BIODIESEL PRODUCTION FROM JATROPHA CURCAS VIA TWO-STEPS CATALYZED PROCESS

GUGANESWARAN A/L SINNATHAMBY

UNIVERSITI MALAYSIA PAHANG

“I hereby declare that I have read this dissertation and in
my opinion this thesis is sufficient in terms of scope and
quality for the award of the degree of
Bachelor of Chemical Engineering ”

Signature : ....

Supervisor : ASSOC. PROF. DR ABDURAHMAN HAMID NOUR

Date : ....

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GUGANESWARAN A/L SINNATHAMBY

A thesis submitted in fulfillment

of the requirements for the award of the degree of

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I declare that this thesis entitled "*Biodiesel Production From Jatropha Curcas Via Two Steps Catalyzed Process*" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : ....
Name of Candidate : GUGANESWARAN A/L SINNATHAMBY
Date : 27 NOVEMBER 2010

Dedicated especially to my beloved Father, Mother, Siblings, Lecturers, 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. The fact that Jatropha oil cannot be used for nutritional purposes without detoxification makes its use as energy or fuel source very attractive. The effect of main factor which are, temperature, particle size of the meal and reaction time were investigated to optimize the extraction operating conditions for achieving maximum oil yield. The lipid fraction of Jatropha curcas oil seed were extracted and to study the analyzed for their chemical and physical properties such as acid value, percentage free fatty acids (% FFA), iodine value, peroxide value and saponification value as well as viscosity, and density. The fatty acid composition of the extracted lipid was revealed using the (GCMS) method. Biodiesel production process is the transesterification of the used two-steps 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 acidcatalyzed esterification, the temperature is set at 40°C, acid catalyst of 2%w/wH2SO4. These studies have been performed based on 3 effect, temperature, catalyst concentration and time. As a result, the best condition that has been determined for maximum biodiesel production were 1.5% catalyst concentration of potassium hydroxides based on weight of jatropha curcas oil that were used methanol to jatropha curcas oil of 6:1 and, process were done at temperature 60^0C and the time is about 60 minutes. Biodiesel yield and moisture content in biodiesel production from jatropha curcas oil were measured. Oil yield content of jatropha kernel was found about 50–60% for different extraction time. Both oleic acid (45.24%) and linoleic acid (31.58%) were detected as the dominant fatty acids while palmitic acid and stearic acid were the saturated fatty acids found in the Jatropha curcas oil. 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. Salah satu cara untuk mengurangkan kos pengeluaran biodiesel adalah menggunakan bahan baku lebih murah yang mengandungi asid lemak seperti minyak dimakan, lemak haiwan, minyak sisa makanan dan oleh produk-produk dari pemurnian minyak sayuran. Pengaruh faktor utama iaitu, suhu, saiz zarah dari masa makan dan reaksi yang diselidiki untuk mengoptimumkan ekstraksi keadaan operasi untuk mencapai hasil minyak maksimum. Pecahan lemak minyak biji jatropha di ambil dan untuk mempelajari dianalisa kimia dan sifat fizikal seperti bilangan asid, asid peratusan lemak bebas (% FFA), nilai iodin, nilai peroksida dan nilai penyabunan serta viskositi, dan kerapatan . Komposisi asid lemak dari lipid diekstrak diturunkan dengan menggunakan kaedah (GCMS). proses pengeluaran 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 40 ° C, asid mangkin 2% w/wH2SO4. Pengajian-kajian ini telah dilakukan berdasarkan 3 kesan, suhu, konsentrasi mangkin dan masa. Akibatnya, keadaan terbaik yang telah ditetapkan untuk pengeluaran biodiesel maksimum adalah 1.5% mangkin konsentrasi kalium hidroksida berdasarkan berat minyak jatropha yang digunakan metanol untuk minyak jatropha dari 6:1 dan, proses dilakukan pada suhu 60^0C dan masa sekitar 60 minit. Biodiesel hasil dan kadar air dalam pengeluaran biodiesel dari minyak jatropha diukur. Menghasilkan kandungan minyak jatropha kernel dijumpai sekitar 50-60% untuk masa ekstraksi yang berbeza. Kedua-dua asid oleik (45,24%) dan asid linoleat (31,58%) yang dikesan sebagai asid lemak yang dominan, manakala asid palmitat dan asid stearat adalah asid lemak tepu ditemui di minyak jatropha.

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^{o}C - Temperature

l - Length

ρ - Density

s - Time (second)

M - Mega

Hz - Hertz

Ml - Milimeter

G - Gram

Wt - Weight Percent

CHAPTER I

INTRODUCTION

1.1 Background

Alternative fuels for diesel engines are becoming increasingly important due to diminishing petroleum reserves and the environmental consequences of exhaust gases from petroleum-fuelled engines. The energy source, fossil fuel, upon which we have come to rely on so deeply is in higher demand than ever before, that more energy is needed all around to fulfill this demand. (Pramanik , 2003). Fossil fuel alone seems to be insufficient to cater to the needs of the global community. In light of this, it is in the world's best interest to devote a substantial amount of resources towards alternative forms of energy. Biofuel , as biodiesel in this context, is at the forefront of these alternatives due to its ability to fuel conventional diesel engines with minimum or no modifications, as well as form blends with fossil diesel.

Biodiesel is defined as fatty acid methyl esters prepared from any kind of feedstock including vegetable oils, animal fats, single cell oils, and waste material. Fatty acid ethyl esters can also be defined as and used to produce biodiesel. (Knothe et al., 2002). However, due to the relatively high price of ethanol compared to methanol, the use of ethyl esters has not so far been established. The preparation of fatty acid methyl esters can be achieved by a process called transesterification, which is the exchange of alcohol or acid moiety of an ester.

Alcoholysis is the transesterification of an ester with an alcohol, in which methanolysis is the term used in the case of methanol. The reaction requires a catalyst, usually a strong base, such as sodium or potassium hydroxide, and produces new chemical compounds called methyl esters. It is these esters that have come to be known as biodiesel.Because its primary feedstock is a vegetable oil or animal fat, biodiesel is generally considered to be renewable. (Veljkovic´ et al., 2006). Since the carbon in the oil or fat originated mostly from carbon dioxide in the air, biodiesel is considered to contribute much less to global warming than fossil fuels. (Openshaw et al, 2000). Diesel engines operated on biodiesel have lower emissions of carbon monoxide, unburned hydrocarbons, particulate matter, and air toxics than when operated on petroleum-based diesel fuel.

All feedstocks that contain fatty acids or glycerol can be used for biodiesel production including jatropha *curcas* 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

The current energy crisis has beckoned upon us to look towards an energy alternative that is feasible and sustainable in the long run. Being a direct solution to the current shortage of liquid fuel, biodiesel is one of the most popular alternatives of all time. This research seeks to solve this uncertainty in feedstock sustainable selection, of the researched types of biodiesel feedstock , namely Jatropha *curcas* oil. *Jatropha curcas* is a wonder plant with a variety of applications and enormous economic potentials. Oil from the seeds can be used as alternative fuel and for making biodiesel which aims to overcome energy crisis problems. In this study, extraction of Jatropha *curcas* oil from seeds was optimized using organic solvent based on the amount of the extracted oil. Using the virgin oil as a feedstock we would not require additional steps in biodiesel production, such as prefiltration and preheating as well as a relatively high catalyst concentration, that may incur additional costs of processing.

Ultrasonic transesterification in biodiesel production can reduce processing time to 25% of the time needed otherwise. Industrially, along with producing 99% yield, it is highly more efficient that conventional agitation that can take up to 12 hours, reducing this time frame to less than 60 minutes. The amount of catalyst required can also be reduced by up to 50% due to the increased chemical activity in the cavitations formed due to ulltrasonication. In addition to this, it also extensively reduces the amount of excess alcohol required for processing while increasing the purity of the glycerin formed. This type of processing, coupled with a comparative research of the two said feedstock, would provide a feasible, sustainable, and efficient choice of feedstock for biodiesel production.

1.3 Objectives

The main objective of the present work was to study on the effect of two step catalyst reaction in producing biodiesel from jatropha *curcas* oil using ultrasonic transesterification, with alkali catalyst potassium hydroxide and , acid catalyst of 2%w/wH_2SO_4 as the catalyst. A second objective was to Optimized of oil extraction from jatropha *curcas* seeds.

1.4 Scope of Research

1.4.1 To comparatively study the effect of catalyst concentration and reaction time on the yield and purity of biodiesel produced from jatropha *curcas* oil using ultrasonic transesterification.

1.4.2 The effect main factor which are temperature, particle size of the meal and reaction time were investigated to optimize the extraction operating conditions for achieving maximum oil yield.

1.4.3 To comparatively study the combustion characteristics of biodiesel produced from jatropha *curcas* oil and analyze the products using Gas Chromatography.

1.5 Rationale and Significance

The rationale of this proposed research project is to provide empirical evidence to compare the purity and yield between biodiesel production from Jatropha *curcas*. The results of this research would signify the identification of a feedstock for biodiesel production that is feasible, sustainable and efficient for Malaysia. The identification of this feedstock will be a basis for the production of biodiesel on an industrial scale to counter the current global shortage of fuel.

The numerous advantages of using Ultrasonic transesterification would bring about volumes of significance in the biodiesel production industry. This is due to the fact that aside from giving relatively high yield, it would monumentally reduce the length of processing time needed for production, and this would go well to supply the ever increasing rate of demand for alternative liquid fuel. With Ultrasonic transesterification, the biodiesel production industry in Malaysia would be able to cater to the needs of Malaysians at a faster rate, thereby eliminating the need for any dependence on foreign alternative fuel that may arise in the future. Malaysia would be able to deal with its own fuel crisis, at an optimal rate using its abundant feedstock resources and ultrasonic transesterification.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Diesel-petroleum based has released problems such as toxicity, water, land and air pollution, fire risk, non-biodegradability and limited resources had opened a unique opportunity to produced new environmental acceptable fuel and lubricants derived from natural ester like vegetable oil. Reported that, the world production of 17 major oils and fats are over 100 billion tones and out this 79% are from vegetable oil (Hamm and Hamilton, 2002).

Research, development and application of vegetable based oil in industrial and automotive sectors are rapidly increasing. The attractive part of vegetable oil is they are neutral, non-toxic, biodegradable, and relatively non-polluting and derived from renewable raw material. During the last decade, due to strict government and environment regulation almost of all country in the world, there has been constant demand for environmentally friendly fuel (Reijnders , 2006). Most of fuel originates from petroleum stock which is toxic to environment and difficult to dispose. Vegetable oils with high oleic acid content are considered to be potential candidates to substitute conventional mineral oil base fuel oils and synthetic esters.

Although biodiesel cannot entirely replace petroleum-based diesel fuel, there are at least five reasons that justify its development (Gerpen, 2005):

1) It provides a sufficient market for excess production of vegetable oils and fats.

2) It decreased, although will not eliminate, most country's dependencies on imported petroleum.

3) Biodiesel is renewable and does not contribute to global warming due to its closed carbon cycle. A life cycle analysis of biodiesel showed that generally CO_2 emissions were reduced by 78% compared with petroleum-based diesel fuel (Sheehan *et al*, 1998).

4) The exhausts emissions of carbon monoxide, unburned hydrocarbons, and particulate emissions from biodiesel are lower that with regular diesel fuel. Unfortunately, most emissions test has shown a slight increased of nitrogen oxides (NO_x).

