# ELUCIDATION OF SONOCHEMICAL REACTION KINETICS OF BIODIESEL PRODUCTION FROM JATROPHA OIL

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## ELUCIDATION OF SONOCHEMICAL REACTION KINETICS OF BIODIESEL PRODUCTION FROM JATROPHA OIL

VALERIAN VICTOR KONG

Thesis submitted to the Faculty of Chemical and Natural Resources Engineering in partial fulfillment of the requirements for the degree of Bachelor of Engineering

Faculty of Chemical & Natural Resources Engineering UNIVERITI MALAYSIA PAHANG

JUNE 2012

### SUPERVISOR'S DECLARATION

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 degree of Bachelor of Engineering.

Signature: Name of Supervisor: D.M. DR. REDDY PRASAD Position: Date: 18<sup>th</sup> JUNE 2012

### **STUDENT'S DECLARATION**

I hereby declare that the work in the thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature: Name: VALERIAN VICTOR KONG ID Number: KA08035 Date: 18<sup>TH</sup> JUNE 2012 Dedicated especially to my beloved Father, Mother, Siblings, Lecturers, Dear, Friends and the ones who give me inspiration and support that made this work possible.

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### ABSTRACT

Biodiesel, an alternative renewable fuel made from transesterification of vegetable oil with alcohol, is becoming more readily available for use in blends with conventional diesel fuel for transportation applications. One way of reducing the biodiesel production costs is to use the less expensive feedstock containing fatty acids such as inedible oils, animal fats, waste food oil and by products of the refining vegetables oils. Biodiesel production process is the transesterification of the used twosteps catalyzed process with jatropha oil and methanol, in the presence of alkali catalyst, to yield the ethyl ester as a product and glycerine as a by-product. In the acid treatment or the acid-catalyzed esterification, the temperature is set at 60°C, acid catalyst of 1% w/w H<sub>2</sub>SO<sub>4</sub>. These studies have been performed based on 2 effects, temperature and oil to methanol molar ratio with fixed parameter of 1% w/w NaOH and 20 kHz of frequency for optimization and lastly with time which is used for kinetic study. As a result, the best condition that has been determined for maximum biodiesel production was 1:6 of oil to methanol molar ratio. However, the temperature does not effect to the biodiesel yield. Biodiesel yield in biodiesel production from jatropha curcas oil were measured by using <sup>1</sup>H NMR spectrometer analysis. These processes which using ultrasonic reactor is easy and faster than other biodiesel production process because cavities caused by the ultrasound at the catalyst surface increase the catalyst activity and reduce the activation over potential loss.

### ABSTRAK

Biodiesel, bahan bakar alternatif boleh diperbaharui yang terbuat dari pengtransesteran minyak sayuran dengan alkohol, menjadi lebih mudah sedia untuk digunakan dalam campuran dengan bahan bakar solar konvensional untuk aplikasi pengangkutan. Biodiesel adalah pengtransesteran dari dua digunakan-langkah proses mangkin dengan minyak jatropha dan metanol, dengan adanya mangkin alkali, untuk menghasilkan ester etil sebagai produk dan gliserin sebagai produk-oleh. Pada perlakuan acid atau pengesteran acidcatalyzed, suhu ditetapkan pada 60 °C, asid mangkin 1% w/w H<sub>2</sub>SO<sub>4</sub>. Pengajian-kajian ini telah dilakukan berdasarkan 2 kesan, suhu dan nisbah methanol untuk minyak dengan 1% pemangkin konsentrasi NaOH dan 20 kHz frekuensi untuk pengoptimum dan masa untuk pengajian kinetik. Akibatnya, keadaan terbaik yang telah ditetapkan untuk pengeluaran biodiesel maksimum adalah 1:6 nisbah minyak untuk methanol. Namun, suhu tidak membawa sebarang kesan terhadap penghasilan biodiesel. Biodiesel hasil dalam pengeluaran biodiesel dari minyak jatropha diukur dengan analisa dari alat <sup>1</sup>H NMR spectrometer.

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### LIST OF ABBREVIATIONS

<sup>1</sup> H NMR	Proton Nuclear Magnetic Resonance
ASTM	American Society for testing and materials
СО	Carbon monoxide
FFA	Free Fatty Acid
GC-FID	Gas Chromatography-Flame Ionized Detector
$H_2SO_4$	Sulphuric acid
JCO	Jatropha curcas oil
kHz	kilo hertz
MHz	mega hertz
NaOH	Sodium Hydroxide
NO <sub>x</sub>	Nitrogen oxide
N <sub>2</sub> O	Nitrous oxide
SO <sub>x</sub>	Sulphur oxide

### **CHAPTER 1**

### **INTRODUCTION**

### **1.1 BACKGROUND**

Biodiesel is an alternative fuel for diesel engines that is receiving great attention worldwide. Ever since energy demands have been steadily increasing along with the growth of human population and industrialization, it attracts the most attention because it is renewable, it can be used either pure or in blends with diesel fuel in unmodified diesel engine and it reduces some exhaust pollutants. Moreover, growing consumption of energy has rapidly depleted non-renewable sources of energy. Rising price of fossilbased fuels and potential shortage in the future have led to a major concern about the energy security in every country.

Biodiesel fuel is defined as alkyl esters of long-chain fatty acids (Knothe et al., 2002). It is produced in the alcoholysis or also known as transesterification reaction of natural triglycerides such as vegetable oil or animal fats with short-chain alcohol such as methanol or ethanol. The reaction requires the presence of base or acid catalysts, or enzymes, heating and efficient mixing, or it is conducted in non-catalytic but supercritical conditions. Base-catalyzed alcoholysis, as being much faster than acid-catalyzed, is mostly used commercially. Potassium and sodium hydroxide are usually used as a catalyst in the biodiesel production because of low price, ease handling in transportation and storage and the possibility to be prepared water-free. The main disadvantage of strong base alkaline hydroxides is the formation of undesired soaps in a

direct reaction with esters and triglycerides. To counter the disadvantages, two-step transesterification is the best solution for preventing the formation of undesired soaps.

