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JUDUL : SCALE UP STUDY ON PRODUCTION OF BIODIESEL FROM JATROPHA OIL

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SCALE UP STUDY ON PRODUCTION OF BIODIESEL FROM JATROPHA CRUDE OIL

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“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 : Prof. Dr. Badhrulhisham bin Abdul Aziz
Date : ....

DECLARATION

I declare that this thesis entitled *"Scale Up Study On Production Of Biodiesel From Jatropha Crude Oil"* 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 : Ainul Nadirah Binti Izaharuddin

Date : November 2010

DEDICATION

Dedicated to the memory of

My beloved parents and siblings,
My supervisor and lecturers,
And all supportive friends

ACKNOWLEDGEMENT

Bismillahirrahmanirrahim,
In the name of Allah The Most Gracious and The Most Merciful

Alhamdulillah, praise to Allah, finally, Final Year Project has been successful finished. Firstly, I would like to thank to my supervisor, Prof. Dr. Badhrulhisham bin Abdul Aziz. Eventhough he is Deputy Vice Chancellor of Universiti Malaysia Pahang, he still can do his work as a good supervisor.

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Thank you.

ABSTRACT

Scale up is a very important activity in designing new industrial plants especially in specialty or fine chemicals production. In this work, bench scale and pilot plant scale up factors are examined in producing biodiesel from Jatropha oil. The production of biodiesel in bench scale is compared to the pilot plant scale production. There are two processes involved in this work i.e. esterification process and transesterification process. The esterification process used H2SO4 as a catalyst while in transesterification process used NaOH as a catalyst. The ratio between Jatropha oil to methanol, the time reaction, and the temperature are similar in both scales. From the result, it was found that for bench scale and pilot plant scale, there are some differences in the value of the final yield. The difference value between the bench scale and pilot plant run was caused by several factors such as handling, operating conditions etc.

ABSTRAK

Peningkatan skala merupakan kegiatan yang sangat penting dalam perancangan kilang industri baru terutama pengeluaran bahan kimia yang khusus atau yang kecil. Dalam kajian ini, skala makmal dan skala pilot plant peningkatan skala dikaji dalam menghasilkan biodiesel dari minyak buah jarak. Pengeluaran biodiesel dalam skala makmal dibandingkan dengan pengeluaran skala pilot plant. Dua proses yang terlibat dalam eksperimen ini iaitu proses pengesteran dan pengtransesteran. Proses pengesteran digunakan H_2SO_4 sebagai pemangkin sementara dalam proses pengtransesteran menggunakan NaOH sebagai pemangkin. Nisbah antara minyak buah jarak dengan Metanol, masa, dan suhu adalah sama pada kedua-dua skala. Dari hasil tersebut, didapati bahawa untuk skala makmal dan skala pilot plant, ada beberapa perbezaan dalam nilai akhir pengeluaran. Perbezaan antara skala makmal dan skala pilot plant disebabkan oleh beberapa faktor seperti pengendalian, keadaan operasi dll

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g - Gram
h - Hour
ρ - Density
^{o}C - Degree Celsius
kg - Kilogram
C - Concentration
L - Liter
mm - Mililiter
μm - Mikrometer
mL - Mililiter
min - Minute
V - Volume
mg - Miligram

CHAPTER I

INTRODUCTION

1.4 Introduction on scale up production

The starting point generally consists of laboratory results that concern a chemical transformation whose translation into economic gain appears viable. Process development should serve to treat quantities of raw materials industrially, amounting to tons or millions of tons, whereas only grams or kilograms of these raw materials are used in the laboratory. This is the precise function of change of scale or scale up. The problem is to reproduce the laboratory results on a large scale: in other words, to achieve the same conversions, yields and selectivity, and, in some cases, possibly improve the results.

To go directly from the laboratory to the industrial scale is rarely feasible. As a rule, one or more additional experiments are necessary. Specifically, the problem is to define these additional steps in order to gather all the information required at minimum cost and as quickly as possible. It is here that the methodology of process development, and hence of scale up, becomes decisive for the success of the operation.

In laboratory-type experiments, certain aspects of the process are investigated, by handling relatively small amounts of raw materials in order to reduce the material constraints to the minimum. In Pilot-plant experiments, at a scale that varies within wide proportions, but in which all the industrial constraints are taken into account: impurities in raw materials, operation over long periods, materials, equipment reliability, etc. It is during pilot-plant experiments that scale up problems must be dealt with. The pilot-plant experiments alone cannot yield all the answers needed to solve the problem of scale up, and that additional experiments are necessary.

1.5 Introduction on biodiesel

Bio-diesel or biodiesel refers to a diesel-equivalent, processed fuel derived from biological sources. Biodiesel is the name for a variety of ester-based oxygenated fuel from renewable biological sources. It can be made from processed organic oils and fats.

Chemically, biodiesel is defined as the monoalkyl esters of long chain fatty acids derived from renewable biolipids. Biodiesel is typically produced through the reaction of a vegetable oil or animal fat with the methanol or ethanol in the presence of a catalyst to yield (m)ethyl esters (biodiesel) and glycerin (Demirbas,2002). Fatty acid (m)ethyl esters or biodiesels are produced from natural oils and fats. Generally, methanol is preferred for transesterification, because it is less expensive than ethanol.