5) When added to regular diesel fuel in an amount equal to 1-2%, it can convert fuel with poor lubricating properties, such as modern ultra-lowsulfur diesel fuel, into an acceptable fuel.

In 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 annual production of biodiesel in Europe was 1,210,000 tones. The production increased 2.2 times in three years (Kann *et al*, 2002).

2.2 Biodiesel

At the forefront of the array of alternative energy sources that are being researched and developed today, is biofuel. Having physical and chemical properties that are compatible with its fossil counterpart has placed biodiesel as one of the most suitable alternatives to complement today, and perhaps even replace fossil diesel tomorrow. Its ability to fuel conventional diesel engines with minimum or no modifications, and to form blends with fossil diesel make it the most practical, and feasible alternative energy source to invest in.

There are many ways how biodiesel serves to benefit the environment more than fossil diesel. One major aspect of life cycle assessments is the potential of global warming, expressed as carbon dioxide, CO_2 equivalents. CO_2 is produced during the whole production process of fuels, biological based and fossil based alike. Due to the positive energy balance of biodiesel and the fact that biodiesel mainly consists of renewable material one could expect a large saving of greenhouse gases compared to fossil fuel. Now, while this remains true in the case of $CO_{2,}$ certain parties argue that if other greenhouse gases like N_2O and CH_4 are considered, which have 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 2.7kg of saved CO_2 equivalents for every kg of substituted fossil diesel fuel. Pure biodiesel is also completely free of sulfur and, this inadvertently reduces sulfur dioxide exhaust from diesel engines to virtually zero.

2.2.1 Characteristic of Biodiesel

Biodiesel is well known as an alternative fuel for diesel engines that is chemically produced by reacting the virgin or used vegetable oil or animal fats with an alcohol such as methanol in order to accelerate the reaction (Leung *et al*, 2006).

Figure 2.1 shows an example of biodiesel. However, it colors cab be 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.

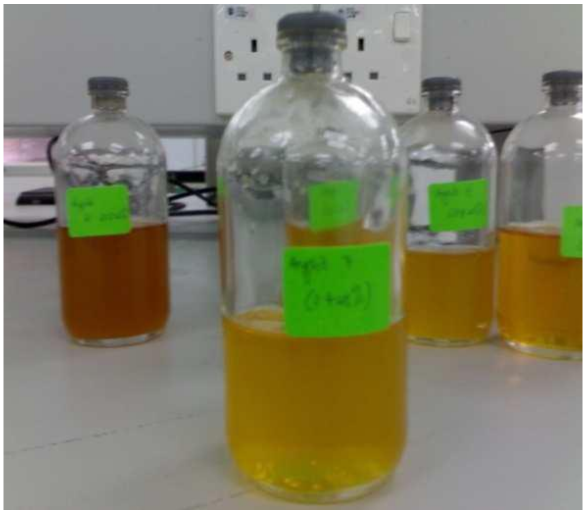


Figure 2.1: Example of biodiesel

Moreover, biodiesel is also clean burning diesel fuel replacement made from natural, renewable source, such as new and used vegetable oils or animal fats. It will run 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, is also known as Alcoholysis. It is the displacement of alcohol from an ester by another alcohol in a similar manner in that of hydrolysis, except than alcohol is used instead of water. Each reaction step is reversible. This process is used widely in reducing the viscosity of vegetable oils. Methanol and ethanol are most frequently used, especially methanol because of its low cost and its physical and chemical advantages. If methanol is used in this process it is called methanolysis. Thus, fatty acid methyl esters or FAMEs, known as biodiesel fuel are formed. The FAME's obtained by transesterification are similar to conventional diesel fuel in its main characteristics and can be used as an alternative fuel or used in blends with fossil diesel for diesel engines. (Song *et al.*,2007)

Figure 2.2 shows the overall process of transesterification which is normally series of three consecutive steps which are reversible reactions. In the first steps diglycerides, are obtained from triglycerides. From diglycerides, monoglycerides are then produced. In the last step, from monoglycerides, glycerol is formed. In all these reactions, esters are produced. The excess of alcohol is usually more appropriate to improve the reaction towards the desired final product (Marchetti *et al*, 2007).

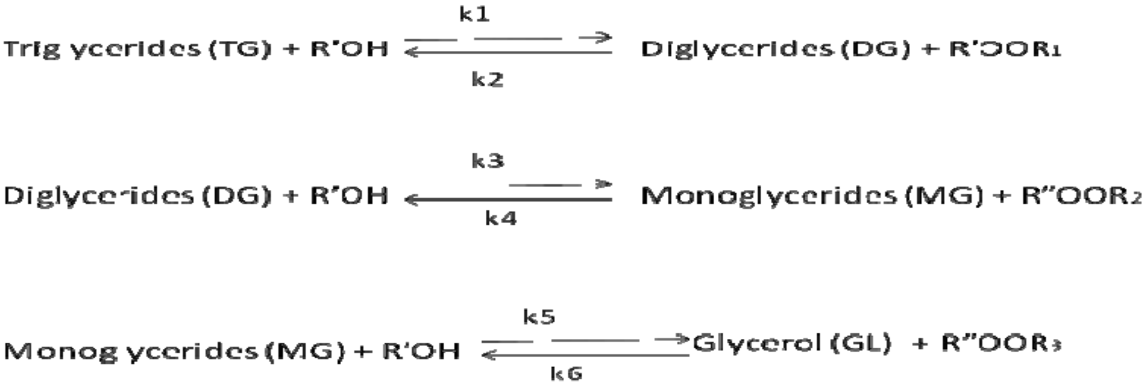


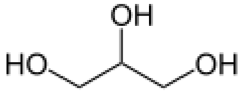
Figure 2.2: Consecutive steps of transesterification

2.4 Glycerine washing and methanol recovery process

The transesterification reaction between oil and an alcohol such as methanol to produce biodiesel yields glycerine as a byproduct. This glycerine needs to be separated out of the product and the methanol recovered. Since the methanol used in the reaction is in excess to allow for sufficient reaction, a considerable amount of methanol can be recovered for reuse. Among the methods available for the removal of methanol are vacuum evaporation, distillation, and water washing. An economical method of methanol removal would be the water washing method since it acquires a relatively low cost. The glycerine can be removed from the product by decantation.

2.5 Glycerine

Glycerine, a byproduct form the transesterification reaction to produce biodiesel, is a colorless, odorless, viscous liquid that is widely used in pharmaceutical formulations. It also goes by the names, glycerol and glycerin. Glycerine is a sugar alcohol of sweet-taste and low toxicity. It has three hydrophilic alcoholic hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature. Its substructure is a central component of many lipids.(Subramanian *et al.,* 2000)



2.6 Alkali catalyst

Either sodium hydroxide (NaOH) or potassium hydroxide (KOH) can be used with methanol or ethanol and the chosen oil. It is best to produce the alcoxy before the reaction to obtain a better global efficiency. The alcoxy reaction is

$$\mathrm{R2CH2OH + NaOH \rightarrow H2O + R2CH2ONa}$$

The alcohol–oil molar ratio that should be used varies from a ratio of 1:1–6:1. However, 6:1 is the most used ratio, leading to an important conversion for the alkali catalyst without using an immense amount of alcohol. The types of alcohol considered are usually methanol and ethanol. Methanol has fewer safety problems because it is less toxic compared to ethanol, thus its usage would have significantly smaller safety issues. 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).

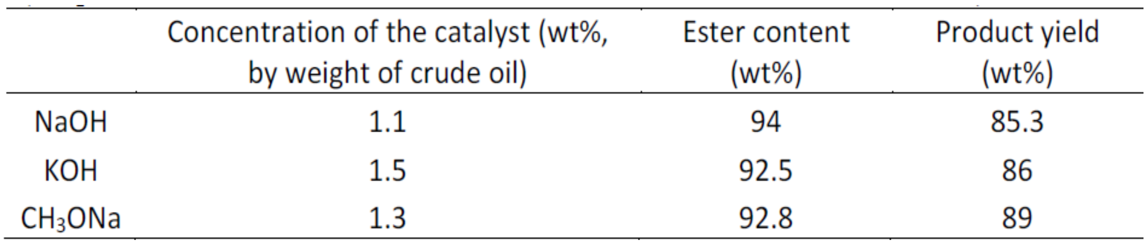
2.7 Acid catalyst

In this process, the triglycerides are used with the alcohol. In this case, instead of a base an acid is used. The most common acid used is sulfuric acid sometimes sulfonic acid. This catalyst gives a very high yield in esters but the reaction occurs very slowly. It normally takes more than a day to finish. If an excess of alcohol is used in the experiment, a better conversion of triglycerides is obtained. However, recovering glycerol becomes more difficult, which is why an optimal relationship between the alcohol and raw material should be determined experimentally considering each process as a new problem. The operation condition is usually in the form of a molar ratio of 30:1. The amount of catalyst that should be added to the reactor varies from 0.5 to 1 mol% (Song *et al.,*2007).

2.8 Amount of Catalyst

The three catalyst (KOH, NaOH, and CH3ONa) exhibit the same trend on the conversion of the TG to esters but different amount of catalyst will be required to achieve the same conversion (Leung *et al*, 2006). Table 2.1 shows the maximum ester content of the biodiesel product was reached at 1.1, 1.3, and 1.5wt% of the catalyst concentration for NaOH, CH3ONa, and KOH respectively. The amount of NaOH used was smaller than those of KOH and CH3ONa for the same mass feedstock oil, since NaOH has the smallest molar mass (40 g/mol), followed by CH3ONa (54 g/mol), and KOH (56 g/mol). However, in term of concentration, CH3ONa was about 10% lesser than NaOH and KOH.

Table 2.1: Comparison of different types of catalyst in the transesterification of JCO (temperature of 70°C, reaction time of 30 minutes, methanol/oil ratio of 7.5:1)



	Concentration of the catalyst (wt%, by weight of crude oil)	Ester content (wt%)	Product yield (wt%)
NaOH	1.1	94	85.3
KOH	1.5	92.5	86
CH_3ONa	1.3	92.8	89

As shown in Table 2.2, the biodiesel yield with NaOH and KOH as catalyst were lower than CH3ONa. This happen during the preparation of the catalyst NaOH or KOH is added and dissolved in the anhydrous methanol forming sodium or potassium methoxide together with small amount of water according to the following equilibrium equation.

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

The water in the reaction system predominantly reacts with oils (TG) and the Na+ (or K+) to form sodium (or potassium) soaps. This is the saponification reaction of TGs leading to the loss of TGs and hence reduction in final product yields. On the other hand, the pure CH3ONa catalyst only dissociates into CH3O- and Na+ without forming any water as side product in the reaction that will cause a drop in product yield.

2.9 Ultrasonic Transesterification

Ultrasonication increases the rate of the transesterification reaction of the chosen oil into biodiesel as well as significantly reduces the amount of excess alcohol required for processing. It also increases the purity of the glycerin formed. This allows a change from the production from batch processing into continuous flow processing. Biodiesel is normally produced in batch reactors that use heat and mechanical mixing as its energy input.

Ultrasonic cavitational mixing achieves a better degree of mixing on a commercial scale. Ultrasonic mixing is an effective means to achieve better mixing levels in commercial processing. It provides the activation energy needed for the industrial transesterification process. Power ultrasonic reactors have been used to produce biodiesel through the methanolysis of soybean with sodium hydroxide as a catalyst. (Kumar and sharma, 2008).

When the reaction is carried out via ultrasonic wave, transesterification is efficiently activated, with short time of reaction. 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).