All feedstocks that consist of fatty acids or glycerol can be used for biodiesel production including jatropha oil. In European countries, rapeseed oil is used due to its widespread availability. Soybean oil is used in the Unites States of America, while palm oil is used widely in tropical regions such as Malaysia. The use of methyl esters as fuel requires a low proportion of saturated fatty acids in order to make the fuel function at low temperatures. In colder climates, rapeseed oil and olive oil have proven to be one of the best options. The usage of palm oil is ideal in Malaysia due its abundant availability as well as its suitability in warm climates. Palm oil can also be used as blends with other types of oil. Feedstock chosen is also influenced by national and international specifications of biodiesel that need to be fulfilled.

### **1.2 PROBLEM STATEMENT**

Energy is a basic requirement for every sector of economic development in a country. As a result, the growth of industries, transport, agriculture and other human needs depends hugely on the petroleum fuels. In the recent years, the fossil fuel resources are depleting rapidly with consequent environment degradation. Being a fast solution to the shortage of liquid fuel, biodiesel is one of the most popular alternatives of all time. This research seeks to solve this uncertainty in the feedstock sustainable selection, of the types of biodiesel feedstock, namely Jatropha oil.

Ultrasonic transesterification in biodiesel production can reduce its processing time. Years before, conventional agitation has been used for producing biodiesel with requirement time up to 12 hours. With ultrasonic method, the processing time of biodiesel yield only take less than 60 minutes. The requirement of catalyst also reduced by 50% due to the increased chemical activity in the cavitations formed due to sonication. Moreover, the amount of excess alcohol required also reduced abundantly while increasing the purity of the glycerine formed.

### 1.3 OBJECTIVES

The objective of this research was to prepare biodiesel by sonochemical methods which are using two-step transesterification with ultrasonic aid, alkali catalyst sodium hydroxide and acid catalyst of sulphuric acid. Second objective is to optimize reaction condition for biodiesel production from jatropha oil with the temperature and molar ratio of oil to methanol as the manipulated parameters. The third objective is to study the sonochemical reaction kinetics of biodiesel production from jatropha oil.

### **1.4 SCOPE OF STUDY**

**1.4.1** To compare the effect of temperature, molar ratio of oil to methanol, and frequency of ultrasonic on the yield of biodiesel from jatropha oil using ultrasonic transesterification.

**1.4.2** To study the sonochemical kinetics based on the yield of biodiesel from jatropha oil.

**1.4.3** To analyze the product using Nuclear Magnetic Resonance (<sup>1</sup>H-NMR).

### **1.5 RATIONALE AND SIGNIFICANCE**

The rationale of this proposed research project is to provide experiential evidence to compare the purity and yield of jatropha biodiesel. The outcome of this research would denote the identification of a feedstock for biodiesel production that is accomplishable, sustainable and efficient in Malaysia. The classification of this feedstock will be a basis for biodiesel yield on an industrial scale to counter the current global shortage of fossil fuel.

The big advantages of using ultrasonic transesterification would bring about amount of significance in the biodiesel production industry. This is because aside from giving relatively high yield, it would significantly reduce the length of processing time needed for production, and this will eventually goes well to supply the highly increasing rate of demand for alternative liquid fuel. With this method, biodiesel production industry in Malaysia would be able to provide the needs of Malaysian at a rapid rate, hence dismissing the dependence on foreign alternative fuel that may arise in the future. As a result, Malaysian fuel crisis could be deal at an optimal rate by using its abundant feedstock resources and ultrasonic transesterification.

### **CHAPTER 2**

### LITERATURE REVEW

### 2.1 INTRODUCTION

Fossil-based fuels have many disadvantages such as atmospheric pollution and environmental issues. Fossil fuels emissions are top contributors of greenhouse gases which may lead to global warming. Combustion from fossil fuels is major source of air pollutants, which consist of CO,  $NO_x$ ,  $SO_x$ , hydrocarbons, particulates and carcinogenic compounds. Based on the report, 17 major oils and fats world production are 100 billion tones and out this 79% are from vegetable oil (Hamn and Hamilton, 2002).

This has attracted to research, development and application of vegetable based oil in industrial and automotive sectors which has rapidly increasing. Currently, dieselpowered vehicles represent about one-third of vehicles sold in Europe and United States (Jayed et al., 2009). The global consumption of petroleum diesel is 934 million tonnes per year (Kulkarni and Dalai, 2006). Biodiesel is one of the most assuring alternative fuels for diesel engines. The arrogation of biodiesel has significantly increased from 2005 especially in USA (Pahl, 2008). There are several advantages of biodiesel as compared to fossil diesel. Among of it is (1) It helps to reduce carbon dioxide and other pollutants emission from engines, (2) Engine modification is not needed as it has familiar properties to diesel fuel, (3) It comes from renewable sources whereby people on grow their own fuel, (4) Diesel engine performs better in biodiesel due to a high cetane number, (5) High purity of biodiesel would eliminate the use of lubricant, (6) Biodiesel production is more efficient as compared to fossil fuels as there will be ni underwater plantation, drilling and refinery and (7) Biodiesel would make an area become independent of its need for energy as it can be produced locally ( Jain and Sharma, 2010; Jayed et al., 2009; Nie et al., 2006; Robles-Medina et al., 2009; Shah et al., 2004; Su and Wei 2008; Vieira et al., 2006).

During the year of 1997, the production of biodiesel fuel was 550,000 tones in Europe, 10,000 tones in Malaysia and 9000 tones in North America. In 2000, the yearly production of biodiesel in Europe was 1,210,000 tones. The production has increased 2.2 times in three years time (Kann *et al*, 2002).

### 2.2 BIODIESEL

Today, biofuel is at the most priority of the array of alternative energy sources that are being researched and developed. With similarity of physical and chemical properties that are compatible with its fossil counterpart, biodiesel has placed as one of the most appropriate alternative to complement, and might even substitute fossil diesel tomorrow. Its ability to fuel conventional diesel engines with minimum or no modification, and to form blends with fossil diesel make it the most feasible alternative energy source to invest in.