The general definition of biodiesel are Biodiesel is a domestics, renewable fuel for diesel engines derived from natural oils like soybean oil, and which meets the specifications of ASTM D 6751. Biodiesel is technically defined by using ASTM D 6751. Biodiesel is a diesel engine fuel comprised of monoalkyl eters of long chain fatty acids derived from vegetable oils or animal fats, designated B100, and meeting the requirements of ASTM D 6751.

Biodiesel, defined as the monoalkyl esters of fatty acids derived from vegetable oil or animal fat, in application as an extender for combustion in CIEs (diesel), has demonstrated a number of promising characteristics, including reduction of exhaust emissions. Chemically, biodiesel is referred to as the monoalkyl-esters especially (m)ethyl ester of long-chain-fatty acids derived from renewable lipid sources via transesterification process.

Vegetable oil has too high a viscosity for use in most existing diesel engines as a straight replacement fuel oil. There are a number of ways to reduce vegetable oil's viscosity which are dilution, microemusification, pyrolysis, and transesterification.

Transesterification (also called alcoholysis) is the reaction of a fat or oil triglyceride with an alcohol to form esters and glycerol. A catalyst is usually used to improve the reaction rate and yield. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the products side.

The biodiesel reaction requires a catalyst such as sodium hydroxide to split the oil molecules and an alcohol (methanol or ethanol) to combine with the separated esters. The main byproduct is glycerin. The process reduces the viscosity of the end product. Transesterification is widely used to reduce vegetable oil viscosity (Pinto et al., 2005). Biodiesel is a renewable fuel source. It can be produced from oil from plants or from animal fats that are byproduct in meat processing.

One popular process for producing biodiesel from the fats/oils is transesterification of triglyceride by methanol (methanolysis) to make methyl esters of the straight chain fatty acid. The purpose of the transesterification process is to lower the viscosity of the oil. The transesterification reaction proceeds well in the presence of some homogeneous catalyst such as potassium hydroxide (KOH) and sodium hydroxide (NaOH) and sulfuric acid, or heterogeneous catalysts such as metal oxides or carbonates. Sodium hydroxide is very well accepted and widely used because of its low cost and high product yield (Demirbas,2003a).

The mechanism of the acid-catalyzed transesterification of vegetable oils is shown in Figure 1.1, for a monoglyceride. However, it can be extended to di- and triglycerides. The protonation of the carbonyl group of the ester leads to the carbocation II which, after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate III, which eliminates glycerol to form the new ester IV, and to regenerate the catalyst H^+.

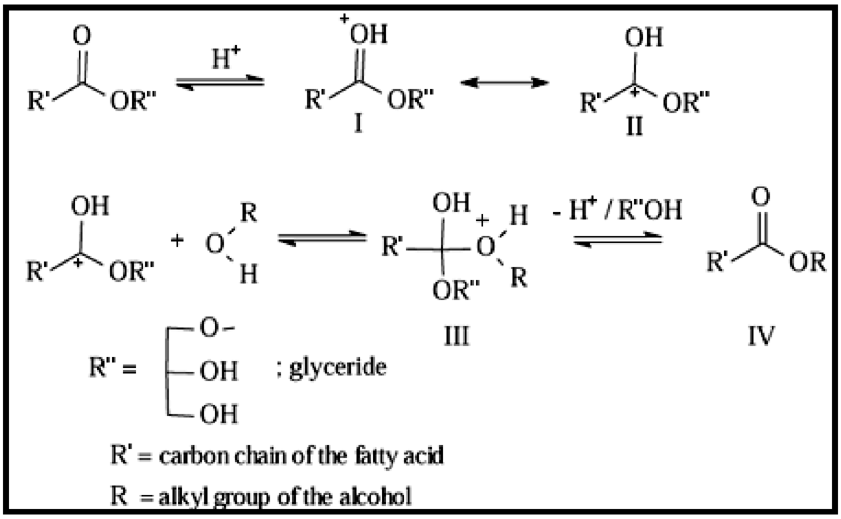


Figure 1.1: Mechanism of acid catalyzed transesterification of vegetable oil.

Removal of this alcohol also removes the water formed by the esterification reaction and allows for a second step of esterification or proceeding directly to alkaline – catalyzed transesterification. Note that the methanol-water mixture will also contain some dissolve oil and FFAs that should be recovered and reprocessed. Figure 1 shows a schematic diagram of the processes involved in biodiesel production from feedstock containing low levels of free fatty acids (FFA) (Gerpen, J.V., 2007).

