas oil is above 10.1 %. So for reduce free fatty acid we need do esterification process using 1%w/w of acid catalyst and molar ratio methanol to oil is 18:1. After esterification, the free fatty acid of the feedstock was testing and the result is 0.402%. It is important because is too high free fatty acid it cause smaller the conversion efficiency. The next stage is transesterification conducted with 6:1, 9;1 and 12:1 molar ratio methanol to jatropha for reaction times of 3, 5 and 7 minutes for 1% catalyst sodium hydroxide (NaOH) at a temperature of 65^0C with frequency arrange 17kHz to 22kHz and ultrasonic power output 240watt. The standard physical properties test to determine the biodiesel qualities are flash point, water content, acid value, density and dynamic viscosity. From test bed for continuous reactor using tubular reactor the maximum producing biodiesel is 89 % was obtained with molar ratio methanol to oil 6:1 at 7 minutes reaction time.

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CHAPTER 1

INTRODUCTION

This chapter deals with the research background and the associated objectives necessary for the research work. The subsequent section sets the scope of the works and the intended objectives for completing the tasks. At the end of this chapter, detailed proposal of research project.

1.1 Background of Study

Biodiesel is the process that formed from the ester of vegetable oils and animal fats. It is an alternative renewable fuel to replace diesel fuel in compression ignition engines. An energy content of biodiesel that is about 12% less than petroleum based diesel fuel on a mass basis. Biodiesel has a higher molecular weight, viscosity, density, and flash point compare with diesel fuel. In engine tests, when biodiesel is compared with conventional diesel fuel, the power and fuel consumption are in nearly direct proportion to the fuel's energy contents.

As we known, biodiesel is an oxygenated fuel, 10% to 11% oxygen by weight, and produces less unburned hydrocarbons (HC), carbon monoxide (CO), and particulate matter (PM) than diesel-fuelled engines. From photosynthesis process, carbon dioxide can be recycled in growing the oilseeds used to produce biodiesel almost CO_2 neutral. When 100% biodiesel fuelling use oxides of

nitrogen (NOx) are increased 10% to 15%. Biodiesel fuels are good for environment because they are readily biodegrable, a benefit in case of spills (Gerpen *et al.,* 2007).

According to Gerpen *et al.,*(2007) the National Biodiesel Board (NBB) suggests two definitions for biodiesel. For general definition "biodiesel is a domestic, renewable fuel for diesel engines derived from natural oils like soybean oil, and which meets the specifications of ASTM D 6751." The second definition is more to technical, biodiesel is "a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100, and meeting the requirements of ASTM D 6751".

Biodiesel an alternative fuel for diesel engines is becoming increasingly important due to diminishing petroleum reserves and the environmental consequences of exhaust gases from petroleum-fuelled engines. Biodiesel, which is made from renewable sources, consists of the simple alkyl esters of fatty acids methyl ester (FAME) has become a promising green and renewable fuel (Berchmans & Hirata, 2008; Na-Ranong & Kitchaiya, 2014). Biodiesel has been studied as an alternative fuel for diesel engines for over a decade (Samniang *et al.*, 2014). Nowadays, the world is currently being produced biodiesel to replace diesel fuel (Fernandes *et al.,* 2013).

Biodiesel feedstock used for production includes algae, animal fats and vegetable oils like palm, jatropha, rapeseed, sunflower etc. Brazil and US for example are promoting ethanol as a potential biofuel derived from sugar cane and corn, and Asian countries like Malaysia, Indonesia and India have been promoting palm oil and jatropha as biodiesel throughout widely (Yee *et al.,* 2009; Silitonga *et al.,* 2011; Ong *et al.,* 2011). Figure 1.1 shows advantages and disadvantages of using biodiesel as compared to diesel fuel.

Advantages
Biodiesel has 10-11% of oxygen; this makes biodiesel a fuel with high combustion characteristics Biodiesel reduces net carbon-dioxide emissions by 78% on the lifecycle basis when compared to conventional diesel fuel and reduces smoke due to free soot. Biodiesel has superior lubricating properties. This improves lubrication in the pump and injector units, which decreases engine wear, tear and increases engine efficiency Biodiesel has higher cetane number (about 60-65 depending on the vegetable oil) than petroleum diesel which reduces ignition delay. Biodiesel may not require engine modification up to B20. However, higher blends may need some minor modification Production can be raised easily and is less time consuming
Disadvantages
Biodiesel has 12% lower energy content than diesel: leads to increase fuel consumption of about 2-10%. Biodiesel causes excessive carbon deposition and gum formation (polymerization) in engine and oil get contaminate and suffer from flow problem. Biodiesel has higher cloud point and pour point, higher nitrogen oxide emissions, lower volatilities that cause formation of deposits in engine due to the incomplete combustion. Transesterification process is expensive (cost of fuel increases), these oil required expensive fatty acid separation or use of less effective or expensive acid catalyst. Use of biodiesel in internal combustion engine may lead to engine durability problems including injector cocking, filter plugging and piston ring sticking, etc. Lower engine speed and power, high price, high engine wear, engine compatibility

Figure1.1: Advantages and disadvantages of biodiesel

Malaysia had launched the National Biofuel Policy to encourage more sources from renewable energy (Ministry of plantation industries and commodities, Malaysia, 2006).The policy was eventually launched in March 2006 and is underpinned by five strategic thrusts, with short-term, medium-term and long-term implementation periods. Figure 1.2 show the summary of the National Biofuel Policy (Hsiao *et al.,* 2011).