The major aspect of life cycle assessment that biodiesel serves to benefit the environment more than fossil fuel is the potential of global warming, known as carbon dioxide,  $CO_2$ .  $CO_2$  produce during the process of fuel production, biological based and fossil based like. Since that biodiesel mainly consists of renewable material, one could expect a large saving of greenhouse gases compared to conventional fuel. While the case of  $CO_2$  still consider true, certain sides argue if other greenhouse gases like  $N_2O$  and  $CH_4$  are considered, which contribute to a higher global warming potential, the advantages of biodiesel are slightly diminished. Even so, the relative savings of greenhouse gases for the use of biodiesel over fossil diesel is 2.7 kg of saved  $CO_2$  equivalent for every kg of substituted fossil diesel fuel. Most biodiesel fuels inherently contain little or no sulphur; this eventually reduces sulphur dioxide exhaust from diesel engines to virtually zero.

#### 2.2.1 CHARACTERISTIC OF BIODIESEL

Biodiesel is an alternative diesel fuel, form chemically by renewable biological sources such as vegetable oils and animal fats with an alcohol to accelerate the reaction (Leung et al, 2006). It is biodegradable and nontoxic, has low emission profiles and so is environmentally beneficial (Krawczyk, 1996).

Figure 2.1 shows an example of biodiesel. Its colors cab is varied between golden and dark brown because it depends on the production feedstock. It is practically immiscible with water, has high boiling point and low vapor pressure. Typical methyl ester biodiesel has a flash point of ~150°C (300°F), making it rather non-flammable. Biodiesel has density of ~0.88g/cm3, less than water. Biodiesel that unpolluted with starting material can be regarded as non-toxic. It also has similar viscosity with petro-diesel that produces from petroleum.

Moreover, biodiesel is also environmental friendly burning diesel fuel replacement made from natural, renewable source, such as new and used vegetable oils or animal fats. It adapts in any diesel engine with a little or no modification and can be mixed with regular diesel fuel in any ratio. Biodiesel is non-toxic and biodegradable

### 2.3 TRANSESTERIFICATION

Transesterification, also called alcoholysis, is the reaction of a fat or oil with an alcohol with an alcohol to form esters and glycerol. It is the displacement of alcohol from an ester by another alcohol which is similar to hydrolysis process except that alcohol is used instead of water. Each reaction step is reversible. A catalyst is usually used to improve the reaction rate and yield. Since the reaction is reversible, excess alcohol is used to shift the equilibrium to the product side.

Alcohols are primary and secondary monohydric aliphatic alcohols having 1-8 carbon atoms (Sprules and Price, 1950). Methanol and ethanol are most frequently used, especially methanol because of its low cost and its physical and chemical advantages which is polar and shortest chain alcohol. It can rapidly react with triglycerides and sodium hydroxide is easily dissolved in it.

Figure 2.2 shows the overall reaction of transesterification process which consist of three consecutive steps; the triglyceride is converted to diglyceride, monoglyceride and finally glycerol. A mole of ester is liberated at each step. The reactions are reversible, although the equilibrium lies towards the production of fatty acid esters and glycerol. The excess amount of alcohol is commonly more suitable to boost the reaction towards the desired final product (Marchetti et al, 2007).



### Figure 2.2: Consecutive steps of transesterification

#### 2.4 GLYCERINE WASHING AND METHANOL RECOVERY PROCESS

Glycerine is a byproduct of transesterification reaction between oil and methanol. This glycerine will be separated out of the product and the methanol recovery. A considerable amount of alcohol can be discovered for reuse since the methanol used excessively to allow for the transesterification. To recover alcohol, vacuum evaporation, distillation, and water washing are among available method. An efficient method of methanol removal would be the vacuum evaporation since it evaporates the alcohol within its boiling point and recovers all. The glycerine can be removed from the product by decantation.

### 2.5 GLYCERINE

Glycerine or also known as glycerol is a simple polyol which is formed as a byproduct of the production of biodiesel through transesterification process. It is a colourless, odourless, viscous liquid that is widely used in pharmaceutical formulations. It has three hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature (Subramanian *et al.*, 2000).

### 2.6 ALKALI CATALYST

The common catalyst applied during alkaline transesterification at industrial level application includes the homogeneous catalysts such as sodium hydroxide, potassium hydroxide, etc.

The benefits homogeneous catalyst such as sodium hydroxide and potassium hydroxide has been efficient at industrial level for the biodiesel yield. However, the biodiesel and glycerol produced have to be purified to remove the catalyst and need to wash with hot distilled water twice or thrice.

Producing alcoxy before the reaction is a best move to gain a better global efficiency. The alcoxy reaction is

 $R_2CH_2OH + NaOH \rightarrow H_2O + R_2CH_2ONa$ 

The amount of catalyst that should be added to the reactor varies from 0.5 to 1 % w/w. The alkali process is more efficient and less corrosive than the acid process (J.M. Marchetti et al., 2003).

### 2.7 ACID CATALYST

Acid catalyst is used for acid catalyzed transesterification which the amount of free fatty acid content in the oil is high. Sulfuric acid, sulfonic acid and hydrochloric acid are common used as acid catalyst.

Despite of the fact that acid catalyst can used to produce biodiesel with high free fatty acid content oil, acid catalysts have been neglected due to slow reaction rate. However, it is still being used to lower its free fatty acid content before alkali transesterification process. The amount of catalyst that should be added to the reactor varies from 0.5 to 1% (Song *et al.*,2007).

#### 2.8 AMOUNT OF CATALYST

Three different homogeneous catalysts which is sodium hydroxide (NaOH), potassium hydroxide (KOH), and sodium methoxde (CH<sub>3</sub>ONa) shows the same pattern on the alkali transesterification but different amount of catalyst will required to achieve the same conversion (Leung *et al*, 2006). The optimum requirement of the catalyst were 1.1, 1.3, 1.5 wt% for NaOH, CH<sub>3</sub>ONa, and KOH respectively for the maximum ester content production. The amount of NaOH required was less than the amounts of both CH<sub>3</sub>ONa and KOH for the same conversion of methyl ester as NaOH has lower molar mass (40 g/mol), compared to CH<sub>3</sub>ONa has 54 g/mol and KOH with 56 g/mol.