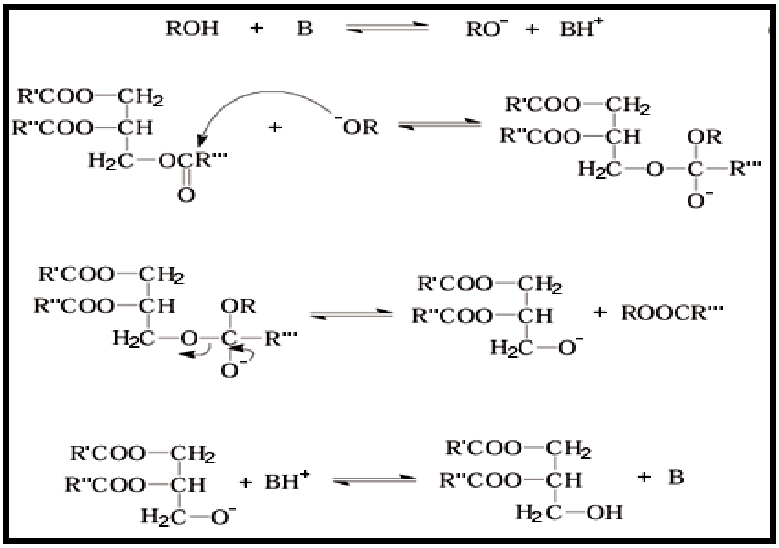


Figure 1.2: Mechanism of base – catalyzed transesterification of vegetable oils

The overall process is a sequence of three consecutive and reversible reactions which di- and monoglycerides are formed as intermediates. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol. Transesterification reactions are reversible and typically require excess methanol reactant to help push the equilibrium in the direction of the product biodiesel and glycerol.

Oils and fats are primarily water-insoluble hydrophobic substances of plant and animal origin and are made up of three moles of fatty acids and are commonly referred as triglycerides and one mole of glycerol. Fatty acids vary in carbon chain length and in the number of unsaturated bonds (double bonds). The fatty acids found in vegetable oils are summarized in Table 1.1. Table 1.2 shows typical fatty acid composition of common oil sources.

To obtain crude oil or fats, natural vegetable oils and animal fats were extracted using solvent or mechanical pressed. These usually contain free fatty acid phospholipids, sterols, water, odorants and other impurities. Even refined oils and fats contain small amounts of free fatty acid and water. The free fatty acid and water give significant effects on the transesterification reaction of glycerides using alkaline or acid catalyst.

They also interfere with the separation of fatty acid alkyl esters and glycerol because of soap formation in product.

1.5.1 Composition of Biodiesel

Biodiesel is mixture of fatty acid alkyl esters. If methanol is used as a reactant, it will be mixture of fatty acid methyl ester (FAME). Based on the feedstock, biodiesel has different proportions of fatty acid methyl esters. Most edibles oil and fats contain mainly fatty acids ranging from lauric acid (dodecanoic acid) to arachidic acid (eicosanoic acid). Besides the linear saturated fatty acids, branch fatty acids, mono-unsaturated. Di-unsaturated and higer unsaturated fatty acids can also occur (frank david column selection for the analysis of FAME). Table 1.3 shows the chemical composition of common fatty acids and their methyl esters present in the biodiesel.

Table 1.1: Chemical properties of vegetable oil on the basis of their fatty acid composition, % by weight (Ma 1999).

Vegetable Oil	**16:0**	**18:0**	**20:0**	**22:0**	**24:0**	**18:1**	**22:1**	**18:2**	**18:3**
Corn	11.67	1.85	0.24	0.00	0.00	25.16	0.00	60.60	0.48
Cottonseed	28.33	0.89	0.00	0.00	0.00	13.27	0.00	57.51	0.00
Cramble	2.07	0.70	2.09	0.80	1.12	18.86	58.51	9.00	6.85
Peanut	11.38	2.39	1.32	2.52	1.23	48.28	0.00	31.95	0.93
Rapeseed	3.49	0.85	0.00	0.00	0.00	64.40	0.00	22.30	8.23
Soybean	11.75	3.15	0.00	0.00	0.00	23.26	0.00	55.53	6.31
Sunflower	6.08	3.26	0.00	0.00	0.00	16.93	0.00	73.73	0.00
Jatropha	14.1	3.7	0.3	0.2	0.00	34.3	0.00	29.0	0.3

Table 1.2: Typical fatty acid composition-common oil source (Ma, 1999)

Fatty acid	**Soybean**	**Cottonseed**	**Palm**	**Lard**	**Tallow**	**Coconut**	**Jatropha**
Lauric	0.1	0.1	0.1	0.1	0.1	46.5	0.0
Myristic	0.1	0.7	1.0	1.4	0.8	19.2	0.1
Palmitic	0.2	20.1	42.8	23.6	23.3	9.8	14.1

Stearic	3.7	2.6	4.5	14.2	19.4	3.0	3.7
Oleic	22.8	19.2	40.5	44.2	42.4	6.9	34.3
Linoleic	53.7	55.2	10.1	10.7	2.9	2.2	29.0
Linolenic	8.6	0.6	0.2	0.4	0.9	0.0	0.3

Table 1.3: Chemical structures of common fatty acid and their methyl esters.