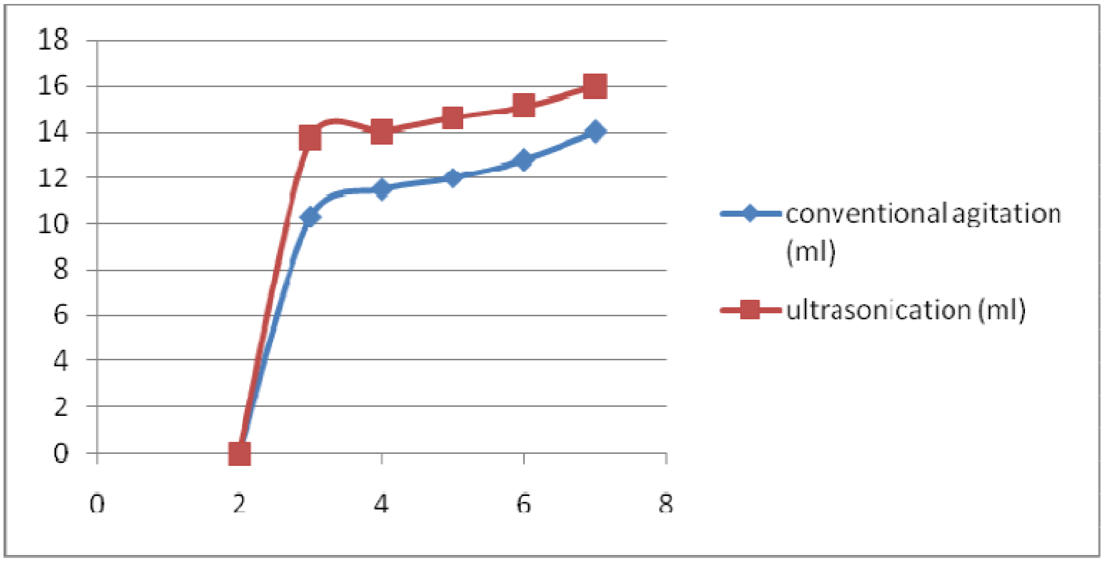


Figure 2.3: Result of rapeseed oil transesterification with potassium hydroxide using conventional agitation and ultrasonication

2.10 Ultrasound

Ultrasound is the process of propagation of the compression (rarefaction) 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 implies 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 quite clear 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).

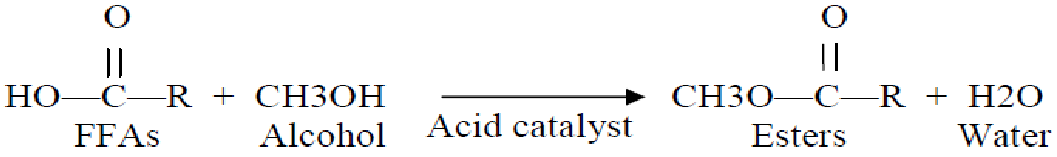
The cavitation phenomenon is also accompanied by the emission of visible radiation, which is given the name sonoluminescense. Some researchers take advantage 19 of this phenomenon doing estimation of the bubbles collapse conditions from the intensity of the light emitted by the system, this area are being explored too.

Another important phenomenon called "acoustic streaming", has been identified when ultrasound is applied to liquid systems. It consists mainly 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). For the ultrasound agitations case , ultrasound application generate shockwaves when they collapse by implosion, forcing the oil and methanol to join.

2.11 Acid-Catalyzed Pre-Treatment

When jatropha curcas oil is used, an acid catalyzed is preferred, but it requires more excess methanol, high pressure and high cost stainless steel equipments. In addition, the yield of the product is low when the common sulfuric acid is used. Hence, a combine process with acid catalyzed pre-treatment 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 second step, sodium hydroxide is added to catalyze the transesterification reaction in which TG is reacted with methanol. Without waste water, reusing the catalyst and low cost of reaction tank, these to 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.



$$\underset{\text{FFAs}}{HO-\overset{\overset{O}{||}}{C}-R} + \underset{\text{Alcohol}}{CH3OH} \xrightarrow[\text{Acid catalyst}]{} \underset{\text{Esters}}{CH3O-\overset{\overset{O}{||}}{C}-R} + \underset{\text{Water}}{H2O}$$

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 pre-treatment step, sodium hydroxide catalyst and methanol can be added to the oil and the transesterification reaction can begin.

2.12 Gas Chromatography

Gas chromatography (GC) is a type of chromatography in which the mobile phase is a carrier gas. This carrier gas is usually an inert gas such as helium or an unreactive gas such as nitrogen. The stationary phase is a microscopic layer of liquid or polymer on an inert solid support, inside glass or metal tubing, called a column. The instrument used to perform gas chromatographic separations is called a gas chromatograph.

A gas chromatograph is a chemical analysis instrument for separating chemicals in a complex sample such as a sample of newly produced biodiesel. A gas chromatograph uses a column, through which different chemical constituents of a sample pass in a gas stream at different rates depending on their various chemical and physical properties and their interaction with the stationary phase. The chemicals are identified and detected electronically as they exit the end of the column. The stationary phase functions to separate different components causing each one to exit the column at different retention times. The carrier gas flow rate, as well as temperature can also be used to alter the order or time of retention.

CHAPTER 3

METHODOLOGY

3.1 Materials

The materials to be used in this study are Jatropha curcus seeds collected from the Jatropha plantation Industrial Biomass Sdn Bhd , potassium hydroxide (KOH) in granular form, and methanol. Fossil diesel is also needed in order to make a comparative analysis.

3.2 Raw material preparation

Jatropha curcas l. seeds were cracked and the shells were carefully removed. The kernels were grinded with a sieve plate and shaker grinder by using sieve plates. The seeds were categorized into two particle size classes : 10µm and below and 1mm and above.

3.3 Optimization of oil extraction

The effect of three main factors which are type of temperature, particle size of the meal and reaction time were investigated to optimize the extraction operating conditions for achieving maximum oil yield. Jatropha curcas seeds were cracked and the shells were carefully removed. The kernels were grinded with a sieve plate and mechanical grinder and defatted in a soxhlet apparatus. The seeds were categorized into two particles size 10µm and below and 1mm and above. 30g of grinded meal was extracted with solvent namely n-hexane. The extraction temperature was fixed at boiling point of the solvent while the reaction time was varied between 4 hr, 6hr and 8hr.

At the end of the extraction, the micelle was filtered using a vacuum filtration (Millipore glass base and funnel) to remove suspended solids. Subsequently, the solvent was separated from the oil using rotary vacuum evaporator at boiling point of solvent and was collected in the receiving flask. The oil which was remained in the sample flask was weighed after the process was completed. The percentage of extracted oil was calculated by dividing the amount of obtained oil by the amount of the seeds multiply by 100. All experiments were repeated at least twice. Extracted seed oil was stored in freezer at 4 ◦C for subsequent physicochemical analysis.

3.4. Chemical and Physical analysis of seed oil

3.4.1. Acid value, % FFA.

Acid value of seed oil was determined according to Method EN14104 . Percentage freefatty acids (FFAs) were calculated using oleic acid as a factor.

3.4.2. Iodine value

Iodine value of seed oil was determined according to Method EN14111

3.4.3. Saponification value

The saponification value was determined according to MPOB Official Test Method 2004.

3.4.4. Peroxide value

The peroxide value was determined according to AOAC Official Method 965.33

3.4.5. Kinematics Viscosity

Viscosity of seed oil was carried out using ASTM D 445-94 was used at 40^0C temperature.

3.4.6. Density

The density of the samples was determined at 15 °C by using density meter ASTM D1292-85(90).

3.4.7 Analysis of Fatty Acid Compositions.

Fatty acid composition of seed oil was determined using gas chromatography mass spectrometry (GCMS) equipped with flame ionization detector and capillary column (30m×0.25mm). About 0.1 ml oil was converted to methyl ester using 1ml NaOMe (1 M) in 1ml hexane before being injected into the GC. The detector temperature was programmed at 250ºC with flow rate of 1.5 ml/min. The injector temperature was set at 250 ºC. Hydrogen was used as the carrier gas. Colomn temperature 50 ^{0}C for 1min increase to 70 ^{0}C at 5^0C /min held for 9min. further programe 200 ^{0}C at 15C/min held for 10min. final temperature 230 ^{0}C held for 4min and solid ratio of 50:1. The identification of the peaks Characteristic and Composition of *Jatropha Curcas* Oil Seed from Malaysia and its Potential as Biodiesel Feedstock was achieved by retention times by means of comparing them with authentic standards analyzed under the same condition.

3.5 Catalyst Preparation

- Acid catalyst preparation
  - 2%wH_2SO_4 / wJCO is prepared.
  - 2% of JCO weight is calculated and taken as H_2SO_4 weight.
  - The calculated weight is then weighed by weighting scale.

- Alkali catalyst preparation
  - Catalyst ratio to Jatropha curcas oil of 0.5, 1.0, 1.5, 2.0 and 2.5% wt KOH /wJCO is first calculated.
  - The calculated weight is then will be weighted by weighing scale.

3.6 Acid-Catalyzed Esterification

The FFAs is first converted to ester in using an acid catalyst that is acid sulfuric (H_2SO_4). This step is called as pre-treatment step. In the pre-treatment step, JCO at calculated amount is put into the ultrasonic batch reactor and pre-heated at 60°C in order to accelerate the reaction rate. At the same time, methanol and catalyst KOH are added in a beaker to allow them to mix before added into the JCO in the ultrasonic batch reactor. KOH does not readily dissolved into methanol, the best way to assure them to mix well. When the particles of KOH cannot be seen, the methoxide (alcohol and catalyst mixture) is ready to be added. The reaction took placed for 1 hours, at the temperature of 40°C. In this step, molar ratio of methanol to Jatropha curcas oil is 6:1 and the ratio of acid catalyst to Jatropha curcas oil is 2%wtH_2SO_4 / wJCO. Table 3.1 shows the molar ratio and the weight of all the substances needed to run this part of experiment.

Table 3.1: Weight of Substances needed during the acid catalyzed esterification (Refer Appendix A)

Molar ratio of methanol: JCO	6 :1
Weight of JCO (g)	50
Weight of methanol (g)	8.33
Catalyst weight percent (wtH2SO4 / wJCO)	2%
Catalyst weight (g)	2

3.7 Alkali Catalyzed Transesterification

After the acid pre-treatment, esterifies Jatropha curcas oil is gone through the alkali-catalyzed transesterification. In order to speed up the reaction, the oil is preheated at 60ºC. Heating with electrical element such as heating plate is usually the easiest way to bring the oil at the required temperature Methanol and catalyst

In this step, the reactor is initially filled up with water as the medium of the ultrasonic wave. The preferred amount of esterifies waste cooking oil which has been through the acid catalyzed pre-treatment is weighed in a beaker. The oil is placed in the ultrasonic batch reactor with its related equipment and will be heated to a predetermined temperature. The catalyst is added to the ultrasonic batch reactor. The reaction is timed as soon as soon as the catalyst-methanol mixture is added to the reactor and continued for a fixed time. The mixture then transferred into a beaker to allow the glycerol to separate from the crude ester layer by gravity for one night.

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:

I. Phase I

The purpose of phase one is to investigate the effect of temperature on biodiesel yield, FFA content and also the acid value. The fixed and the manipulated variables of this phase is shown in Table 3.2(a) and Table 3.2(b) respectively.