In contrary, in terms of yield,  $CH_3ONa$  proved to be better than NaOH and KOH due to no water was form as side product since  $CH_3ONa$  dissociates into  $CH_3O^-$  and Na<sup>+</sup>. Meanwhile, NaOH and KOH forms sodium or potassium methoxide when dissolved in methanol and forms water as side product. This side product will then reacts with Na<sup>+</sup> (or K<sup>+</sup>) to form soaps with the saponification reaction of triglyceride leading to the reduction of final product yields.

 $CH_3OH + NaOH (or KOH) \rightarrow CH_3ONA (or CH_3OK) + H20$ 

#### 2.9 ULTRASONIC TRANSESTERIFICATION

In the ultrasound-assisted transesterification, the formation, growth and implosive collapse of micro bubbles known as ultrasonic cavitation induced acoustically in the bulk of the liquid phase increase the mass transfer between the two phases by equip both heating and mixing (J.Ji, 2006). Cavitation causes a localized increase in temperature at the phase boundary and supplies the mechanical energy for mixing and the required activation energy for initiating the transesterification reaction.

The collapse of the cavitation bubbles disrupts the phase boundary and cause emulsification by ultrasonic jets that affect one liquid to another. These effects speed up the transesterification reaction rate and shorten time required, while high final yields of biodiesel are commonly achieved.

When the reaction is carried out via ultrasonic wave, transesterification is efficiently mobilized, with short time required. As the result, a drastic reduction in the quantity of by-product and a short separation time is obtained and at the same time can reduce the energy consumption. Biodiesel is primarily produced in the batch processes, in which a basic homogenous catalyst is introduced to catalyze the reaction. Ultrasound allows for the continuous processing. Besides reducing the reaction time, ultrasonication also reduces the separation time compared to the conventional agitation method.

When using the ultrasonication, the amount of excess alcohol required can be reduced. Most commonly, the sonication is performed at an elevated pressure (1 to 3 bar, gauge pressure) using a feed pump. Industrial biodiesel processing does not require much ultrasonic energy. In addition, ultrasonication is an effective means to increase the reaction speed and conversion rate in the commercial processing.

Figure 2.3 shows the typical result of the transesterification of rapeseed oil with potassium hydroxide studied by Carmen Stavarache. The blue line is the control sample, was exposed to intense mechanical mixing while the red line represent the sonicated sample with respect to the volume ratio, catalyst concentration and temperature. The horizontal axis shows the time after mixing or sonication, respectively. The vertical axis shows the volume of glycerin that settled at the bottom. This is the simple means of measuring the reaction speed. In this diagram, the sonicated sample (red line) reacts much faster than the control sample (blue line).



Figure 2.3: Result of rapeseed oil transesterification with potassium hydroxide using conventional agitation and ultrasonication

#### 2.10 ULTRASOUND

Ultrasound is the process of propagation of the compression waves with frequencies above the range of human hearing (above 15-16 KHz) (Shutilov, 1998). Typical commercial ultrasonic instruments known as "probe system" have a piezoelectric transducer powered by a generator that couples energy into chemical reaction by means of horn or velocity transformer. The converter vibrates in a longitudinal direction and transmits this motion to the horn tip immersed in the solution, causes cavitation

Cavitation indicates the opening of holes in liquids. Depending on the circumstances, this holes can be filled either by gases already dissolved in the liquid, in which case the phenomenon is sometimes called as gaseous cavitation or pseudocavitation, or, in the absence of such dissolved gases, by the vapor of the liquid itself (vapor cavitation or true cavitation). It is apparently that the conditions for the appearance of these two kinds of cavitation can be quite different.

The applications of ultrasound in chemical processing enhance both the mass transfer and chemical reactions, this science called as sonochemistry. It offers the potential for shorter reaction cycles, cheaper reagent and less extreme physical conditions, leading to less expensive and perhaps chemical producing smaller plant. Existing literature on sonochemical reacting system is chemistry-intensive, and applications of this novel mean of reaction in remediation and pollution prevention seems almost unlimited. For example, environmental sonochemistry is a rapidly growing area that deals with the destruction of organic in aqueous solutions. However, some theoretical and engineering aspects are not yet fully understood (Adewuyi, 2001). The cavitation phenomenon is also accompanied by the emission of visible radiation, which is given the name sonoluminescense. Some researchers take advantage 19 of this phenomenon doing estimation of the bubbles collapse conditions from the intensity of the light emitted by the system, this area are being explored too.

Another important phenomenon called "acoustic streaming", has been denoted when ultrasound is applied to liquid systems. It consists of a hydrodynamic vertical flow near the sound source and its intensity depends on the ability of the medium to absorb the acoustic energy (usually the energy absorbed by the medium generates an increase in temperature). This ability can be modified by the presence of the electrolysis salts. Other undesired effect of the sonochemical processes are erosion of emitter and reactor surface, creation of noise and acceleration of by-product formation (Loning et al, 2002).

#### 2.11 ACID-CATALYZED PRE-TREATMENT

Since Jatropha oil contains high FFAs which are up to 15%, acid catalyzed transesterification is preferred. However, it needs more excess methanol, high pressure and high cost stainless steel equipments. In addition, the amount of product is low when the common sulfuric acid is used. Therefore, a two step process, with acid catalyzed pre-treatment which known as acid esterification process to remove FFAs, followed by base transesterification is developed to synthesize biodiesel from Jatropha oil. The first step would be the esterification of FFAs with methanol by acid catalyst which is acid sulfuric (Yong *et al*, 2007). At the next step, sodium hydroxide is added to catalyze the transesterification reaction in which triglyceride is reacted with methanol. Without waste water, reusing the catalyst and low cost of reaction tank, these steps shows the potential application in fuel industry.

The esterification pre-treatment step would convert the FFAs to esters (Canaki et al, 2006). Figure 2.4 shows the esterification process. The acid catalyst and methanol should be added, allowed to react, and then settled.

$$\begin{array}{cccc} O & O \\ \parallel \\ HO \_C \_R + CH3OH \\ FFAs & Alcohol \end{array} \xrightarrow[Acid catalyst]{} CH3O \_C \_R + H2O \\ Esters & Water \end{array}$$

Figure 2.4: Esterification of FFAs to ester using methanol and acid catalyst

The mixture of water and methanol can then be removed. Once the mixture is removed and the oil can go on the transesterification step. It is best to carry this reaction out in at least two stages this way, as water is a by-product of the esterification reaction, and the addition of water causes the reaction to become slow. In addition the presence of water in the oil can make the transesterification reaction turn into a saponification reaction, and unwanted gels and emulsion can form with the biodiesel. After the pretreatment step, sodium hydroxide catalyst and methanol can be added to the oil to begin transesterification reaction.