Fatty acid / Formula	Common acronym	Methyl ester / Formula
Palmitic acid / $C_{16}H_{12}O_2$	C16:0	Methyl palmitate / $C_{17}H_{34}O_2$
Stearic acid / $C_{18}H_{36}O_2$	C18:0	Methyl stearate / $C_{19}H_{38}O_2$
Oleic acid / $C_{18}H_{34}O_2$	C18:1	Methyl Oleate / $C_{19}H_{36}O_2$
Linoleic acid / $C_{18}H_{32}O_2$	C18:2	Methyl linileate / $C_{19}H_{34}O_2$
Linolenic acid / $C_{18}H_{30}O_2$	C18:3	Methyl linolenate / $C_{19}H_{24}O_2$

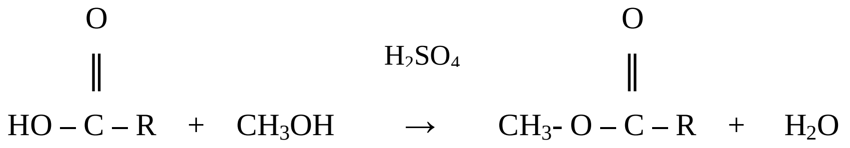
1.5.2 Mechanism of Esterification and Transesterification

Special treatment are required if the oil or fat contains significant amounts of FFAs. Used cooking oils typically contain 2-7% FFAs and animal fats contain from 5-30% FFAs. Some very low quality feedstock, such as trap grease, can approach 100% FFAs. When an alkali catalyst is added to this feedstock, the free fatty acids react with the catalyst to form a soap and water as shown in the reaction below:

$$\mathrm{HO-\overset{\overset{O}{\|}}{C}-R} \quad + \quad \mathrm{KOH} \quad \rightarrow \quad \mathrm{K^{+-}\,O-\overset{\overset{O}{\|}}{C}-R} \quad + H_2O$$

Fatty Acid Potassium Hydroxide Potassium Soap Water

Up to 5 % FFAs, the reaction can still be catalyzed with an alkali catalyst but additional catalyst must be added to compensate for that lost to soap. The soap created during the reaction is either removed with the glycerol or is washed out during the water wash. When the FFA level is above 5%, the soap inhibits separation of the glycerol from the methyl esters and contributes to emulsion formation during the water wash. For these cases, an acid catalyst such as sulfuric acid can be used to esterify the FFAs to methyl ester as shown in the following reaction:



$$HO-\overset{\overset{O}{\|}}{C}-R \quad + \quad CH_3OH \quad \xrightarrow{H_2SO_4} \quad CH_3-O-\overset{\overset{O}{\|}}{C}-R \quad + \quad H_2O$$

Fatty Acid Methanol Methyl ester Water

1.6 Objective of Study

To study on difference between lab scale production and pilot plant production of biodiesel production from Jatropha oil.

CHAPTER II

LITERATURE REVIEW

This chapter contains the literature cited in this study. Section 2.1 presents a brief history of scale up study on chemical processes. In section 2.2 is about the process of biodiesel briefly and in section 2.3 is about the Jatropha crude oil.

2.1 Scale up on chemical processes

2.1.1 Scale up

The term ‘scale up’ should not be understood only in the sense of increasing the dimensions while preserving similar systems. Often, the transposition of one system to another offers a better solution to a problem (for example, a pilot plant operating in up flow for an industrial unit operating in down flow). ‘ The development of an industrial process is a creative activity, which is aimed at finding and coordinating all the information and data required for the design, construction and start up of a new industrial unit, in order to guarantee an economically profitable operation’ (Trambouze et al. 1975).

The typical activity of process development work remains the pilot plant experiment. This investigation is necessary for one or more of the following reasons:

- The passage from laboratory apparatus to the industrial installation raises scale-up problems that are too complex to be solved without an experiment performed with components of intermediate size.
- The operating conditions must be investigated in a representative unit, in which the influence of oil the parameters, such as the type of feed, impurities, recycle, etc., can be taken into account.
- The study of long-term effects, such as catalyst, the activation, buildup of by-products or impurities, corrosion mechanisms, etc.
- The need to show potential customers an operating pilot plant to convince them of the value of the process and its operational character. This applies especially if the innovative character of the process is a special feature.
- The need to produce representative sample in sufficient quantities for various tests.

This list offers a glance at the essential characteristics of a pilot plant, and especially the requirements that a pilot plant has to meet to perform its role: the pilot plant must simultaneously be transposable or scalable and representative. A pilot plant must therefore be designed to account for these two requirements, while minimizing its complexity and size, which condition the cost of its construction.

However, this work can only be reasonably undertaken if a sufficiently clear idea has first been derived of the future industrial technology. As we pointed out, the success of a scale up depends on this first prospective phase. Based on the information obtained from laboratory experiments and from the literature, one can imagine an industrial unit whose size would correspond to the presumed need of the market. This means working out the details on paper, so as to compare different technological alternatives, to identify constraints or impossibilities, and finally to select the most interesting industrial flow sheet from the technical economic standpoints.

It is at this level that the type of reactor must be chosen, essentially based on the chemical reactions to be carried out, the phases present, and the industrially feasible technologies. In difficult situations, this choice may not be very clear, so that many possible technologies must be considered. Figure 2.1 shows the essential steps in process development for scale up.