Table 3.2: Fixed and manipulated parameter for alkali catalyzed transesterification (Phase I)

(a): Fixed Parameter

Parameter	Value
Catalyst weight percent (%wtH_2SO_4 / w JCO)	2
Reaction time (hr)	1
Ultrasonic wave (Hz)	60
Settling time	6 hr
Agitator speed (rpm)	150

(b) Manipulated Parameter

Sample	Temperature (ºC)
1	30
2	40
3	50
4	60

II. Phase II

The purpose of phase two is to investigate the effect of catalyst weight percentation biodiesel yield,and moisture content . The fixed and the manipulated variables of this phase is shown in Table 3.3(a) and Table 3.3(b) respectively. The calculated weight of various catalyst weight percent is shown in Table 3.4.

Table 3.3: Fixed and manipulated parameter for alkali catalyzed transesterification (Phase II)

(a): Fixed Parameter

Parameter	Value
Temperature	Best temperature from Phase I
Reaction time (hr)	1hr
Ultrasonic wave (Hz)	60
Settling time	6hr
Agitator speed (rpm)	150

(b) Manipulated Parameter

Sample	Catalyst weight percent (%wt KOH / w JCO)
1	0.5
2	1.0
3	1.5
4	2.0
5	2.5

Table 3.4: Weight of alkali Catalyst (Refer Appendix B for the manual calculation)

JCO (g)	%wt KOH/wJCO	Weight KOH (g)
50	0.5	0.5
50	1.0	1.0
50	1.5	1.5
50	2.0	2.0
50	2.5	2.5

3.8 Draining of Glycerol

After the transesterification reaction, the solvent vessel concerned must be left untouched for approximately 6 to 8 hours, so that the glycerol will settle at the bottom of the vessel. This should occur since glycerol is more denser than biodiesel. After 6 to 8 hours has elapsed, drain off the glycerol that has settled at the bottom of the container using the decantation technique.

3.9 Methanol Recovery

After the settling time, the glycerol layer and the methyl ester layer is separated. The methyl ester layer (the upper part) is put in the rotary evaporator to remove the remaining 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 process of methanol recovery.

Figure 3.5: Methanol recovery

3.10 Washing

After methanol recovery, the methyl ester will be washed with warm deionized water for several times until wash water becomes clear. The methyl ester or biodiesel needs to be washed so that it can remove the residue methanol and soapy deposits. The biodiesel and wash water will be foaming two layers and can be separated. The amount of wash water is equal to the amount of oil, and can be drained throughout the washing process. At this point, the biodiesel is usually a pale yellow color. This can be seen in the Figure 3.6.

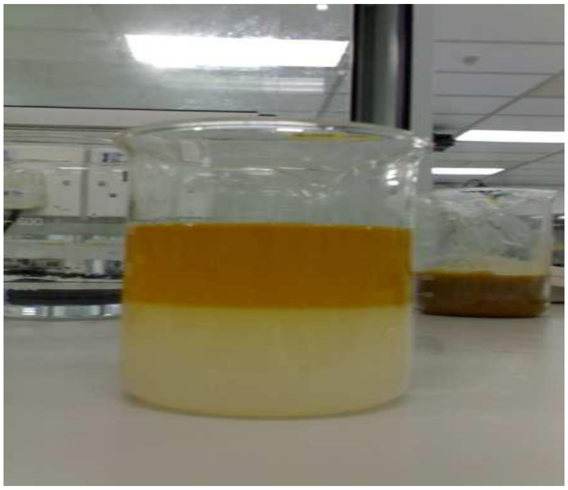


Figure 3.6: Biodiesel after 1 hour washed with hot water

3.11 Biodiesel Yield

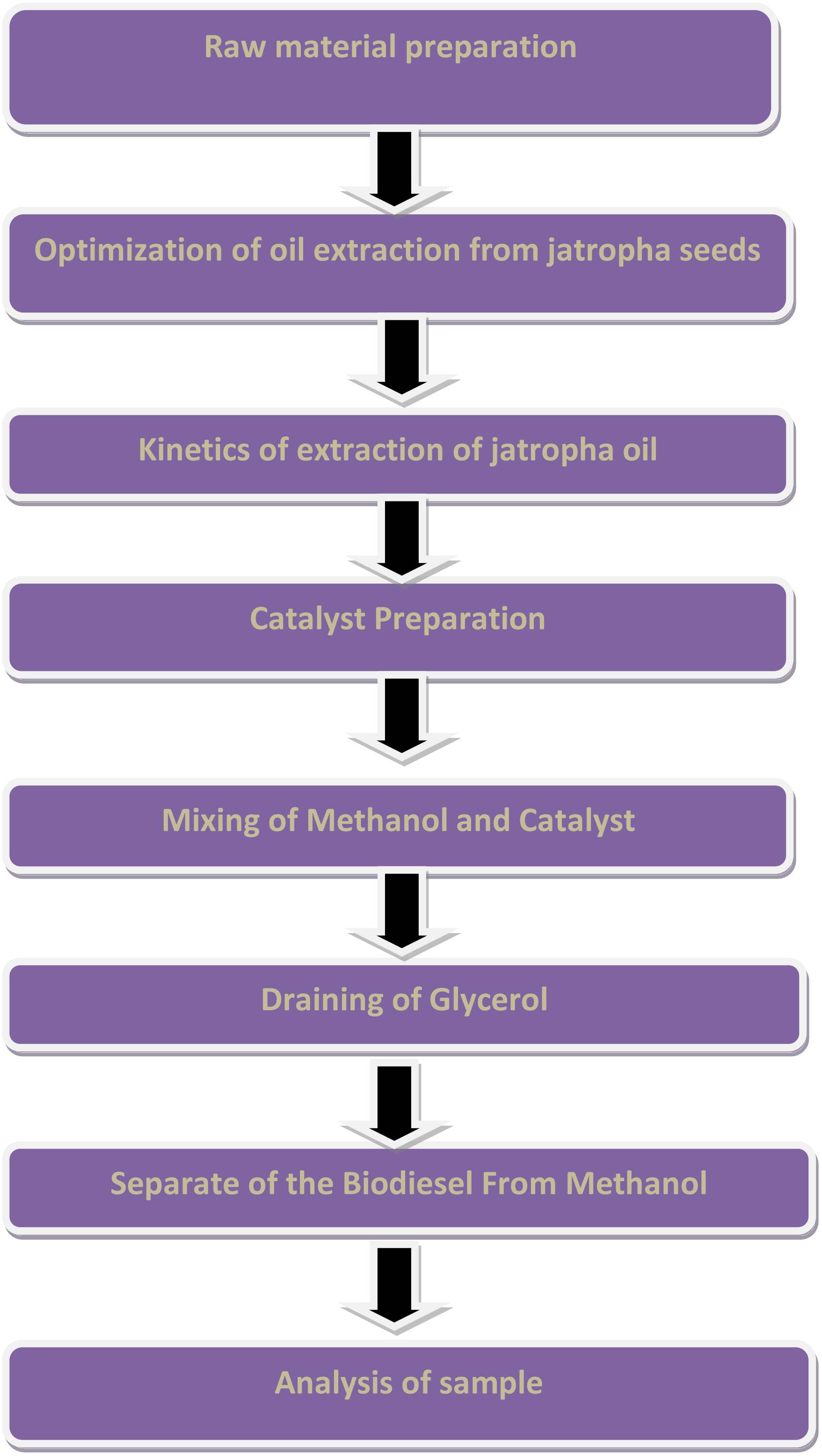
The biodiesel yield are measured by determine the amount of biodiesel product divided with the amount of the value of raw Jatropha curcas oil used. The density of Jatropha curcas oil is 887g/L and density methanol is 765g/L. The calculation of the biodiesel yield is shown in equation 3.1.

$$\% \text{ Yield} = \frac{\text{Final sample product}}{\text{Jatropha curcas oil}} \times 100 \qquad (3.1)$$

3.12 Moisture content

Biodiesel which have high quality is basically has low moisture content. Moisture or water content in biodiesel can lead to tank corrosion. Moreover, biodiesel and its blends are susceptible to growing microbes when water is present in fuel. The solvency properties of the biodiesel can cause microbial slime to detach and clog fuel filters. In this experiment, moisture content in biodiesel sample will be measured using Karl-Fischer titration. The biodiesel samples were used about 10 ml and the experiments were running in 300s.

3.13 FLOW CHART



CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This study is carried out to investigate the effect of temperature, reaction time and catalyst weight percent to the biodiesel yield, FFA content and physical parameters value by two-step catalyzed transesterification of Jatropha curcas oil, assisted by the ultrasonic radiation.

4.2 Effect of reaction time on oil extraction

Table 4.1: Particle size 10µm

Time, hr	grinded meal, g	Oil weight, g			Extracted oil , %
		Test 1	Test 2	average	
4	30	15.1	15.3	15.2	50.66
6	30	17.5	18.1	17.8	59.33
8	30	18. 3	18.4	18.35	61.17

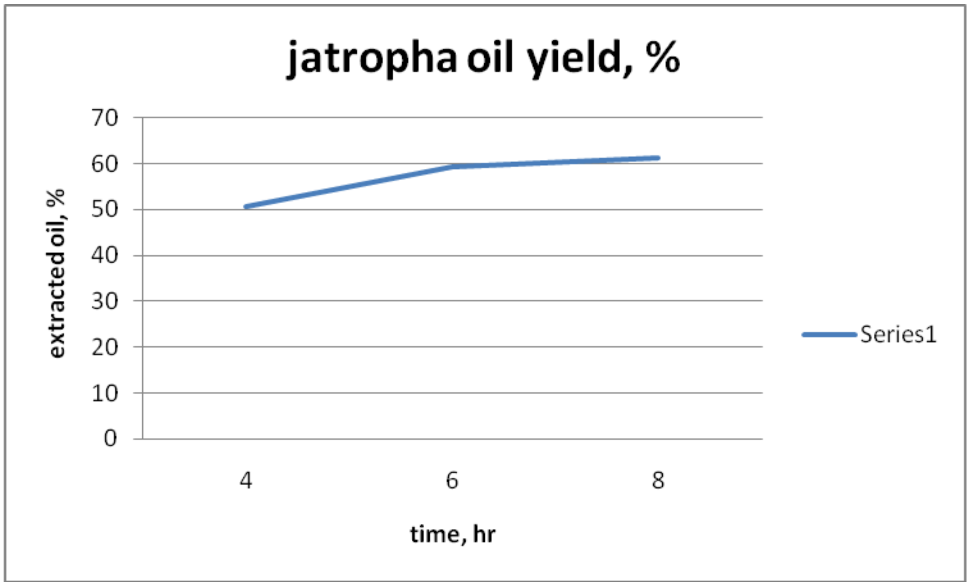


Figure 4.1 : Graph percentage of extracted oil vs time for particle size 10µm

Table 4.2: Particle size 1mm

Time, hr	grinded meal, g	Oil weight, g			Extracted oil, %
		Test 1	Test 2	average	
4	30	12.5	12.3	12.4	41.33
6	30	14.6	14.9	14.75	49.17
8	30	15. 3	15.4	15.35	51.17