### 2.12 SONOCHEMISTRY

Sonochemistry is the application of ultrasound to chemical reactions and processes. Ultrasound is defined as sound of a frequency that is too high for the human ear to detect. Ultrasound is the part of the sonic spectrum which ranges from about 20 kHz to 10 MHz and can be roughly subdivided in three main regions: low frequency, high power ultrasound (20-100 kHz), high frequency, medium power ultrasound (100 kHz-1 MHz), and high frequency, low power ultrasound (1-10 MHz). The range from 20 kHz to around 1 MHz is used in sonochemistry where as frequencies far above 1 MHz are used as medical and diagnostic ultrasound. Several studies on the tranesterification of various vegetable oils with different types of alcohols in the presence of a base-catalyst using low-frequency ultrasound (20 to 40 kHz) have been published so far.

### 2.13 NUCLEAR MAGNETIC RESONANCE ( NMR) SPECTROSCOPY

Nuclear Magnetic Resonance (NMR) spectroscopy is (arguably) the most powerful tool available for determining the structure of organic compounds. This technique relies on the ability of atomic nuclei to behave like a small magnet and align them with an external magnetic field. When irradiated with a radio frequency signal the nuclei in a molecule can change from being aligned with the magnetic field to being opposed to it. Therefore, it is called "nuclear" for the instrument works on stimulating the "nuclei" of the atoms to absorb radio waves. The energy frequency at which this occurs can be measured and is displayed as an NMR spectrum. The most common nuclei observed using this technique are 1H and 13C, but also 31P, 19F, 29Si and 77Se NMR are available.

In recent study, a quantitative <sup>1</sup>H NMR method has been discovered by which long chain ethyl esters can be readily quantified in unpurified biodiesel products, and the results compared with those obtained using a conventional GC-FID method (Isac, 2010).

#### **CHAPTER 3**

### METHODOLOGY

#### 3.1 MATERIALS

The materials to be used in this research are Jatropha oil that bought from Benua Asia Sdn Bhd, Sodium Hydroxide in granular form, Sulfuric Acid and methanol. A Sonics VCX 750 series ultrasonic unit with a maximum power output of 750 watt and frequency of 20 kHz was used. The ultrasonic horn employed was a 20 kHz titanium alloy; with tip diameter of 13 mm and 10ml to 250ml of processing capability.

### 3.2 CHEMICAL AND PHYSICAL ANAYSIS OF SEED OIL AND BIODIESEL

#### 3.2.1 Acid Value, %FFA

Acid Value of Jatropha oil was determined according to method determination of FFA in the sample vegetable oil using isopropanol as the solvent.

### 3.2.2 Saponification Value

The saponifaction value was determined according to method for determination of saponification value.

### 3.2.3 Kinematic Viscosity

Viscosity of Jatropha oil was determined by using ASTM D 445-94 was used at  $40^{0}$ C temperature.

### 3.2.4 Density

The density of the samples was determined at  $15^{\circ}$ C by using density meter ASTM D1292-85(90).

### 3.2.5 Flash Point

The flash point of the samples was determined by using ASTM D93-02.

#### **3.2.6** Moisture Content

The moisture content of the samples was determined by using water determination test.

### 3.3 CATALYST PREPARATION

Acid Catalyst preparation:

- $1\% \text{ w/w H}_2\text{SO}_4$ / Jatropha oil is prepared.
- 1% of Jatropha oil weight is calculated and taken as H<sub>2</sub>SO<sub>4</sub> weight.
- The calculated weight is then weight by weighting scale.

Alkali Catalyst preparation:

- 1% w/w NaOH/ Jatropha oil is prepared.
- 1% of Jatropha oil weight is calculated and taken as NaOH weight.
- The calculated weight is then weight by weighting scale.

#### 3.4 ACID CATALYZED ESTERIFICATION

Acid catalyzed esterification is also known as pre-treatment step. In this process, the FFAs from the Jatropha oil are converted to ester by using an acid catalyst which is sulfuric acid ( $H_2SO_4$ ). Jatropha oil at required amount is into the ultrasonic batch reactor and preheated at 60°C in order to accelerate the reaction rate. In this step, molar ratio of methanol to Jatropha oil is 6:1 and acid catalyst to Jatropha oil is 1% w/w. The reaction took placed for 1 hour, at the temperature of 60°C, with frequency 20 kHz direct sonication. Table 3.1 shows the value of required amount of all the substances that needed to run this experiment.

**Table 3.1**: Weight of substances needed during the acid catalyzed esterification.

Molar ratio of methanol: JCO	6 :1
Weight of JCO (g)	50
Weight of methanol (g)	8.33
Catalyst weight percent (wtH <sub>2</sub> SO <sub>4</sub> / wJCO)	1%
Catalyst weight (g)	0.5

During the acid pre-treatment is ongoing, methanol and base catalyst NaOH are added into a beaker and mixed together until the catalyst dissolve completely. When the NaOH particles visually disappeared, sodium methoxide is ready to be added for the next step of experiment which is base-catalyzed transesterification.

### 3.5 ALKALI CATALYZED TRANSESTERIFICATION

After the acid catalyzed esterification, the FFAs of esterifies Jatropha oil will be determined. If the value of FFAs is lower than 1%, then it will carry on to the base catalyzed transesterification. Heating the oil with heating plate is usually the easiest way to bring the oil at the required temperature.

Direct sonication method with sonotrode will be used during base catalyzed transesterification. The preferred amount of esterifies Jatropha oil which has been gone through the acid catalyzed esterification is weight in a beaker. The beaker is placed on the heating plate to heat until it reaches to a predetermined temperature. The catalyst added into the beaker of oil and the sonotrode is dipped into it. The reaction is timed as soon as the catalyst-methanol mixture is added into the beaker and continued until a fixed time. After that, the mixture then transferred into a separatory funnel to allow the glycerol to separate from the ester layer by gravity and settled overnight.