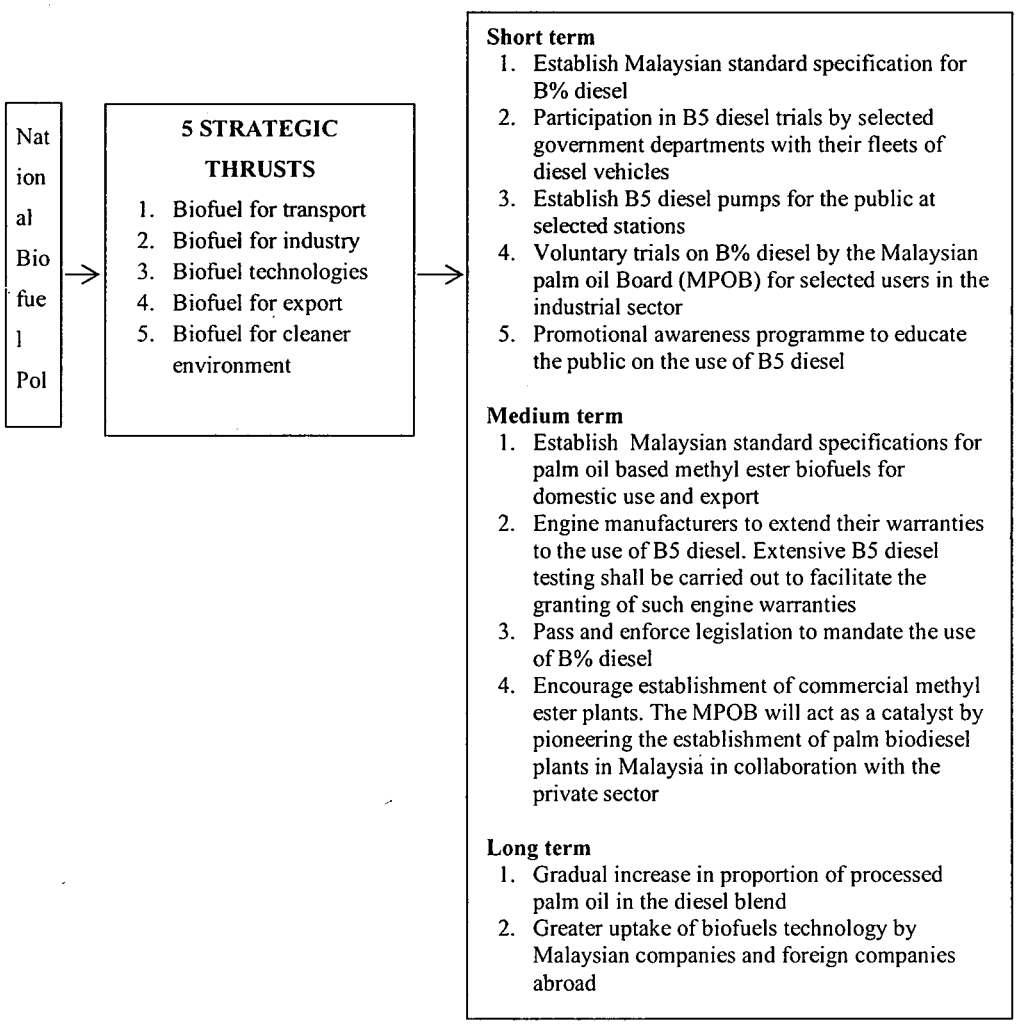

Figure 1.2: Implementation of National Biofuel in Malaysia

Malaysia has introduced a 5 % biodiesel blended composition which is 5 % consist of Palm oil methyl ester (POME) and known as B5 since mid-year 2011. Currently, extensive research also has been conducted in Malaysia to promote the usage of Jatropha and Algae biodiesel as they are easily obtained (Khan *et al.,* 2014; Akbar *et al.,* 2009). Compatible with climate change in Malaysia make Jatropha a promising alternative fuel. Apart from that, Algae also has attracted many researchers as it is easy to be found especially in Sabah and Sarawak. However, the use of Algae as an alternative fuel is still in its infancy (Khan *et al.,* 2014).

1.2 Problem Statement

The batch transesterification process requires large reactors and longer reaction and separation times because the reaction and separation stages are usually carried out in the same tank. In contrast, the reactor for continues process can be smaller than that the batch process for the same production capacity. Several types of continuous reactors have been studied and applied for biodiesel production (Lertsathapornsuk *et al.,* 2008; Zhang *et al.,* 2010) On the laboratory scale, continuous reactor system assisted by microwave has been demonstrated. Other continuous flow processes using a rotating packed bed, supercritical methanol or gas liquid reactor have been found to be more effective for the transesterification (Chen *et al.,* 2010; He *et al.,* 2007; Behzadi & Farid, 2009) It is believed that the transesterification of the TG with methanol is an equilibrium reaction system. Therefore, the equilibrium can be shifted to the right, i.e., the formation of FAME, by performing a multistep transesterification processes. To minimize the influence of glycerine on the back reaction, the glycerine in the reaction mixture should be taken out after each step. The important of establishing for proper processing biodiesel route as a driving force for the development of the new technology of processing for several decades. A variety of sonochemical apparatus are commercially available with several design: ultrasonic cleaning baths, direct-immersion ultrasonic horns and flow reactors are common examples. Cleaning bath has insufficient intensity for most applications. Recently, the ultrasound clamp on tubular reactor development received less attention in other country because they are still not aware the potential of such as technology because it is really new. Therefore, it is great potential for Malaysia to become a leader can patent the as ultrasound process.

1.3 Objectives of Study

a) To design a new continuous process for biodiesel using ultrasound clamp on tabular reactor for producing pure biodiesel from jatropha curcas oil.
b) To fabricate and test the application of sonochemistry technique in biodiesel production through optimal and low cost production technique for enhancing their capabilities and effective process.
c) To verify and to evaluate a test bed for continuous reactor using tubular reactor.