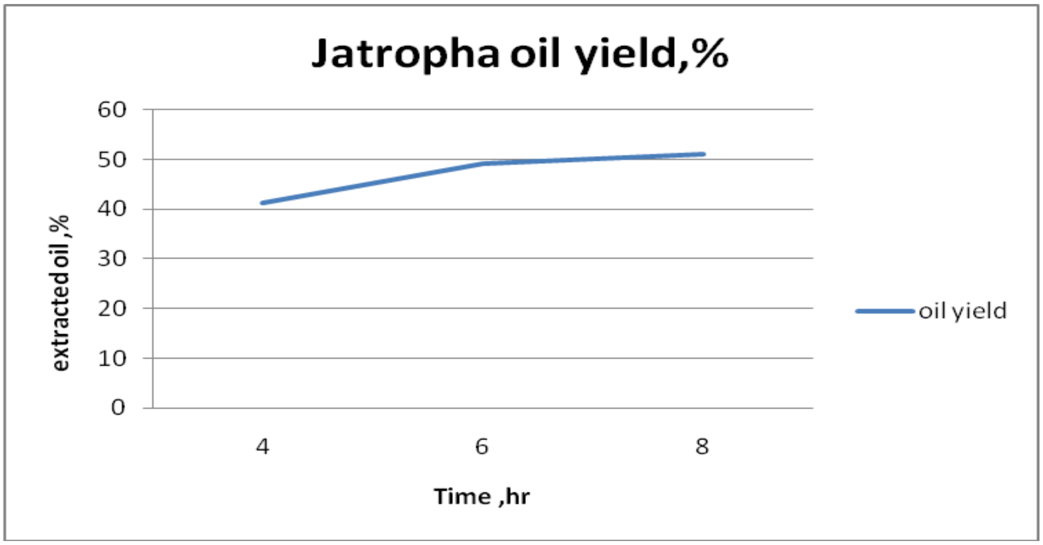


Figure 4.2 : Graph percentage of extracted oil vs time for particle size 1mm

Figures 4.1 & 4.2 and table 4.1 & 4.2 shows the total amount of oil extracted from Jatropha curcas seeds at different reaction times. The amount of extracted oil by hexane did not change significantly after 6 h. Most of the oil is extracted after 6hr although maximum extracted oil is achieved after 8 h with 61.17 % and 51.17 %. The extraction rate is fast at the beginning of the extraction but gets slow gradually. The reason is that when the meal is exposed to the fresh solvent, the free oil on the surface of seeds is solubilized and oil gets extracted quickly inducing a fast increase in the extraction rate.

Furthermore, since the oil concentration is low in the solvent at the beginning of the extraction process, the oil diffuses quickly from the meal to the liquid phase due to the mass transfer effect. As the time passing by, the concentration of oil increases in the solvent resulting in a decrease in the diffusion rate. When the maximum amount of extractable oil is obtained, the oil yield level remains invariable even by extending the reaction time. By increasing the temperature approaching to the boiling point of the solvent, both the diffusion coefficient and the solubility of the oil in the solvent are enhanced, thus improve the extraction rate (Richardson and Harker , 2002). The optimum extraction temperature for n-haxane would be near their boiling point to ensure the maximum recovery of oil.

4.3 Effect of particle size on oil extraction

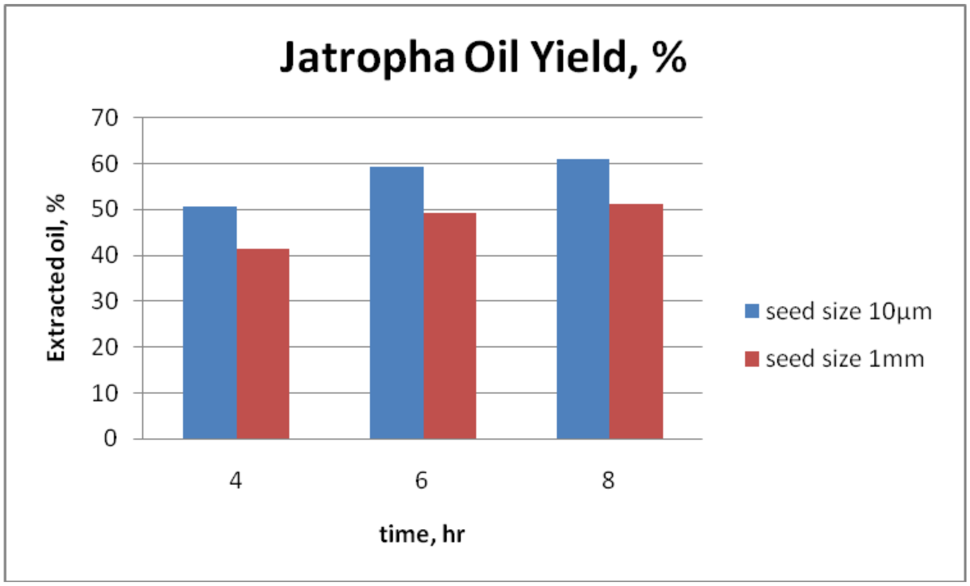


Figure 4.3 : graph show comparison on extracted oil yield vs time for different particle size

The effect of particle size of meal on extraction yield is shown in Figure 3. The extraction was carried out using two different meal sizes namely 10µm and below and 1mm and above. The highest percentage of oil yield was obtained from the smallest size particle (10µm) which is 61.17 % using hexane. Less oil is extracted from the larger particles (>1 mm) compared to the smaller size particles. The reason is that larger particles with smaller contact surface areas are more resistant to solvent entrance and oil diffusion. Therefore, less amount of oil will be transferred from inside the larger particles to the surrounding solution in comparison with the smaller ones.

4.4 Chemical and physical properties of extracted oil

Table 4.3: Fatty acid composition & Chemical and physical properties of Jatropha Curcas oil.

No	PROPERTIES	JATROPHA CURCAS OIL
1	Fatty acid composition ,%	
	Palmitic acid $C_{16:0}$	14.07
	Stearic acid $C_{18:0}$	8.29
	Oleic acid $C_{18:1}$	45.24
	Linoleic acid $C_{18:2}$	31.58
	Linolenic acid $C_{18:3}$	0.81
2	Density @15°C (g/ml)	0.8879
3	Iodine value , g/100 g	108.46
4	Saponification value ,	196.71
5	Peroxide value , meq/kg	2.26
6	Viscosity at 40°C (cp)	30.69
7	Kinematics Viscosity at 40°C (Cst)	34.56
8	Acid value, % FFA.	3.84
9	Pour point , °C	-7
10	Cloud point, °C	-11
11	Flash point , °C	189
12	Moisture content , wt%	0.03
13	Physical state at room temperature	liquid

The fatty acid composition and other physico-chemical properties of Jatropha curcas oil is presented in Table 3. Jatropha curcas oil contains 22.36% saturated acids (Palmitic and Stearic) and 77.63% unsaturated acids (Oleic, Linoleic and Linolenic). Saturation fatty acid alkyl esters increase the cloud point, cetane number and stability. The free fatty acid content of unrefined jatropha oil was about 1.9%. The yield of esterification process decreases considerably if FFA value is greater than 2%. It has been found that the alkaline catalyzed transesterification process is not suitable to produce esters from unrefined oils having FFA greater than 2% due to presence of moisture leading to soap formation and lack of phase separation. The high FFA content (>2% w/w) will happen soap formation and the separation of products will be exceedingly difficult, and as a result, it has low yield of biodiesel product.

The iodine value is a measured of the unsaturation of fats and oils. Higher iodine value indicated that higher unsturation of fats and oils. The limitation of unsaturated fatty acids is necessary due to the fact that heating higher unsaturated fatty acids results in polymerization of glycerides. This can lead to the formation of deposits or to deterioration of the lubricating.

Peroxide value of *jatopha* oil seed showed a low value (as crude seed oil) of 2.26meq/kg, proving the oxidative stabilities of the seed oil relatively. The high iodine value and oxidative stability shows that the seed oil upholds the good qualities of semidrying oil purposes (Eromosele et al., 1997). High saponification value indicated that oils are normal triglycerides and very useful in production of liquid soap and shampoo industries.

Viscosity defined as resistance liquid to flow. Viscosity increased with molecular weight but decreased with increasing unsaturated level and temperature. The viscosity of Jatropha oil seed must be reduced for biodiesel application since the kinematic viscosity of biodiesel were very low compared to vegetable oils. High viscosity of the jatropha oil seed are not suitable if its use directly as engine fuel, often results in operational problems such as carbon deposits, oil ring sticking, and thickening and gelling of lubricating oil as a result of contamination by the vegetable oils (Pramanik, 2003). Generally, the density of oil decreases with molecular weight, yet increase with unsaturation level. From the experiment was conducted, the density of *jatropha* seed oil were 0.8879 g/ml.

4.5 Effects of catalyst concentration

The effects of KOH on the transesterification process of the Jatropha curcas oil were investigated with the concentration varying from 0.5, 1, 1.5, 2.0, and 2.5% (based on the weight of raw Jatropha curcas oil). The reaction conditions during the whole process were fixed at reaction time of 60 min and temperature at 40^0C.

Table 4.4 : Analysis data on biodiesel samples based on different catalyst concentration

Catalyst concentration (%)	Yield (%)	Moisture content (%)
0.5	56.72	0.02
1.0	74.20	0.03
1.5	92.52	0.03
2.0	83.40	0.04
2.5	70.16	0.04