The best value of each parameter involved in the process was determined while the rest were kept constant. After each best value was obtained, the value was taken for the next research of the best value of the following parameter. The alkali-catalyzed transesterification part is to optimizing the reaction condition for biodiesel production. The parameters that need to be investigated are temperature of the process, molar ratio of jatropha oil with methanol, and the frequency of ultrasonic wave. Once the parameters have been optimized, the production of biodiesel will be carrying on to investigate the amount of esters along the time.

The reaction was investigated step by step. The best value of each parameter involved in the process was determined while the rest were kept constant. After each best value was attained, the value was adopted for the investigation of the best value of the next parameter. The alkali-catalyzed transesterification part is divided into two major parts which are:

### 1. Optimization

The purpose of optimization is to investigate the effect of temperature and oil to methanol molar ratio on the biodiesel yield. The fixed and the manipulated variables of this part is shown in Table 3.2(a) and Table 3.2(b) respectively.

Table 3.2: Fixed and manipulated parameter for alkali catalyzed transesterification

Parameter	Value
Catalyst weight percent (%wtH2SO4/wJCO)	1
Reaction time (min)	30
Ultrasonic wave (kHz)	20
Settling time	8 hr

(a): Fixed Parameter

### (b): Manipulated Parameter

			Molar Ratio (Oil: Methanol)		
re		40	1:1	1:3	1:6
Temperatu	(°C)	50	1:1	1:3	1:6
		60	1:1	1:3	1:6

### 2. Kinetic Study

The purpose of kinetic study is to observe the biodiesel yield with optimized condition in respective of time. The optimized condition of this stage is shown in Table 3.3.

**Table 3.3**: Optimized condition for alkali catalyzed transesterification.

Parameter	Value
Catalyst weight percent (%wtH2SO4/wJCO)	1
Reaction time (min)	30 & 45
Ultrasonic wave (kHz)	20
Temperature (°C)	Best temperature from Optimization
Molar ratio (oil: methanol)	Best molar ratio from Optimization

### 3.6 GLYCEROL DRAINING

After transesterfication reaction, the separatory funnel contain must be left untouched for approximate 6 to 8 hours, so that the glycerol settled at the bottom layer since it is denser than biodiesel layer. After it is settled properly, drain off the glycerol using the decantation technique.



Figure 3.1: Separatory funnel (Top layer: biodiesel; Bottom layer: glycerol)

### 3.7 METHANOL RECOVERY

The methyl ester layer which is the upper part layer in the separatory funnel, inserted into the rotary evaporator to remove the residual methanol in the methyl ester. The temperature of the rotary evaporator was set at 65-67°C, above than the methanol boiling point which is 64.5°C. Figure 3.5 shows the methanol recovery process.



Figure 3.2: Rotary evaporator

### 3.8 WASHING

After methanol recovery, process of washing methyl ester will be done with warm deionized water for several times until the appearance of methyl ester becomes clear. This process is required to remove the residue methanol and soap deposits. Two layers of biodiesel and wash water will be form and can be separated. The amount of wash water is equal to the amount of oil, and can be drained out. Litmus paper is used to determine the pH of wash water after used. If the pH of wash water is neutral, the washing process is stop from continuing. Then, sodium sulphate is added to the biodiesel sample for removing the moisture and filtered with filter paper.

### **3.9 QUANTIFICATION OF BIODIESEL BY NMR ANALYSIS**

9 biodiesel samples of optimization part, 1 biodiesel sample of kinetic study and 1 sample of JCO as standard were sent to analyze quantitatively by <sup>1</sup>H NMR spectroscopy. Samples (0.050mL) were dissolved in 0.5 mL of deuterated chloroform (CDCL<sub>3</sub>) and transferred to an NMR probe. Spectra were recorded at room temperature with tetramethylsilane (TMS) as internal standard.



### **CHAPTER 4**

### **RESULT AND DISCUSSION**

### 4.1 INTRODUCTION

This study is carried out to prepare biodiesel by sonochemcial methods, optimizing reaction condition for biodiesel production from jatropha oil and study the sonochemical reaction kinetics.

# 4.2 FREE FATTY ACID PERCENTAGE (FFA%) IN ESTERIFICATION PROCESS

Test	t, time (min)	FFA %
1	0	31.16
2	15	11.04
3	30	8.5
4	45	5
5	60	1.09
6	75	1.08

Based on the Table 4.0, the results of FFA percentage with time using 1% of  $H_2SO_4$  acid catalyst, 60°C temperature, 1:6 oil to methanol molar ratio and frequency of 20 kHz shows a reduction of FFA in the Jatropha oil. Since it is almost less than 1%

(w/w), the transesterifcation process can be proceeds with higher yield of biodiesel and less soap formation.

### 4.3 EFFECT OF TEMPERATURE AND OIL TO METHANOL MOLAR RATIO ON BIODIESEL YIELD

The conversion of biodiesel was acquired through Hydrogen Nuclear Magnetic Resonance (<sup>1</sup>H NMR) analysis. This technique is fast, accurate and has a simple procedure compared to chromatographic analyses, such High Performance Liquid Chromatography (HPLC) and Gas Chromatography (GC), which need a sample preparatuin and purification. In <sup>1</sup>H NMR analysis, information regarding all compenents in the mixture is given in one spectrum, without derivating or destroying the sample (G. Knothe, 2004; G. Vigli, 2003; U. Rashid, 2009).