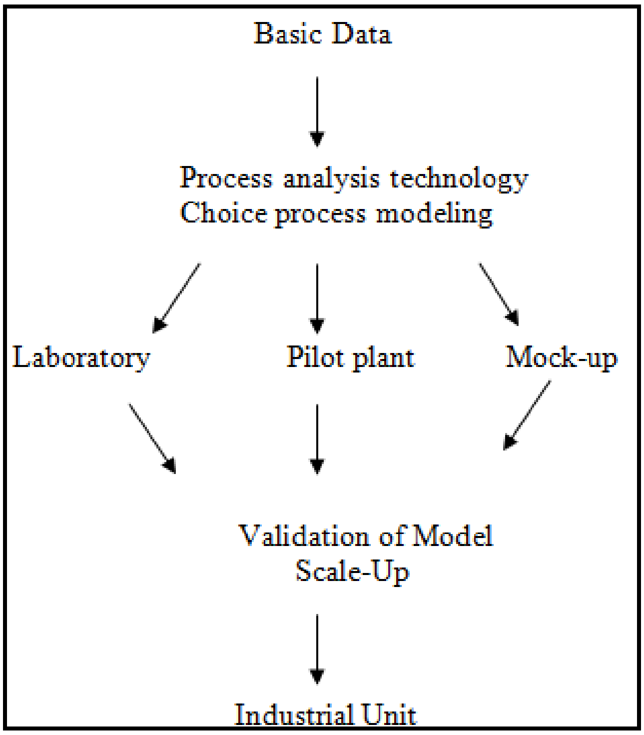


Figure 2.1: Essential steps in process development for scale up

2.1.2 Raw material

The source of the raw material is an important factor. The composition and, especially, the types of impurity and their concentrations depend on the source of the raw material. It is therefore important for the raw material intended for the pilot plant to be perfectly representative of the material to be used industrially.

In this respect, the use of model molecules, which are useful in conducting kinetic studies or constructing chemical models, is only acceptable if the model molecule is mixed within a representative feed. This makes it possible to investigate the inhibiting or catalytic effect of a given chemical species.

2.1.3 Utilities

Utilities generally include:

- Water (cooling water, de-ionized water)
- Steam at different pressures
- Electricity
- Service air (all-purpose compressed air)
- Instrument air
- Heat transfer fluids
- Inert gases
- Gases, liquid and solid fuels

For a pilot plant, the choice of a given form of utility is based essentially on ease of use, keeping in mind the representatives of the pilot plant.

Thus, for example, electricity is usually used in preference to steam or fuel to heat furnaces, reactors and various vessels. The recovery of the heat or cold is usually ignored, unless it is necessary to examine the problem in itself, in order to determine the transfer coefficients or fouling rates.

2.2 Biodiesel Process

The process for making fuel from biomass feedstock used in the 1800s is basically the same as that used today. Biodiesel from vegetable oils is not a new process. Conversion of vegetable oils or animal fats to the monoalkyl esters or biodiesel is called as transesterification. Transesterification of a vegetable was conducted as early as 1853, by scientists E. Duffy and J. Patrick, many years before the first diesel engine became functional. Life for the diesel engine began in 1893 when the famous German inventor Dr. Rudolf Diesel published a paper entitled ‘The theory and construction of a rational heat engine’.

2.2.1 Catalytic Transesterification

The catalyst is dissolved into methanol by vigorous stirring in reactor. The oil transferred into the biodiesel reactor, and then, the catalyst/alcohol mixture is pumped into the oil. The final mixture is stirred vigorously for 2h at 340 K in ambient pressure. A successful transesterification reaction produces two liquid phases; ester and crude glycerin. Crude glycerin, the heavier liquid, will collect at the bottom after several hours of settling. Figure 2.2 shows the schematic of transesterification process.