1.4 Research Question

1.4.1 State the current scenario?

In south East Asia, Malaysia is one of the countries which actively doing the commercial production and utilize biodiesel as fossil fuels replacement/ alternative due to its abundant palm oil resources. The current approved installed capacity for biodiesel production is about 10.2 million tons in Malaysia ("Production Of Biodiesel From Waste Cooking Oil Using," 2012). Generally, the overall biodiesel cost consists of raw material, catalyst, biodiesel processing, transportation local and national taxes (Haas *et al.,* 2006). The existing processing of biodiesel is using the conventional based on stirring method.

1.4.2 What is wrong with current scenario?

The conventional techniques resulted low initial cost, however produced low rates of chemical reactions due to the limitation of the mass and heat transfer process. Actually, the low rates of chemical reaction will mainly influence the cost of biodiesel processing. Therefore, an effort to increase the rates of reaction will be carried by ultrasonic process for cost reduction.

1.4.3 State The Solution?

The ultrasonic clamp-on tubular reactor is a new apparatus of ultrasonic with could be settled with variable frequencies. In our previous work, the optimum parameter such as reaction time, methanol to oil molar ratios, catalyst concentration, water concentration and output power were investigated. Based on the optimum parameter in our previous work, a batch of small pilot plant with semi continuous processes using ultrasound clamp on tubular reactor for biodiesel production from jatropha curcas oil and waste cooking oil was develop (Sebayang *et al.,* 2010). Biodiesel production using ultrasonic clamp on tubular reactor has shown that the reaction time is reduced approximately by 80% compared to the conventional stirring method. The biodiesel oil was then analyzed according to physical and chemical properties. Fatty acid methyl ester (FAME) yield increased about 10wt% compared to conventional stirring method. The biodiesel oil fulfilled biodiesel standard according to EN-14122 (2003). Besides, the biodiesel oil (B5 and B10 according to Malaysian level standard) was tested on performance and emission characteristics in diesel test bed. It indicated that the performance of the biodiesel similar with diesel fuel characteristic

1.4.4 Described the working principle behind the solution?

The ultrasound is well known as a useful apparatus to make a fine emulsion from immiscible liquid. Owing to this aspect, the transesterification reaction of vegetable oil and alcohol can reach equilibrium in a short reaction time with a high yield of alkyl esters even at low temperature (Stavarache, 2006; Georgogianni *et al.,*2009; Sebayang *et al.,* 2010).

1.4.5 Why is your solution better than your competitors?

The reaction time is 80 % faster compared to the conventional process. Therefore, this project is aimed to build continuous transesterification process of vegetable oil based on ultrasonic clamp on tubular reactor system with flow rate capacity 6.6ml/s. This test bed will be up scaled and used in industry. The small scale can be used as teaching model for polytechnics and other technical institution.

1.4.6 Research background including summary of previous research related to the development.

Biodiesel, a liquid fuel consisting of mono-alkyl esters of long chain fatty acids derived from vegetable oils, can be used as a substitute for diesel fuel (Xue *et al.,* 2006). Some of the advantages of using biodiesel fuel are its renewability, easy biodegradability, non-toxicity and safer handling due to its higher flash point compared to those of fossil fuels(He *et al.,* 2007). In addition, biodiesel fuel is also primarily free of sulphur and aromatics, producing more tolerable exhaust gas emissions than conventional fossil diesel (Demirbas, 2008). Biodiesel is synthesized by the transesterification of triglycerides (TG), the main components of vegetable oil and animal fats, with mono-alcohol in the presence of a catalyst, into fatty acid alkyl esters. The TG is converted stepwise to diglycerides (DG), monoglycerides (MG) intermediates and finally to glycerine (GL).The transesterification can be carried out in batch or continuous reactors (Y. Zhang, 2003).

1.4.7 Description of prototype including its originality, innovativeness, special features and indicates strategies to be used that will make the product competitive.

The following figure 1.3 shows the proposed set-up continuous reactor system for biodiesel processing. The whole process (esterification, transesterification, and purification) based on the clamp on tubular system. Figure 1.3 show process schematic diagram of tubular assisted continuous reactor for biodiesel production. The diagram indicated that the whole process (esterification, transesterification and purification) using the clamp on tubular. Proof of concept related to the optimum parameter, such as: reaction time, methanol to oil molar ratios, catalyst concentration, water concentration and output power for the esterification, transesterification and purification process using ultrasound clamp on tubular reactor were investigated (Sebayang *et al.,*2010). Based on the optimum parameter in our previous work, a batch rig plant with semi continuous processes using ultrasound clamp on tubular reactor biodiesel production from jatropha curcas oil and waste cooking oil was developed by our research group (Sebayang *et al.,* 2010). Biodiesel production using ultrasonic clamp on tubular reactor has shown that the reaction time is reduced by approximately 80% compared to the conventional stirring method. The biodiesel oil was then analyzed according to physical and chemical properties. Fatty acid methyl ester (FAME) is obtained about 96.5wt %. The biodiesel oil fulfilled biodiesel standard according to ASTM D6751. Besides, the biodiesel oil (B5 and B10 according to Malaysian level standard) was tested on performance of this biodiesel similar with diesel fuel characteristic in diesel test bed. It was indicated that the performance of this biodiesel similar with diesel fuel characteristic. This continuous process will be a model that can be used as a reference for an industrial size plant later. The process is economical, quicker and much more efficient.