To evaluate the conversion of oils to biodiesel, the appearance of a new signal at 3.7 ppm was examined. The conversion was analyzed by the existence of this peak, as the starting material loss its signals because other secondary products could be formed in the same region of the <sup>1</sup>H NMR spectra. The new signal at 3.68 ppm shows the formation of biodiesel since that peak is in the range of hydrogens from the methyl ester group (- COOCH<sub>3</sub>). To calculate the conversion to the methyl ester ( $C_{ME}$ ), hydrogens from the methylene group adjacent to the carbonyl ( $\alpha$ -CH<sub>2</sub>) at 2.3 ppm. This peak represent all molecules derived from triglycerides, including unreacted oil, mono and diglycerides, soaps and all other long chain types that could be formed during the process. Equation 4.1 describes the conversion of the reaction in the form of a calculation, relating the intergration values of the <sup>1</sup>H NMR signals from the methyl ester (ME) hydrogens and hydrogens on the methylene group adjacent ( $\alpha$ -CH<sub>2</sub>) to the carbonyl.

$$C_{ME} = 100 \times \left(\frac{I_{ME}/3}{I_{\alpha - CH_2/2}}\right)$$
 (Equation 4.1)

 $I_{\rm ME}$  is the integration value of the methyl ester peak and  $I_{\alpha-\rm CH2}$  is the integration value of the methylene group adjacent to the ester group. Factors of 3 and 2 were used because the methyl ester has three hydrogens in every peak (-OCH<sub>3</sub> – 3.68 ppm) and two hydrogens corresponded by the peak from the methylene group adjacent to the carbonyl ( $\alpha$ -CH<sub>2</sub> – 2.3 ppm).



Figure 4.1: <sup>1</sup>H NMR spectrum of jatropha oil



Figure 4.2: <sup>1</sup>H NMR spectrum of biodiesel yield from 40°C and 1:1 oil to methanol molar ratio



Figure 4.3: <sup>1</sup>H NMR spectrum of biodiesel yield from 40°C and 1:3 oil to methanol molar ratio



**Figure 4.4:** <sup>1</sup>H NMR spectrum of biodiesel yield from 40°C and 1:6 oil to methanol molar ratio.

Table 4.1: Temperature 40°C

	Molar	ratio	oil	to	%	yield	of
	methan	ol			biodiesel		
1	1:1				69		
2	1:3				93		
3	1:6				93		



Figure 4.5: Graph percentage of ME yield vs molar ratio oil to methanol at  $40^{\circ}$ C



Figure 4.6: <sup>1</sup>H NMR spectrum of biodiesel yield from 50°C and 1:1 oil to methanol molar ratio



Figure 4.7: <sup>1</sup>H NMR spectrum of biodiesel from 50°C and 1:3 oil to methanol molar ratio



Figure 4.8: <sup>1</sup>H NMR spectrum of biodiesel from 50°C and 1:6 oil to methanol molar ratio

Table 4.2: Temperature 50°C

	Molar	ratio	oil	to	%	yield	of
	methan	ol			biodiesel		
1	1:1				63		
2	1:3				92.4		
3	1:6				92.4		



Figure 4.9: Graph percentage of ME yield vs molar ratio oil to methanol at 50°C



**Figure 4.10:** <sup>1</sup>H NMR spectrum of biodiesel from 60°C and 1:1 oil to methanol molar ratio



**Figure 4.11:** <sup>1</sup>H NMR spectrum of biodiesel from 60°C and 1:3 oil to methanol molar ratio



**Figure 4.12:** <sup>1</sup>H NMR spectrum of biodiesel from 60°C and 1:6 oil to methanol molar ratio

Table 4.3: Temperature 60°C

	Molar	ratio	oil	to	%	yield	of
	methan	ol			biodiesel		
1	1:1				50.7		
2	1:3				90.4		
3	1:6				92		



Figure 4.13: Graph percentage of ME yield vs molar ratio oil to methanol at 60°C

Figure 4.1 represent <sup>1</sup>H NMR spectra of the jatropha oil before transesterification and Figure 4.2, 4.3, 4.4, 4.6, 4.7, 4.8, 4.10,4.11,4.12 are the <sup>1</sup>H NMR spectrum of the produced biodiesel.

To calculate the residual content of tri-,di- and monoglycerides in the resultant methyl esters, the signal corresponding to methylene hydrogens in the glyceride sequence (–CH<sub>2</sub>-CH-CH<sub>2</sub>-) was examined. These peaks were located between 4.1 ppm and 4.4 ppm and correspond to four hydrogens. As can be seen from the six spectra (Figure 4.3, 4.4, 4.7,4. 4.8, 4.11 and 4.12), there are no residual mono-, di-, or triglycerides, which is proved from the total disapperance of peaks between 4.1 ppm until 4.44 ppm. Mono- and diacylglycerides, which are formed as intermediates in transesterification, exhibit signals due to glyceridic hydrogens in the same region as glyceridic hydrogens of triacylglycerides from the feedstock. However, three spectra (Figure 4.2, 4.6 and 4.10) shows that the residual content of tri-, di- and monoglycerides are still present in the biodiesel.

The results from calculation of the integration of peaks from the <sup>1</sup>H NMR data of biodiesel products are shown in Table 4.4.

**Table 4.4:** Overall biodiesel conversion over different temperature and oil to methanol

 molar ratio

		Biodiesel conversion %			
		Molar Ratio (Oil: Methanol)			
		1:1	1:3	1:6	
(C)	40	69	93	93	
srature (	50	63	92.4	92.4	
Tempe	60	50.7	90.4	92	



Figure 4.14: % ME yield versus oil to methanol molar ratio with different temperature.

Based on the result obtained in the optimization stage, the temperature does not give any effect on the biodiesel yield as it shows conversion in range 90.4 - 93% with molar ratio of 1:3 and 1:6. Comparing with literature values from Jiet et.al, and Chand et. al, they manage to yield more than 95% biodiesel in less than 10 minutes. According to Chand et.al, external heating was not used in any of the ultrasonic experiments. Since the temperature was not controlled in any of the sonication experiments, therefore the temperature increased at a very rapid rate during the sonication. Since the samples of  $60^{\circ}$ C exceeds the temperature  $60^{\circ}$ C, the biodiesel yields doesn't reach to its maximum since the methanol began to evaporate.

Moreover, it is well set up that traditional basic catalysis is unable to reach high conversions since it is in non-anhydrous conditions. Even though the acid-catalyzed esterification is done on the early stage for lowering the FFA value, but the soap formation still occurred since the methanol is in non-anhydrous condition.

### 4.4 CHARACTERISTICS OF JATROPHA OIL & BIODIESEL

Based on the table 4.5, it shows that the values of characters decreases as the jatropha oil converts to biodiesel.