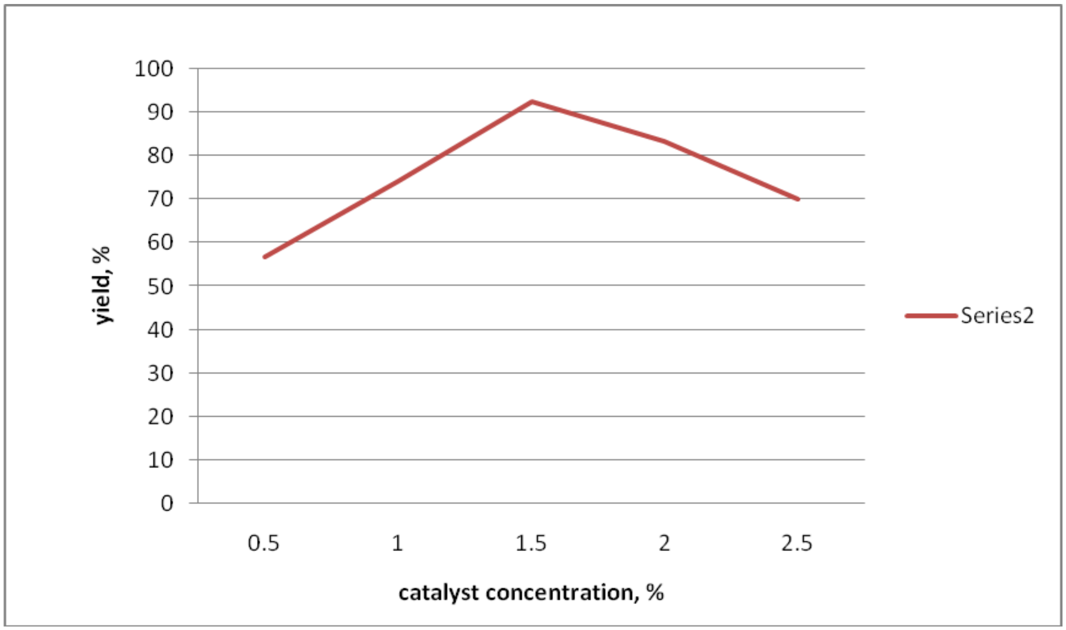


Figure 4.4 : Graph percentage of biodiesel yield vs. catalyst concentration

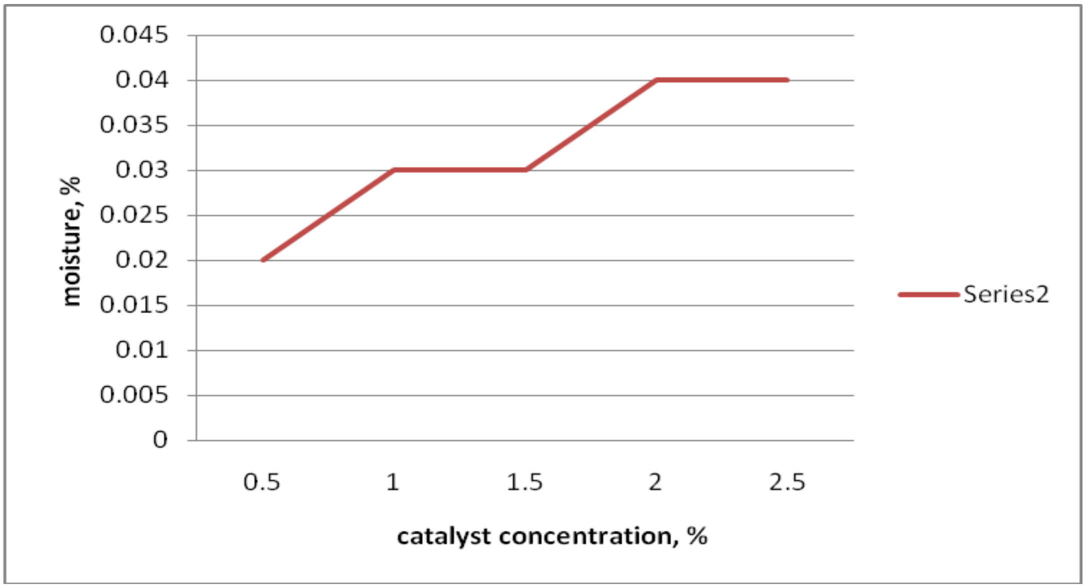


Figure 4.5: Graph percentage of moisture content vs. catalyst concentration

The effects of KOH on the transesterification process of the jatropha curcas oil were investigated with the concentration varying from 0.5, 1, 1.5, 2.0, and 2.5%. The reaction conditions during the whole process were fixed at reaction time of 60 min and temperature at 40^0C.

Figure 4.4 shows that effect of catalyst concentration to yield production. As can be observed, the methyl esters yield were increase proportionally with the catalyst concentration until it reached point maximum which the yield value was 92.52% at 1.5% catalyst concentration. After that, the yield percentages were decrease to the most minimum production of yield (70%) which at catalyst concentration 2.5%. Increase in catalyst concentration does not increase the conversion. This fact was related to the free acidity of the oil. With the increase in the concentration of the catalyst, there was decrease in the yield of methyl esters. This was because the formation of soap in presence of high amount of catalysts increases the viscosity of the reactants and lowered the yield (Encinar *et al.*, 2005). As a result, the best methyl esters yield (92.52%) was achieved for catalyst concentration of 1.5%. At higher concentration over than 1.5% of catalyst, the productions of biodiesel were decreased.

From Figure 4.5, it is shows the moisture content of biodiesel sample is decreasing rapidly constantly until it reached lowest point which at 0.5% catalyst concentration at 0.02%. The highest moisture content 0.04% was recorded at catalyst concentration 2.5%. This was related to OH – molecule in catalyst itself. If high amount of catalyst were used, it will contributed more OH molecule and make the biodiesel have high moisture content. Lowest moisture content is very important for biodiesel because water in sample can contribute to microbial growth, lead to tank corrosion, it participate in the formation of emulsion, as well as cause hydrolysis or hydrolytic oxidation (Knothe *et al.,* 2002).

4.6 Effects of temperature

The effects of temperature on the transesterification process of the jatropha curcas oil were investigated with temperature varying from 30, 40, 50 and 60^{0}C. The reaction conditions during the whole process were fixed at reaction time of 60 min and catalyst concentration (KOH) at 1.5%.

Table 4.5: Analysis data on biodiesel samples based on different temperature

Temperature °C	Yield (%)	Moisture content (%)
30	61.83	0.03
40	67.30	0.03
50	75.51	0.02
60	87.13	0.02

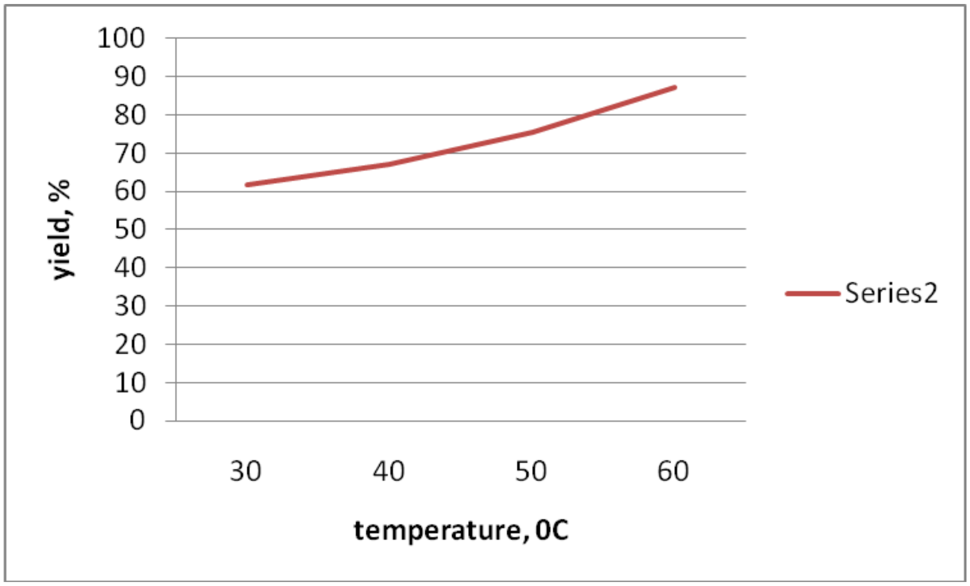


Figure 4.6 : Graph bodiesel yield vs temperature

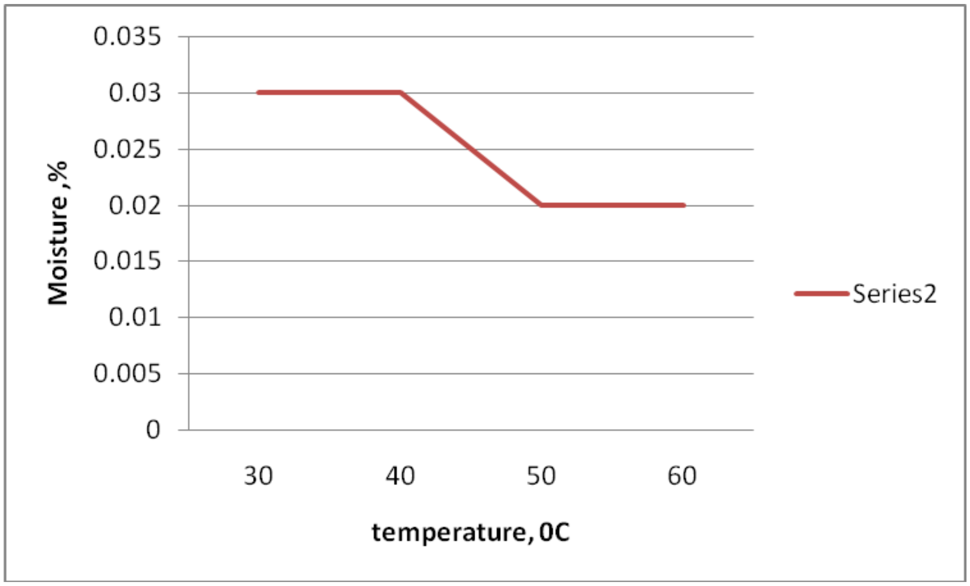


Figure 4.7 : Graph percentage of moisture content vs. temperature

Figure 4.6 shows yield production via temperature. It can be observed that the percentages of biodiesel yield were increased rapidly as the temperature increased from the lowest temperature 30^0C with yield 61.83% until the highest temperature 60^0C with yield 87.13%. High temperature which near the boiling point of alcohol used in the experiment was contributed to the high conversion of methyl esters. Alkaline alcoholysis of oils is normally performed near the boiling point of the alcohol (Srivastava *et al.,* 2004). The reaction temperature above boiling point of alcohol is ignored at as at high temperature it leans to accelerate the saponification of glycerides by the base catalyst before completion of the alcoholysis (Dorado *et al.*, 2004). The boiling point for methanol is 65^0C. Based on results after 60min reaction, the yield of esters at 60^0C which the temperature is the nearest to boiling point of methanol have produced the highest yield which these respectively showing the influence of temperature on ester conversion.

Based on figure 4.7 , at temperature 60^0C with the lowest moisture content which was 0.02%, it because of the water content biodiesel sample have evaporated. This is because higher temperature will evaporate more water molecule compared to lower temperature. This was proven by the high value of moisture content which was 0.03% at temperature 30 ^{0}C. Since the kinetic energy of a water molecule is proportional to its temperature, evaporation proceeds more quickly at higher temperature (Silberberg *et al.*, 2004). So the temperature at 60^0C is chosen as the best temperature.

4.7 Effects of time

The effects of time on the transesterification process of the jatropha curcas oil were investigated with time varying from 20, 30, 40, 50 and 60 min. The reaction conditions during the whole process were fixed at reaction temperature of 60^0C and catalyst concentration (KOH) at 1.5%.

Table 4.6 Analysis data on biodiesel samples based on different time

Time (min)	Yield %	Moisture content %
20	66.50	0.03
30	72.85	0.03
40	78.42	0.02
50	83.51	0.02
60	90.72	0.02