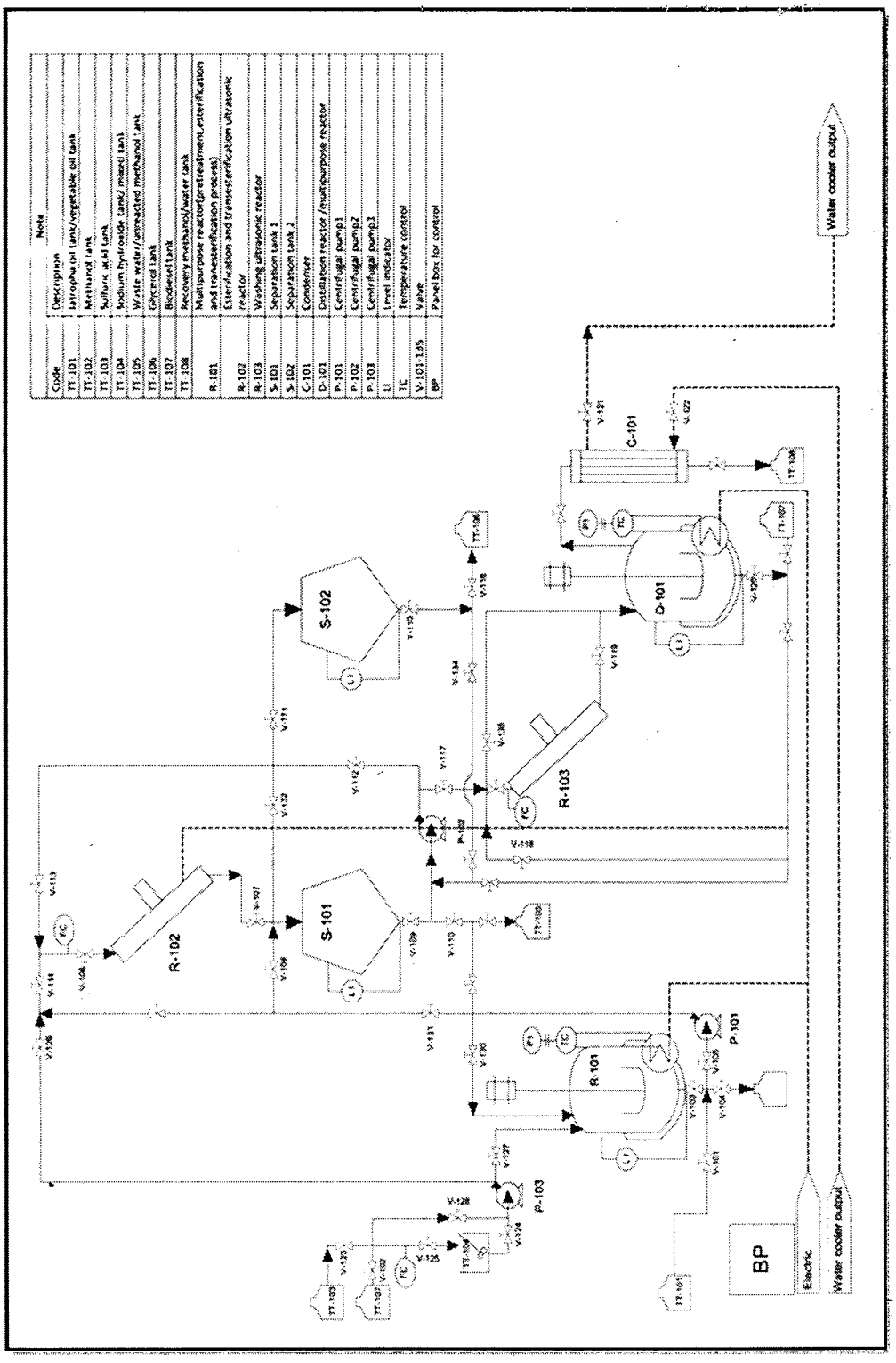

Figure 1.3: Flow process flow diagram of tubular assisted continuous reactor for biodiesel production for the pilot plant.

1.4.8 Describe of the state of the art including information on similar product available in the market and existing market size.

The whole biodiesel process is based on the ultrasonic system. As far as we know, no similar process in the market.

1.4.9 Describe how the developed prototype can contribute to wealth reaction, enhance quality of life and create or consolidate new industries.

This process will improve the production of biodiesel and improve cost saving and time. The process reduces waste and increase productivity. It is also a green technology.

1.4.10 If development cost for the prototype is more than the PRGS ceiling, state how you plan to obtain the remaining fund.

We try to cooperate with the small industry in Malaysia which is interested in Biodiesel processing.

1.4.11 Provide the activities and potential funding sources to bring the developed prototype to commercialization.

Cooperate with the small industry, polytechnic and university to work together and promote the novelty of the product

CHAPTER 2

LITERATURE REVIEW

As we know, that a considerable amount of biodiesel is produced from edible oils. However, the extensive use of edible oils might lead to some negative impacts such as starvation and higher food prices in developing countries. For instance, in Malaysia the biodiesel refineries have created shortages in palm oil. Therefore the price of palm oil for cooking has risen by 70 %. The rising food prices may be beneficial to the poor farm producers but at the same time they are unlikely to benefit the urban poor. So for solve this problem, many of the researchers agree that non-edible oils are the suitable alternative to edible oils for biodiesel production. Hence, the recent focus is to find non-edible oil feedstock for biodiesel production. Besides that, to produce biodiesel have many methods. The method that be used in this study is producing biodiesel using jatropha curcas oil (JCO) using ultrasonic in-line reactor. This chapter will elaborate the state of art in the biodiesel production from initial feedstock to final product through the literature reviews.