	Jatropha Oil	Biodiesel
Density (Kg/m <sup>3</sup> )	921	886
Viscosity (cP)	32.902	4.02
Saponification value (mg KOH/g)	193.995	
FFA %	31.16	0.4
Flash Point (°C)	125	93
Moisture Content %	7.38	6.26

 Table 4.5: Comparison between jatropha oil and biodiesel

### 4.5 KINETIC STUDY

According to Diasakov et. al., the transesterification reaction proceeds in three steps in which TG reacts with methanol to produce diglycerides, which further reacts with methanol to form monoglycerides that lastly reacts with methanol to yield methyl ester and glycerol. Since one mole of methyl ester is generated per mole of methanol reacted at each step, in all, six rate constants are reported in the literature for the whole reaction. However, since transesterification results are only focus on the production of methyl ester, therefore all the intermediate reaction can be ignored.

Since conversion of methyl ester in this study is almost the same with different temperature, the optimize condition for the biodiesel yield will be on 60°C and 1:6 oil to

methanol molar ratio. The kinetics of transesterification has been studied with respect to %ME yield as a function of time.

Figure 4.15 shows <sup>1</sup>H NMR spectrum of biodiesel from 60°C temperature and 1:6 of oil to methanol molar ratio at 45 minute. Based on the calculation, the % ME yield shows that there is no further conversion of biodiesel occur after 30 min. Figure 4.16 and Table 4.6 shows % biodiesel yield over time in range of 0 until 45 min.



**Figure 4.15:** <sup>1</sup>H NMR spectrum of biodiesel from 60°C and 1:6 oil to methanol molar ratio at 45 minute.

Table 4.6: % ME yield over time

Time (Minute)	% yield of
	biodiesel
0	0
30	92
45	92



Figure 4.16: % ME yield vs time

Based on Figure 4.1, there is no signal at 3.68 ppm in the <sup>1</sup>H NMR spectra of jatropha oil since no fatty acid methyl ester exists. From this point, the initial concentration of methyl ester is said to be nil. Since the process occurred in batch reactor, let the transesterification reaction process to be noted as:

Triglyceride + Methanol  $\rightarrow$  Methyl ester + Glycerol

 $A + B \rightarrow C + D$ 

To find sonochemistry rate constant, graphical method is used to conduct the calculation.

1. Rate law

$$r_C = k C_C^{\alpha} C_D^{\beta}$$
 (Equation 4.2)

 $r_{c} = k' C_{c}^{\alpha}$  (Equation 4.3) , where  $k' = k C_{D}^{\beta}$ 

2. Apply CRE algorithm

Mole Balance

$$\frac{dN_C}{dt} = r_C V \text{ (Equation 4.4)}$$

Rate Law

$$r_C = k' C_C^{\alpha}$$

Stoichiometry: Liquid

 $V = V_0$  (Since it is constant volume)

$$C_C = \frac{N_C}{V_0}$$

Combine: Mole balance, rate law, and stoichiometry

$$\frac{dC_C}{dt} = k'C_C^{\alpha}$$

Taking the natural log of both sides of equation

$$\ln\left[\frac{dC_C}{dt}\right] = \ln k' + \alpha \ln C_C$$

The slope of a plot of  $\ln \left[\frac{dc_c^{\alpha}}{dt}\right]$  versus  $\ln C_c$  will yield the rate constant k'.

Given that,

$$C_{A0} = \frac{0.05 \text{ mol}}{5 \times 10^{-5} m^3} \times \frac{1m^3}{1000 \ dm^3}$$
$$= 1 \ mol/dm^3$$

$$C_C = 0.92 \ mol/dm^3$$

Find  $\left[\frac{dC_C}{dt}\right]$  as a function of C<sub>C</sub> from concentration-time data.

t (min)	$C_{\rm C}  ({\rm mol/dm^3})$	$\frac{\Delta C_C}{\Delta t}$ (mol/dm <sup>3</sup> .min)	$\frac{dC_C}{dt}$ (mol/dm <sup>3</sup> .min)
0	0		0.04625
		0.031	
30	0.92		0.015625
		0	
45	0.92		





Figure 4.17: Graph rate of biodiesel formation versus time

Based on graph,

 $\ln k' = 0.04625$ 

 $k' = 1.0473 \text{ min}^{-1}$ 

### **CHAPTER 5**

### CONCLUSION AND RECOMMENDATION

### 5.1 Conclusion

Biodiesel from jatropha curcas oil were produced using ultrasonic reactor through transesterification reaction and catalyst that have been used was sodium hydroxides (NaOH). Reaction by ultrasonic reactor offers a fast and safe alternative to the usual process. The mechanism of the sonic wave had effect on the transesterification reaction. From the results, it is concluded that the best conditions for transesterification reaction for jatropha oil is at molar ratio of 1:6 oil to methanol with reaction temperature does not affect reaction time which provided the highest conversion of biodiesel yield. The two steps process to produce biodiesel was the better procedure for jatropha curcas oil with high FFA content towards achieving the high yield and quality of the product. The reaction rate constant k' has a value of 1.0473 min<sup>-1</sup> which shows the reaction is quite slower than it supposes to be.

### 5.2 Recommendation

To improve the biodiesel production, the temperature of the reactor should be controlled properly since the sonication process will eventually increases the temperature as time goes. Reaction time should be in the range of 10 to 15 minutes for the prevention of the temperature increases until the boiling point of the methanol which will affect the biodiesel yield.

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### APPENDIX A

### MATERIAL, APPARATUS AND EQUIPMENT



Appendix A1: Chemical used in experiment



Appendix A2: Ultrasonic reactor

### **APPENDIX B**

### ESTERIFICATION PROCESS, TRANSESTERIFICATION PROCESS & NMR ANALYSIS



Appendix B1: Esterified Oil (After esterification)



Appendix B2: After transesterification; Biodiesel (upper layer) & Glycerol (bottom layer)



Appendix B3: Methanol recovery



Appendix B4: Biodiesel washing



Appendix B5: Biodiesel



Appendix B6: NMR SPECTROSCOPY