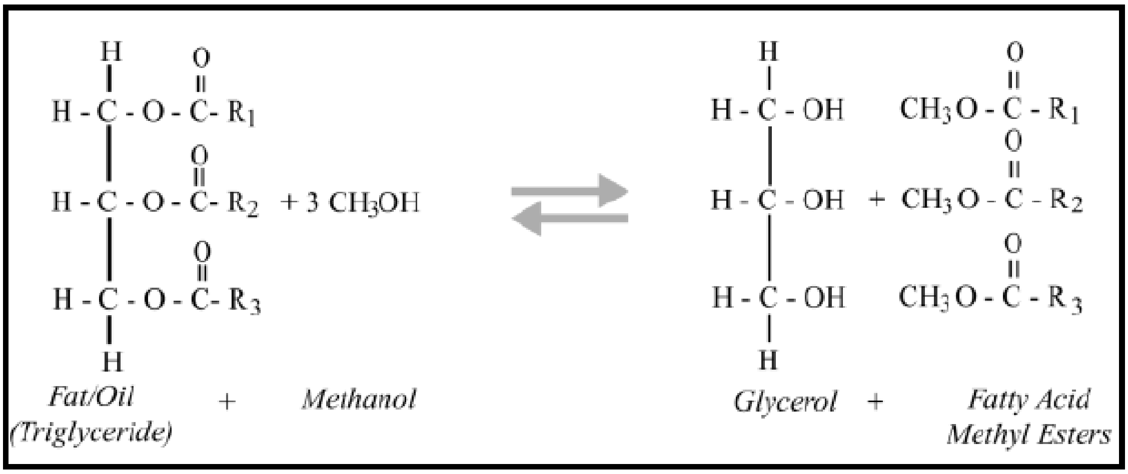


Figure 2.2: Schematic of transesterification process

2.2.2 Background of catalyst in biodiesel production

2.2.2.1 Base catalyst.

Transesterification can be catalyzed by acids, bases or enzymes. Among them, base catalysis is the most popular way and most often used commercially for biodiesel production owing to the high catalytic activity. Also, base catalysts are less corrosive than acidic compounds avoiding the necessity of expensive stainless steel as construction material (Zhang, Y., et al., 2003). Homogeneous base-catalyzed triglyceride transesterification has been thoroughly studied on the laboratory scale. The most common homogeneous basic catalysts used for lipids methanolysis include alkaline metal compounds, such as NaOH and KOH, CH3ONa and CH3OK, Na2CO3 and K2CO3. Alkaline metal alcoxides are the most effective catalysts for the transesterification reaction (Boocock, D. G. B. et al., 1996 and Freedman, B. et al., 1984). As low as 0.5 wt% of catalyst (by the weight of oil) can allow more than 98% biodiesel yielded in very short times. However, in practice, alkaline hydroxides (NaOH and KOH) are more favored because of their cheaper price and easier handling with respect to alkaline alcoxides.

Nevertheless, the use of hydroxides can be problematic considering the formation of water in the initial step of reaction as shows in Fig 1.3 (Schuchardt, U. et al., 1998). Water then hydrolyzes esters to FFAs and consequently causes saponification which in turn translates to catalyst deactivation and productivity loss. Alkaline carbonates can be an alternative choice in order to reduce saponification (Schuchardt, U. et al., 1998) but their use is limited by the weaker base strength.

2.2.2.5 Acid catalysis

Strong liquid mineral acids, such as sulfuric acid, phosphoric acid, hydrochloric acid, and others, are effective for the esterification of FF's with alcohol. They have also been used to catalyze transesterification of TGs to produce biodiesel. However, because of their much lower activity (by 3 orders of magnitude) (Freedman, B. et al. 1986) and much stronger corrosiveness than the base catalysts (Zhang, Y. et al. 2003), the acid catalysts have never enjoyed the same popularity for biodiesel synthesis as its counterpart in both the academic and industrial sectors. Only recently, given the versatility of acid catalysis to deal with FFAs, has its use been proposed as an economically viable alternative to base catalysis for biodiesel formation form low cost feedstock (Zhang, Y. et al. 2003).

2.2.2.3 Esterification of FFAs

As the most common way to synthesize organic esters of enormous practical importance, esterification of carboxylic acids with alcohols, indeed, represents a well-known category of liquid-phase reactions of considerable industrial interest. Simple Brønsted acid catalysts such as H2SO4, HCl, H3PO4 and arylsulfonic acid, are generally known to be effective for the direct esterification. Recently, given their noncorrosiveness and reusability, acidic ionic liquids are proposed as catalysts to offer a new and environmental benign approach for alkyl ester synthesis. Ionic liquids have the potential as dual solvent-catalyst in organic synthesis. And enormous variety of precursors is available to further tune their versatility making them more adapted to a specific reaction.

In most cases, related studies focus on the impacts of reaction parameters on the final free acidity of lipid feedstock without paying much attention to the reaction kinetics. Mainly using H2SO4 as catalyst, the pre-esterification of different lipid feedstocks with high FFA contents have been investigated. In accordance, oils with initial FFA contents up to 19% can be easily reduced to 1% or lower using 1-step reaction at 60^{o}C after short reaction time, regardless the origins of oils. The specific efficiency of a process is adjustable by varying operation parameters. For instance, the use of larger amounts of catalysts speeds up esterification rate therefore substantially shortening the necessitated reaction time. Also, higher catalyst concentration appears to favor a deeper FFA conversion before a reaction platform reaches (Ganeshpure, P. A. et al., 2007). However, excessive amounts of acid were observed to darken the ester products by inducing side reactions (Ramadhas, A. S. et al., 2005). Furthermore, the expedient range of H2SO4 can be interfered with by either the initial FFA content (Sendzikiene, E. et al., 2004) or methanol-to-oil molar ratio (Veljkovic, V. B. et al., 2006). Typically, catalyst concentration ranged between 1 and 2 wt% (with respect to oil) in academic studies using sulfuric acid.

2.2.2.4 Transesterification of Triglycerides

In contrast to the base-catalyzed biodiesel synthesis, much fewer studies have dealt with the use of acid catalysts in transesterification of lipid feedstock. The slow reaction rate has mainly been why it has fallen into disfavor. Indeed, the homogeneous acid-catalyzed transesterification follows a similar mechanistic route as the acid-catalyzed esterification, whereby the catalytic turnover is initiated by the activation of carbonyl carbon followed by nucleophilic attack of alcohol to form a tetrahedral intermediate (Lotero, E. et al., 2005, Schuchardt, U. et al., 1998). Disproportionate of this intermediate complex yields the alkyl monoester and diglyceride. This sequence is repeated twice to transform a triglyceride molecule to three alkyl monoesters and one glycerol as ultimate products. Lotero et al. [1] compared this acid-catalyzed mechanism to the base-catalyzed and pointed out that there is a crucial difference lying between them in the reaction initiation steps which mainly discriminate the catalytic efficiency: the formation of a weak and lump electrophilic species (in acid catalysis) vs. that of a strong and small nucleophile (in base catalysis).