2.1 Feedstock Properties

The renewable product of biodiesel comes from many sources. The sources such as Jatropha Curcas oil (JCO), vegetable oil, animal oil, and waste cooking oil are used as raw material to produces biodiesel in order to replace a petroleum diesel. These raw materials have different contain of fatty acid. Nevertheless, Jatropha oil has more potential to make as feedstock for biodiesel.

Jatropha curcas is a plant that has a place with the Euphorbeaceas family. Inside this variety there are more than 170 species dispersed far and wide, particularly in tropical locales. This plant originates from Focal America (México), and it is conceivable to acquire an oil yield higher than 1500 kg for every hectare. This oil is satisfactory to be utilized as an issue material as a part of the biodiesel production (Heller, 1996).

Jatropha curcas oil produced from the seed of Jatropha plant which is grows in all the common and marginal lands. The species of plant that is used for oil extraction is known as Jatropha Curcas. Most of the Jatropha is very toxible. Therefore, they are not consumable to human and living thing. The main gold of cultivating of Jatropha all over the world is to use as an alternative energy sources. Jatropha oil extraction methods have also gained the same importance like Jatropha cultivation. Since the oil extracted from Jatropha seeds is the main source for biofuel, the extraction methods have also become significant.

The Jatropha curcas (Figure 2.1 parts of Jatropha curcas) is gaining more attention as feedstock for biodiesel production due to its incompetence with food crops. Furthermore, adverse climatic conditions such as, high temperature, low moisture content and soil fertility do not affect its productivity (Balat, 2011). Moreover, Jatropha curcas oil is not suitable for nutrition purposes due to the presence of phorbol ester as toxic constituents, however, without detoxification making it used as energy or fuel source (Akbar *et al.,* 2009).Presently, Malaysia's government is given more concern on non-edible feedstock to produce green fuel in order to avoid the controversial food issues ("FRIM completes Malaysian jatropha pilot , aims for scale," 2012).

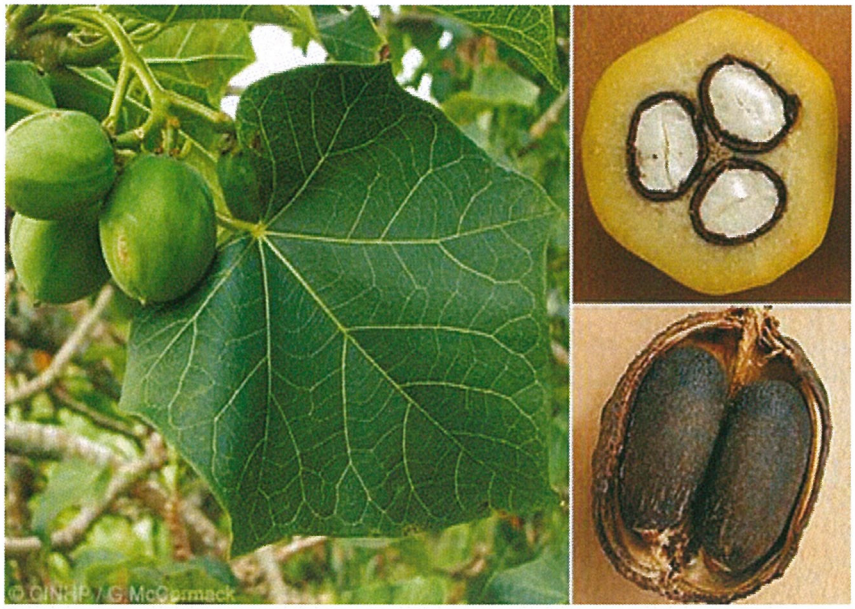

Figure 2.1: The parts of jatropha curcas

The extracted oil from the seeds is being processed to prepare a high quality bio-fuel. This bio-fuel can be an alternatives source that can be used in any diesel engine. The residue that remains after extracting the oil is used as a fertilizer. Jatropha oil (Table 2.1 properties of jatropha curcas oil) is non-edible and also very poisonous. Jatropha has to be made with two processes in order to get a better yield of 92 % otherwise a yield of less than 85 % will only be required("Crude Jatropha Oil - Jatropha Oil - Jatropha Greenhouse Gases - Buy, Sell Jatropha Oil," n.d.).

Table 2.1: Properties of Jatropha Oil

No	Property	Value
1	Density	0.92 g/cm^3
2	Ignition point	340 °C
3	Solidification point	5 Kin
4	Viscosity	75 to 7 x 10^{-6} m^2/s
5	Iodine value	13
6	Saponification value	198
7	Cetane number	23/51
8	Heating value	39.628 MJ/kg
9	Flash point	240/110 °C
10	Carbon residue	0.64
11	Distillation point	295 °C
12	Kinematics viscosity	50.73
13	Sulphur	0.13%
14	Calorific value	9.470 kcal/kg
15	Pour point	8 °C
16	Colour	4.0
17	Acid value	1.0 – 38.2
18	Specific gravity	0.917/0.923(0.881)
19	Solidifying point	2.0
20	Refractive index	1.47
21	Palmitic acid	4.2
22	Stearic acid	6.9
23	Oleic acid	43.1
24	Linoleic acid	34.3
25	Other acids	1.4

2.3 Biodiesel Properties

Biodiesel properties is main criterion of biodiesel quality is the inclusion of its physical and chemical properties into the requirements of the adequate standard. Quality standards for biodiesel are continuously updated, due to the evolution of compression ignition engines, ever-stricter emission standards, revaluation of the eligibility of feedstock used for the production of biodiesel, etc. The quality if biodiesel can be determined from it properties. Currently, the standard that most popular American standard specification for biodiesel fuel (B100) blends Distillate feels (ASTM D6751). Biodiesel standards have developed or establish in various countries and region around the world (Knothe & Gerpen, 2005). The details of specification s of biodiesel refer to ASTM D6751.