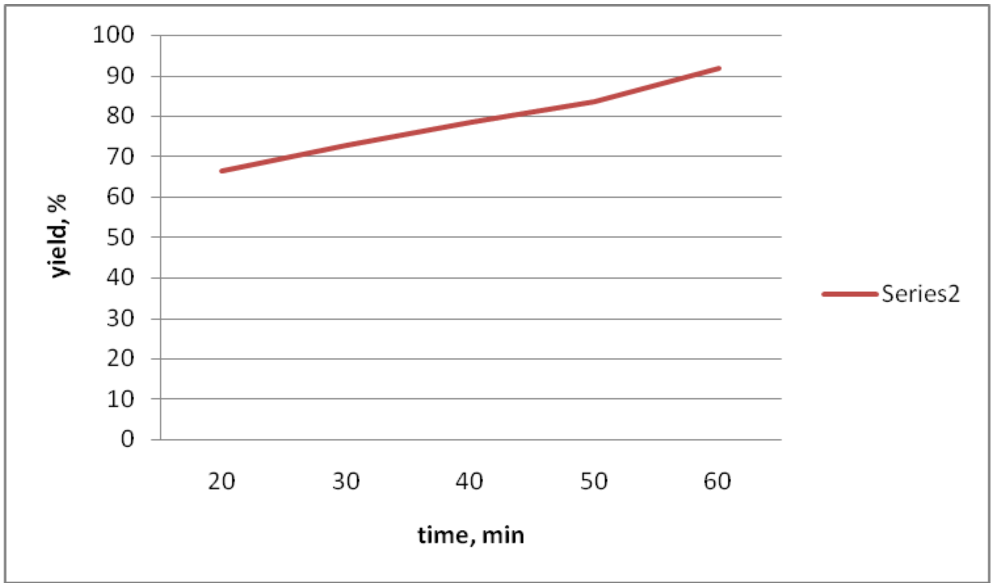


Figure 4.8: Graph percentage of biodiesel yield vs. time

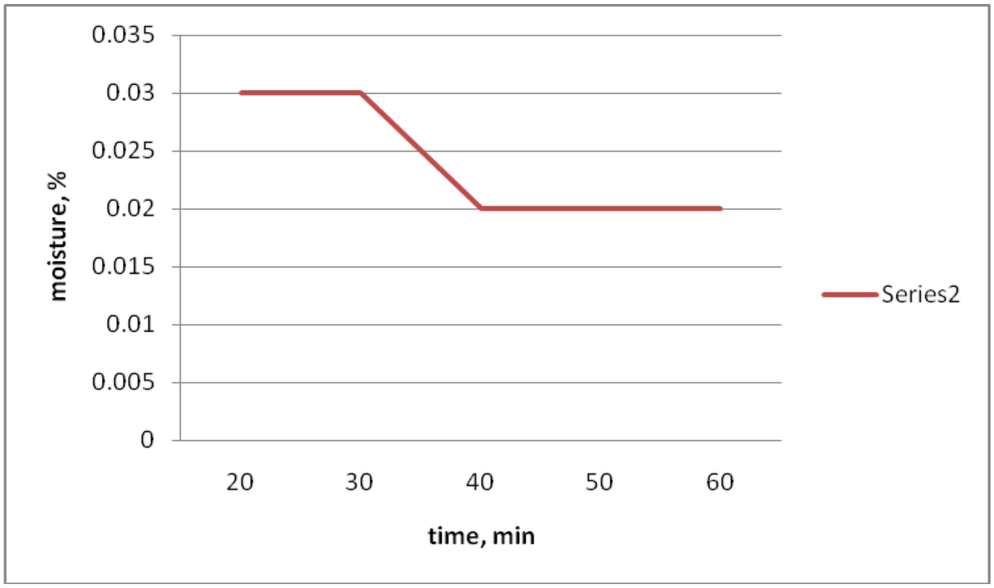


Figure 4.9 : Graph percentage of moisture content vs. time

Based on figure 4.8, the highest yield value was 90.72% with reaction time 60 min and the lowest yield value was 66.5% with reaction time 20 min. For figure 6, the lowest moisture content recorded was 0.02% for 40, 50 and 60 min and the highest was 0.03% at reaction time 20 & 30 min.

Figure 4.8 and 4.9 were the results analysis on biodiesel production based on different time. Based on the results it was showed that biodiesel yield was proportionally increased with reaction time. The longer duration of time, the more conversion of methyl esters can be achieved. These due to time that was taken for the transesterification reaction to completely done. Based on all results analysis, the maximum production methyl esters with the lowest moisture content which was 0.02%, achieved for catalyst concentration 1.5% at 60^0C and for 60 min reaction time.

There were some error occurred during the experiment. These errors were slightly effects some of the results for these studied experiment. When the experiments were running, there are some losses in yield of biodiesel. These losses are obviously occurred because some un-reacted alcohol, residual catalyst and emulsion removed during the washing stage of the production process.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

Two main operating parameters affecting the solid liquid extraction of Jatropha seeds were optimized based on the maximum oil yield extracted from the seeds. The optimum conditions for the lab scale solid liquid extraction were obtained at temperature near the boiling point (68°C), extraction time of 6hr, and 10µm coarse size meals. The major fatty acids in *Jatropha curcas seed* oil were the oleic acid, linoleic acid , palmitic acid and the stearic acid. The oil extracts exhibited good physicochemical properties and could be useful as biodiesel feedstock and industrial application.

Biodiesel from jatropha curcas oil were produced using ultrasonic reactor through transesterification reaction and catalyst that have been used was potassium hydroxides (KOH). 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 waste cooking oil are at 1.5% catalyst concentration, reaction temperature at and at 60^0C a reaction time 60 min 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.

To improve the biodiesel production, there are four recommendations. First, throughout this study, the ultrasonic rector used is only capable to supply frequency about 60Hz. Therefore, it is recommended that an ultrasonic reactor capable of supplying higher frequency, such as 10 MHz or higher, be used for future study to get higher conversion of biodiesel. Secondly, during the transesterification reaction the mixture of oil, catalyst and alcohol should be constantly mixing. Without mixing, the reaction occurred only at the interface of the two layers and considered too slow to be feasible. The higher agitations on the transesterification of oil promoted the homogenization of the reactants and thus lead to higher yields. Thirdly, the raw waste cooking oil has to be preheated at higher temperature such as 100^0C before mixing with catalyst such as alkaline-catalyzed to reduced water content in the oil and due to contributed to high biodiesel yield production. This is because the presence of water, under alkaline conditions may cause ester saponification. Finally For further research we can use nano particle size of meal on extraction for Optimized the oil extraction.