2.3 *Jatropha curcas* L. seed oil for biodiesel production.

Jatropha curcas is a drought resistant shrub or tree belonging to the family Euphorbiaceae, as well a family of carrot and tapioca (Sirisomboon, P. et al., 2007).
Classification of *Jatropha curcas* is shown below:

Division	: Spermatopyta
Subdivision	: Angiospermae
Class	: Dicotyledonae
Ordo	: Euphorbiales
Family	: Euphorbieaceae
Genus	: Jatropha
Species	: *Jatropha curcas* Linn.

Jatropha cucras is well adapted to arid and semi-arid conditions and has low fertility and moisture demand. It can also grow on moderately sodic and saline, degraded and eroded soil (Sirisomboon, P. et al., 2007). The role of *J. curcas* as a substitute for diesel is very remarkable. Table 2.1, shows the major composition fatty acid of *Jatropha curcas L.* seed oil. It is non-edible oil being singled out for large-scale of plantation on wastelands. *J. curcas* plant can thrive under adverse condition. It requires very little irrigation and grows in all type of soils (from coastlines to hill slopes) (Deepak A., et al., 2007). Fig. 2.3 shows a typical *J.curcas* growing on rocks in mountain regions. The production of *J.curcas* seeds is about 0.8kg per square meter per year (R.K. Henning,Fighting)**.** The oil content of *J.curcas* seed ranges from 30% to 40% by weight and the kernel itself ranges from 45% to 60% (K.Pramanik, 2003 and J. B Kandpal, et al. 1995)**.** Fresh *J.curcas* is slow drying, odorless and colorless oil, but turns yellow after aging (K.Pramanik, 2003).

Many researchers have studied its potential for use as neat oil, as transesterified oil (biodiesel), or as a blend with diesel. The calorific value and cetane number of *Jatropha* oil are comparable to diesel, but the density is high. As the density of oil is high, on the whole, a significant improvement of the engine performance, emissions and combustion parameters can be achieved by properly optimizing the injector opening pressure, injection timing, injection rate and enhancing the swirl level when a diesel engine is operated with neat *J.curcas* oil (Narayan, R.J.et al., 2006).

Table 2.1: Fatty acid composition of crudes *Jatropha curcas* (H.J Berchmans et al. 2007)

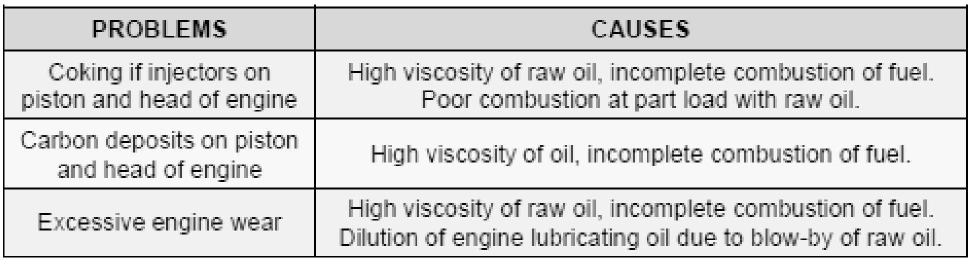
Fatty acid	Formula	Systematic name	Structure	wt%
Myristic	$C_4H_{28}O_2$	Tetradecanoic	14:0	0-0.1
Palmitic	$C_{16}H_{32}O_2$	Hexadecanoic	16:0	14.1-15.3
Palmitoleic	$C_{16}H_{30}O_2$	*cis*-9-Hexadecanoic	16:1	0-1.3
Stearic	$C_{18}H_{36}O_2$	Octadecanoic	18:0	3.7-9.8
Oleic	$C_{18}H_{34}O_2$	*cis*-9-Octadecenoic	18.1	34.3-45.8
Linoleic	$C_{18}H_{32}O_2$	*cis*-9, *cis*-12-Octadecedianoic	18:2	29.0-44.2
Linolenic	$C_{18}H_{30}O_2$	*cis*-6, *cis*-9-*cis*-12 Octadecatrienoic	18:3	0-0.3
Arachidic	$C_{20}H_{40}O_2$	Eicosanoic	20:0	0-0.3
Behenic	$C_{22}H_{44}O_2$	Docosanoic	22:0	0-0.2

Figure 2.3: *Jatropha curcas* L. seed oil plant on rocky substrate

Oil that is produce from *J. curcas* plant has a very high potential of being processes in alternative fuel. As a comparison, diesel fuel is a hydrocarbon containing 8-10 atom carbon per molecule. While, *J. curcas* oil contains 16-18 atom carbon per molecule of hydrocarbon which means the viscosity of *J. curcas* oil is much higher and the energy needed to burn as fuel is quite low.. Transesterification from *J. curcas* oil requires methanol (about 30% by volume of the vegetable oil methanol mixture) for making the methyl ester of vegetable oil.