Table 2 2: ASTM D6751 Standard

Property	Method	Limits	Units
Flash point, closed cup	D 93	130 min	° C
Water and sediment	D 2709	0.050 max	% volume
Kinematic viscosity, 40°C	D 445	1.9 – 6.0	mm^2/s
Sulfated ash	D 874	0.020 max	wt. %
Total sulfur	D 5453	0.05 max	wt. %
Copper strip corrosion	D 130	No. 3 max	
Cetane number	D 613	47 min	
Cloud point	D 2500	Report to customer	° C
Carbon residue	D 4530	0.05 max	wt. %
Acid number	D 664	0.8 max	mg KOH/g
Free glycerin	D 6584	0.02	wt. %
Total glycerin	D 6584	0.24	wt. %
Phosphorus	D 4951	10	ppm
Vacuum distillation end point	D 1160	360 °C max, at T-90	
Storage stability	To be determined	To be determined	To be determined

2.3.1 Flash Point

Flash point is the lowest temperature at which it can vaporize to form an ignitable mixture in air. Flash point is important for proper safety and handling of biodiesel fuel. It is also important for storage of biodiesel so that we can observe the storage temperature to make sure it in safe condition.

2.3.2 Viscosity

Viscosity can be expressed as kinematic viscosity. Kinematic viscosity takes into account the fluid density and measured in unit called "centistokes". When comparing the values, it is important to note the temperature when the measurement was taken. In general view, the viscosity of liquid reduced as the temperature rises. Figure 2.2 shows kinematic viscosity at 40^0C.

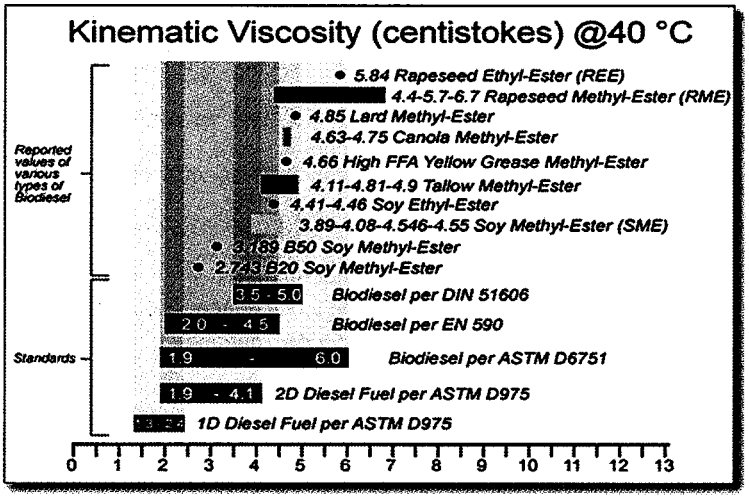

Figure 2.2: Kinematic viscosity at 40 °C

2.3.3 Density

Density is referring to viscosity of biodiesel in several standards. It is important for biodiesel parameters that impact the quality of fuel. Density or volumetric mass density is a mass per unit volume.

2.3.4 Acid Value

The quality of biodiesel is related to acid value of biodiesel. Acid value may increase during storage due to hydrolysis reactions. Purity of biodiesel was determined using acid value. Acid value can formed corrosion on component in engine.

2.3.5 Water content

For run this test, the sample of biodiesel is placed in the syringe and must be weighted and tare to zero. After that, the sample of the biodiesel is put into the machine. The amount of the weighted is different before and after the biodiesel

injected into the water. It will be analyzed and will be key –in into the machine. The water analyzed will print out the amount of moisture in the form of percentage. This test is very important because water reduces the heat of combustion. This means more smoke, harder starting and less power. Water will corrode vital fuel system components, like fuel pumps, injector pumps and fuel lines.

2.4 Biodiesel Production

Jatropha oil is one of source energy has potential to produce biodiesel. But before to produce biodiesel from jatropha is need follow the systematic process starting with titration of oil for test FFA contain. In biodiesel production, oil and fats which have the FFA content above than 2% it need some pre-treatment process to reduce the FFA content. Esterification process is one name of pre-treatment process. Transesterification is alcoholysis, during this process the chemical displacement of alcohol from an ester by another alcohol in a process similar to that of hydrolysis (Egi Augustian, 2012).

General name for a chemical reaction in which two reactants (typically an alcohol and an acid) form an ester as the reaction product is esterification. The commonly alcohol used in biodiesel production is methanol because it is cheap cost and availability. Another alcohol can be used in biodiesel production are ethanol and higher alcohols such as isopropanol, butanol can also be used for the esterification. Besides that, by using higher molecular weight an alcohol improve the cold flow properties of biodiesel but reduces the efficiency transesterification process. By using alkali catalyzed the transesterification process is faster and alkali catalyzed almost widely used in biodiesel production. Another factor, that affect transesterification process are oil temperature, reaction temperature, ratio of alcohol to oil, catalyst type and concentration and reaction time (Hofman *et al.,* 2006).

The last step to meet biodiesel useful as fuel is purification process. Methanol removal, washing-either water washing or dry washing using an absorbent and subsequent drying of the biodiesel before final filtering are processes necessary to make biodiesel quality as per required for the combustion or heating fuel. In the glycerol removal unit operation, the glycerol is neutralized using citric acid to separate the remaining fatty acid and crude glycerol. This remaining fatty acid can be esterified to produce biodiesel provided its minimum amount is sufficient. Glycerol itself is a common feedstock for soap production.