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APPENDIX A

```
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Instrument :    GCMSD
Sample Name: 4HR
Misc Info  : oil
Vial Number: 1
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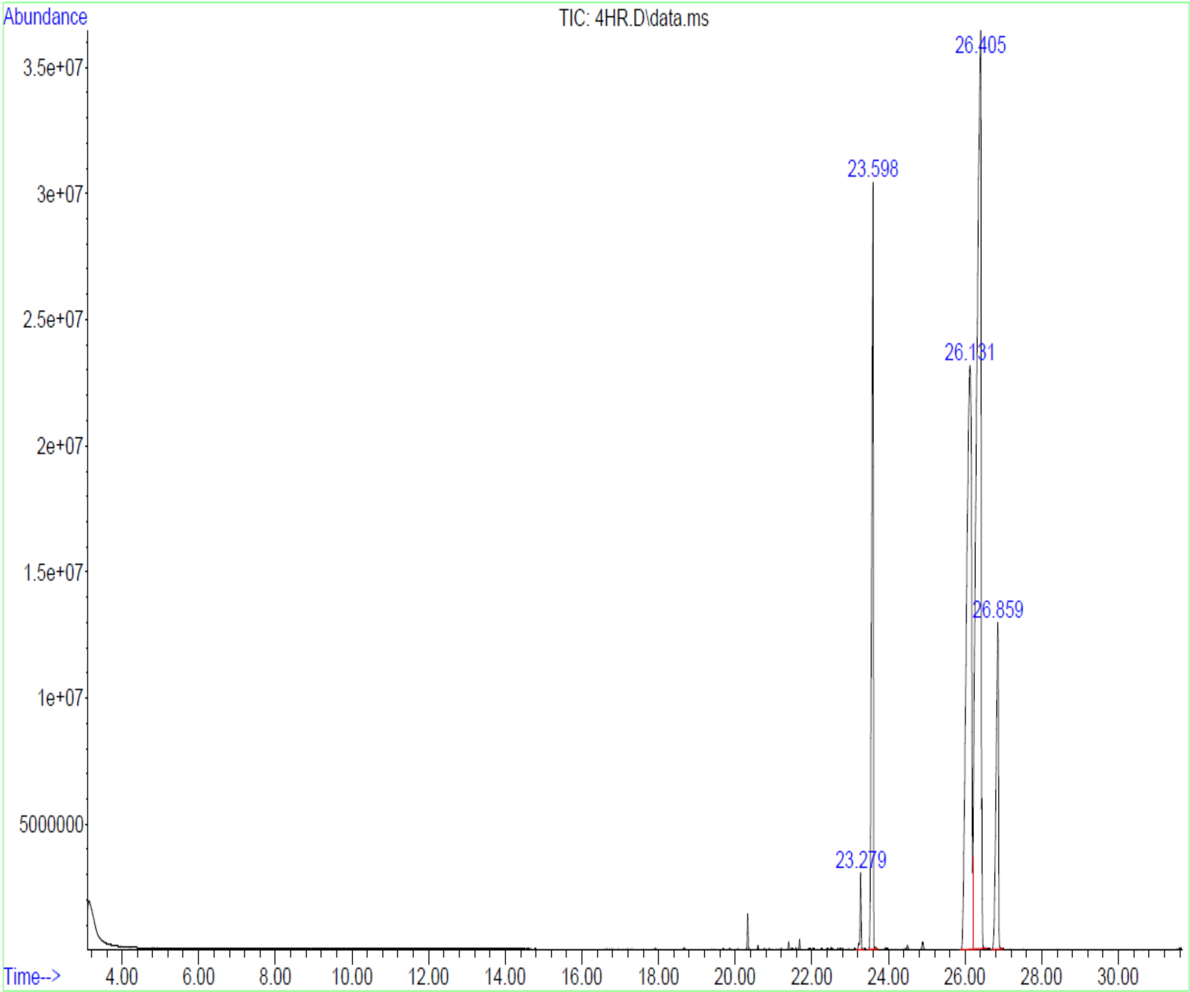

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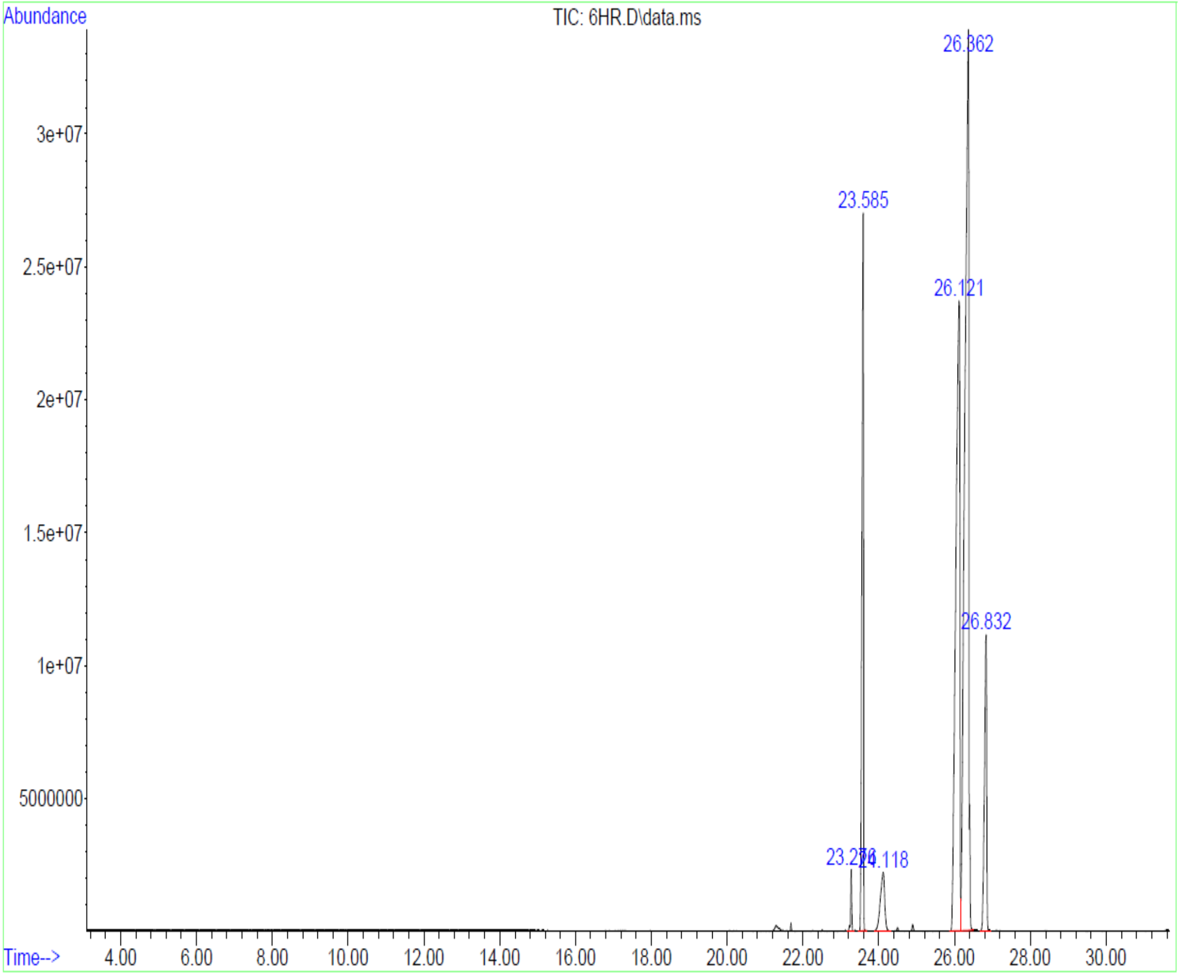

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Misc Info  : oil
Vial Number: 3
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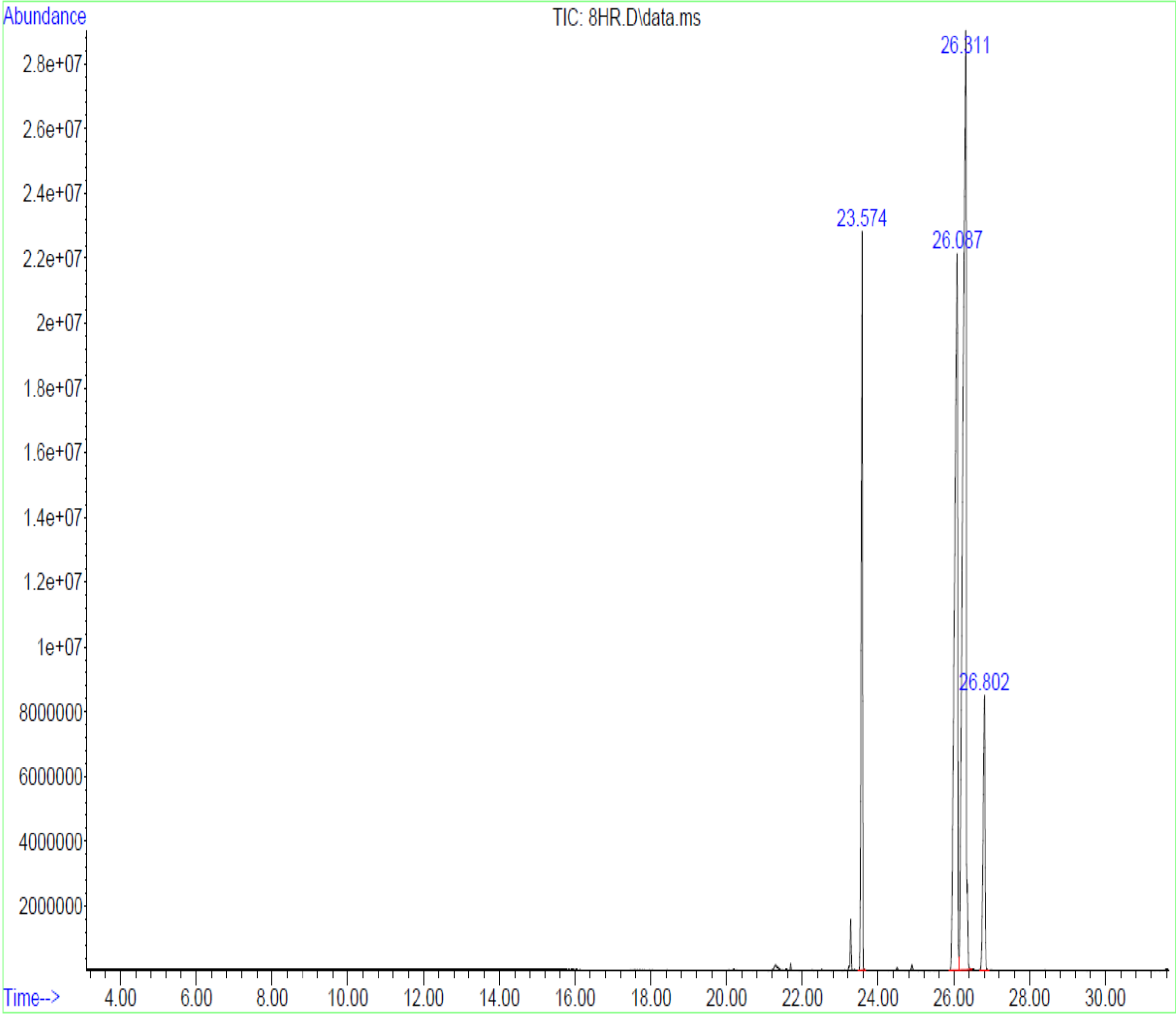

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Sample    : 4HR
Misc      : oil
ALS Vial  : 1   Sample Multiplier: 1

Search Libraries:   C:\Database\NIST05a.L           Minimum Quality:

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                (Z)-
               7-Hexadecenoic acid, methyl ester, 104151 056875-67-3 99
                (Z)-
               9-Octadecenoic acid (Z)-, methyl e 122321 000112-62-9 93
               ster

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               Pentadecanoic acid, 14-methyl-, me 105662 005129-60-2 97
               thyl ester
               Hexadecanoic acid, methyl ester    105644 000112-39-0 96

3  26.128 32.02 C:\Database\NIST05a.L
               9,12-Octadecadienoic acid, methyl  121093 002462-85-3 99
               ester
               9,12-Octadecadienoic acid (Z,Z)-,  121105 000112-63-0 99
               methyl ester
               9,12-Octadecadienoic acid (Z,Z)-,  121106 000112-63-0 99
               methyl ester

4  26.406 45.50 C:\Database\NIST05a.L
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                (E)-
               9-Octadecenoic acid (Z)-, methyl e 122323 000112-62-9 99
               ster
               7-Octadecenoic acid, methyl ester  122298 057396-98-2 99

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               Octadecanoic acid, methyl ester    123708 000112-61-8 98
               Octadecanoic acid, methyl ester    123700 000112-61-8 98
```

```
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Data File : 6HR.D
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Sample    : 6HR
Misc      : oil
ALS Vial  : 2   Sample Multiplier: 1

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Integration Events: ChemStation Integrator - autoint1.e

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                  (Z)-
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                 Hexadecanoic acid, methyl ester    105646 000112-39-0 94

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                 ) ester
                 Hexanedioic acid, bis(2-ethylhexyl 161423 000103-23-1 95
                 ) ester
                 Hexanedioic acid, bis(2-ethylhexyl 161419 000103-23-1 91
                 ) ester

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                 ester
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                  (E)-
                 9-Octadecenoic acid (Z)-, methyl e 122323 000112-62-9 99
                 ster
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                 Octadecanoic acid, methyl ester    123700 000112-61-8 98
```

```
Data Path : D:\Data\GUGA PSM2\
Data File : 8HR.D
Acq On    :  2 Jun 2010  12:58
Operator  : FIZA02062010
Sample    : 8HR
Misc      : oil
ALS Vial  : 3   Sample Multiplier: 1

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Unknown Spectrum:   Apex
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                thyl ester
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                ester
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```
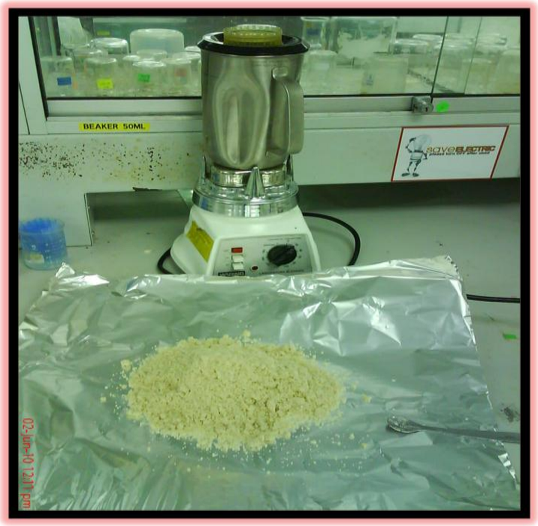

APPENDIX B

Jatropha curcas seeds

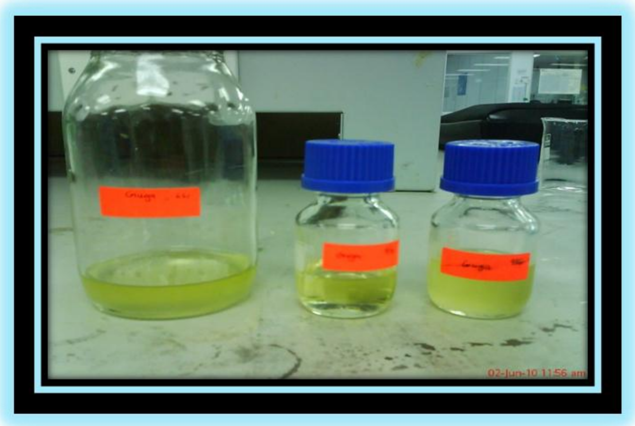
Jatropha curcas kernels



Grinded seeds

Soxhlet extraction

separation

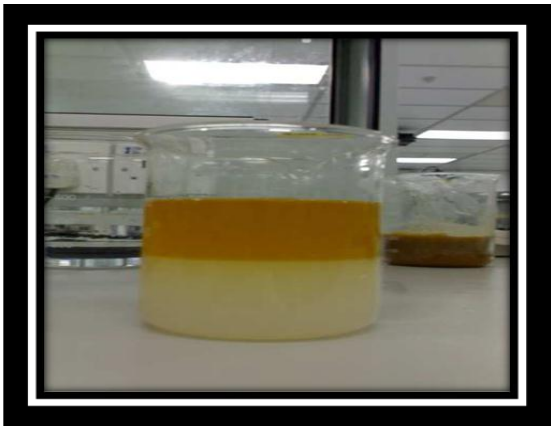


Jatropha curcas oil

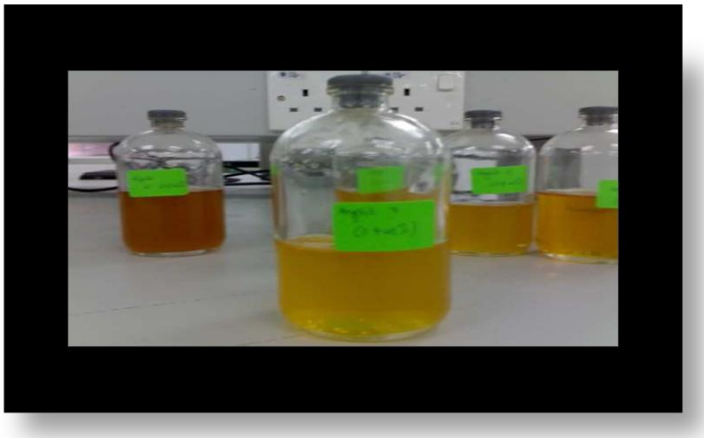
GCMS analysis

Ultrasonic Reactor

separation furnal



washing



biodiesel