2.4.1 Esterification

Esterification is chemical reaction between two reacant(typically an alcohol and acid) form an ester as the reaction product. Acid calalysis affer the advantage of esterification free fatty acids contained in the fatls and oil and therefore, is especially suited for the transesterification of highly acidic fatty material. However,acid catalyzed transesterification are usually far slower than alkali catalyzed reactions and required higher temperature and pressures as well as higher amounts of alcohol. The typical reaction conditions for homogeneous acid-catalyzed methanolysis are temperature of up to 100°C and pressures of up to 5 bars in order to keep the alcohol in a liquid for (Lepper & Friesenhagen, 1984).

Besides that, disadvantages of acid catalysis probably prompted by higher reaction temperatures and increased the formation of unwanted secondary product, such as dialky esters or glycerol esters (Mittelbach *et al.*,1996). It is because the slow reaction rates and high temperatures needed for transesterification, so acid cataylst are only used for esterification reactions. Thus for vegetables oil or animal fats with an amount of free fatty acid larger than approximately 1% two states are possible. The free fatty acids (FFA) can be esterified under acid catalyzed conditions followed by alkine catalyzed in transesterification reaction. This so called esterification has the advantages that

prior to the transesterification most of the free fatty acid is already converted into methyl ester, acoordingly the overall yield is very high.

Berrios *et al.,* (2007) , Knothe & Gerpen, (2005)Gerpen and and Foon *et al.,*(2004) have investigated that esesterification is necessary i f the free fatty acid (FFA) level of oil above 1%(w/w) which is equivalent to 2 mg KOH per gram of triglyceride. While Canakci & Van Gerpen, (2001) recomended acidity reduces below 0.5%. Knothe & Gerpen (2005) found that the biodiesel yield from unferined oil will decrese from 93-98% to 86-87% in the presence of above 5 % FFA and ascribed it to phospholipids that destroys the catalyst effect. The esterification of FFA with methanol in the presence of an acid catalyst is shown in Figure 2.3.

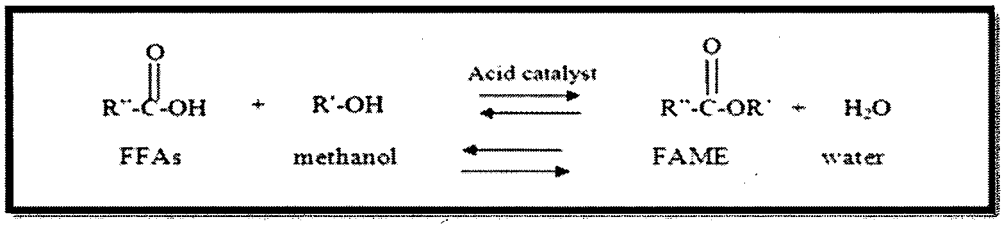

Figure 2.3: Esterification of FFA with methanol to produce methyl esters and water

In addition, by using the oils with higher FFA contents in alkali catalyzed transesterification results in the formation of soaps and causes difficulties in the purification of biodiesel, thereby increasing the overall production cost (N.Saifuddin *et al.,* 2009). A new technique has been develop to produce biodiesel from jatropha curcas seed oil having high free fatty acids (15% FFA). The high FFA level of jatropha curcas oil was reduced to less than 1% by two step pretreatment process. The first step for esterify the FFA with methanol by acid catalysis. This was carried out with 0.60 wt% methanol to oil ratio in the presence of 1wt% H_2SO_4 as acid catalyst in 1 hour reaction at 50°C. After the reaction, the mixture was allowed to settle for 2 hours and the separated methanol-water mixture at the top layer was removed (Berchmans & Hirata, 2008).

When the content is lower than 0.5%, the sulfuric acid is drained, and the solid alkali is introduced into system for complete the transesterification process (Canakci & Van Gerpen, 2001). A common approach in cases where the FFA content of feedstock is in excess of 1.0% is a two-step process in which acid pretreatment of the feedstock to lower its FFA content is followed by transesterification with homogenouse base catalyst to produce biodiesel. Another researches in acid pretretment procedure, FFA are esterified to the corresponding FAME in the presence of heat, excess methanol, and acid catalyst, nomarly sulfuric acid (Ramadhas *et al,* 2005). Esterification of fatty acids accours simultaneously with transesterification reaction of triglycerides.

2.4.2 Transesterification

The majority of the biodiesel today is produced by the alcohols of triglycerides with methanol by the an alkali catalyst, a process frequently referred to as transesterification, Knothe (2010), Knothe and Gerpen, (2005) have listed four method to reduce the high viscosity of vegetables oil to enable their use in common diesel engines without operational problem such as engine deposits: direct blending with petrol-diesel, pyrolysis, micro emulsification and transesterification. Only transesterification reaction leads to biodiesel as the product.

Transesterification is the process is converting vegetable oils into biodiesel Transesterification (also called alcoholysis) is the reaction of a fat or oil with an alcohol to form ester and glycerol. Meher *et al.,*(2006) reported alcoholysis or transesterification is the displacement of alcohol from an ester by another in a similar process to hydrolysis, except that alcohol is used instead of water. This process used for reduce the viscosity of triglycerides. Transesterification of triglycerides produces fatty acid alkyl esters and glycerol. The glycerol layer settles down at the bottom of the reaction vessel. Diglycerides and monoglycerides are the intermediates in this process. The reaction of

triglycerides is shown in Figure 2.4. when NaOH:KOH, K_2CO_3 or other similar catalyst were mixed with alcohol, the actual catalyst alkoxide group is formed. A small amount of water generated inthe rection may cause soap formation during transesterification(Ma & Hanna, 1999).

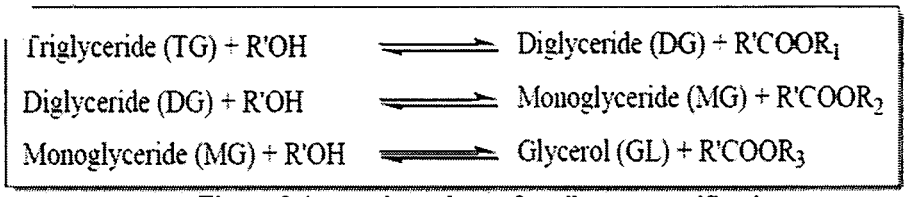

Figure 2.4: reaction scheme for oil transesterification

In this process vegetable oil reacted with an alcohol like methanol or ethanol in presence of a catalyst by either acid or base. Methanol and ethanol are used most frequently especially for methanol due to its low price and its physical and chemical advantages-polar and shortest chain alcohol (Ma & Hanna, 1999).Various components of vegetable oil break down to form new compounds after the chemical reaction. The chemical names of biodiesel, triglycerides are converted into alkyl esters. In the chemical reaction, if methanol is used methyl esters are formed, but if ethanol is used, then ethyl esters are formed. Both of these compounds are biodiesel fuels with different chemical combinations.

Alkaline or basic catalysis is by far the most commonly used reaction type for biodiesel production. The main advantages of this form of catalysed transesterification are a high conversion under the mild conditions in comparatively short reaction times (Freedman *et al.,* 1986). It was estimated that under the same temperature conditions and catalyst concentration methanolysis is might proceed about 4000 times faster in the presence of an alkaline catalyst than in the presence of the same amount of an acidic equivalent (Formo, 1954). Moreover alkaline catalysts are less corrosive to industrial equipment and thus enable the use of less expensive carbon-steel reactor material.

Berchmans and Hirata (2008) have been developing technique to produce biodiesel from jatropha curcas seed oil having high free fatty acids (15% FFA). High FFA of jatropha curcas oil was reduced to less than 1% by two step pre-treatment process. The second step was transesterification process using 32.56

wt%. methanol to oil or same with methanol to oil molar ratio 9:1 and 1.4wt% NaOH to oil as an alkaline catalyst to produce biodiesel at 65°C.the final yield for methyl ester of fatty acid was achieved at 90% in two hours (Berchmans & Hirata, 2008).

Generally the ranges of molar ratios of methanol to triglyceride used have been in between 5.25-6:1. Freedman *et al.,* (1986) suggested that, for maximum yield of the FAME, a molar ratio of 6:1 should be used. He also noted that molar ratios greater than 6:1 did not increase the yield of FAME, will make recovery of FAME and glycerol complicated and increase, therefore the cost of the methanol recovery.

According to Deng *et al.,* (2010) mixtures of Jatropha oil, methanol and catalyst (NaOH) stirred at 600 rpm were reacted for biodiesel production in an ultrasonic reactor at power of 210W on 60 °C. NaOH was used as catalysts for the base-transesterification process to produce biodiesel. It found that in transesterification step 96.4% biodiesel yield with 0.32 mg KOH/g acid value was achieved for 0.5 h transesterification reaction. For transesterification process only take 0.5 hour to achieve 96.4% diesel yield that is half time of the previous work of Berchmans and Hirata(2008).

2.5 Factors Affecting Transesterification Reaction

There are many factors that could affect the yield and conversion of biodiesel. The factor such as types content of free fatty acid and moisture, the amount of alcohol/ triglyceride molar ratio, type and concentration of catalyst used, mixing intensity, reaction time and reaction temperature. These all factors will determine by the final result biodiesel product as the ASTM standard to be officially confirmed that it is usable and can be further commercialized.

2.5.1 Effect of alcohol/ triglyceride Molar Ratio

The most important variables affecting the yield of ester is the molar ratio of alcohol to triglyceride. The stoichiometric ratio for transesterification requires 3 mol of alcohol and 1 mol of triglyceride to yield 3 mol of fatty acid alkyl esters and 1 mol of glycerol. However, transesterification is equilibrium reaction in which a large excess of alcohol is required to drive the reaction right. For maximum conversion to the ester, a molar ratio 6:1 should be used.

The emulsions are caused in part by formations of the intermediate monoglycerides and diglycerides, which have both polar hydroxyl groups and nonpolar hydrocarbon chains. These intermediates are strong-surface active agents. In the process of alcoholysis, the catalyst, either sodium hydroxide or potassium hydroxide, is dissolved in polar alcohol phase, which triglycerides must transfer in order to react. The reaction is initially mass transfer controlled and does not conform to expected homogeneous kinetics.

When the concentrations of these intermediates reach a critical level, emulsions form. The larger nonpolar group in ethanol, relative to methanol, is assumed to be the critical factor in stabilizing the emulsions. However, the concentration of mono- and diglycerides is very low, so then the emulsions become unstable. This emphasizes the necessity for the reaction to be as complete as possible, thereby reducing the concentrations of mono-and diglycerides.

Molar ratio of alcohol plays a vital role in biodiesel yield Leung and Guo, 2006; Zhang et al., 2003: Ma and Hanna, 1999; Freedman et al., 1986). Normally the transesterification reaction requires 3 mole of alcohol for one mole of triglycerides to three mole of fatty acid ester and one mole of glycerol. Excess amount of alcohol increases conversion of fats into esters within a short time. So the yield of biodiesel increases with increase in the concentration of alcohol up to certain concentration.

The required molar ratio of oil to methanol is 1:3 in order to generate three moles of biodiesel from one mole of oil. The molar ratio used in practical

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