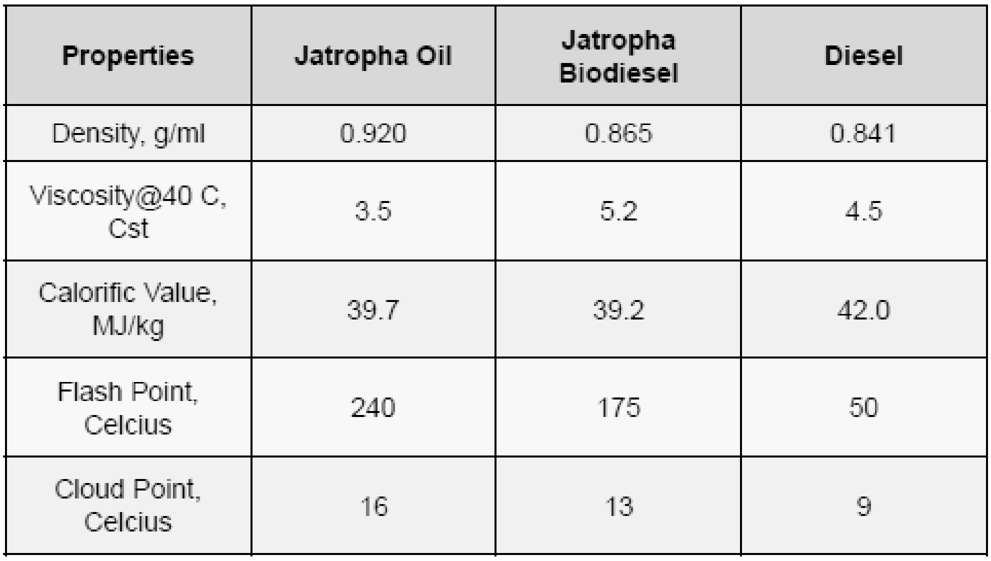
The production of fatty-acid methyl ester from vegetables oils and their use as diesel fuel have been well tested and evaluated in several European countries such as, Austria, France and Italy. Basically, standard biodiesel parameters are density, flash point, cetane number, kinematics viscosity, sulphated ash, iodine number and carbon residue. Table 2.2 shown below is the problems in use of Jatropha oil as fuel in diesel engine. Forson et al. used *J. curcas* oil and diesel blends in compression ignition engines and found its performance and emissions characteristic similar to tat of mineral diesel at low concentration of jatropha oil in blends. Pramanik tried to reduce viscosity of jatropha oil by heating it and also blending it with mineral diesel. Table 2.3 shows the fuel properties of Jatropha oil and its biodiesel.

Table 2.2 : The problems in use of Jatropha Oil as fuel in Diesel Engine



PROBLEMS	CAUSES
Coking if injectors on piston and head of engine	High viscosity of raw oil, incomplete combustion of fuel. Poor combustion at part load with raw oil.
Carbon deposits on piston and head of engine	High viscosity of oil, incomplete combustion of fuel.
Excessive engine wear	High viscosity of raw oil, incomplete combustion of fuel. Dilution of engine lubricating oil due to blow-by of raw oil.

Table 2.3: Fuel Properties of Jatropha Oil and its biodiesel



Properties	Jatropha Oil	Jatropha Biodiesel	Diesel
Density, g/ml	0.920	0.865	0.841
Viscosity@40 C, Cst	3.5	5.2	4.5
Calorific Value, MJ/kg	39.7	39.2	42.0
Flash Point, Celcius	240	175	50
Cloud Point, Celcius	16	13	9

2.3.1 The multi-uses of *Jatropha curcas* Plant

All parts of *J. curcas* can be used for a wide range of purpose. Exploitation of *J. curcas* is described by Openshaw, K., 2000**.** The tree itself has been used for erosion control, fire wood, as hedge plant and for plant protection. The bark is rich in tannin and also yields a dark blue dye. Leaves have been used for rearing of silkworm, in dyeing, medicine, and as an anti-inflammatory substance. Latex has medicinal, pesticide and mollusk control properties. It has been used for wound healing as protease has medicinal use. The flowers attract bees and thus the plant has a potential use in honey production. Seed have been used as insecticide, food/fodder (non-toxic varieties or when detoxified), seed oil for soap production, fuel, lubricant, insecticide, medicine and when mixed with iron oxide, they can be used in varnish. Seed cake is useful as fertilizer or in biogas production. Briquettes can be used as a fuel, nutraceuticals, or, after further processing, as fodder (non-toxic varieties or when detoxified), and seed shell are combustible. Fruits hulls are combustible, contain tannin and can be used as green manure and in biogas production. Lastly, the roots contain yellow oil with strong antihelminthic properties.

CHAPTER III

METHODOLOGY

3.0 Introduction

Scale up experiment was running on lab scale and pilot plant scale. The difference between lab scale and pilot plant scale is the value of capacity and production of biodiesel.

Two steps-catalyzed processes were adopted to prepare biodiesel from J.curcas seed oil. Two step-catalyzed which the first step is acid catalyzed to esterifies FFA followed by alkali catalyzed to complete the reaction was chosen over other reaction due to several reason, among them are;

- It requires low temperature and pressure reaction
- The reaction times short and low cost compared to other method.
- Acid catalyzed process, which requires extra step to convert FFA to methyl ester, thus avoiding soap.
- Alkali catalyzed is a direct biodiesel conversion reaction with no formation of intermediate compounds.
- The high FFA content (>1% 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 acid-catalyzed esterification of the oil is an alternative, but it is much slower than the base catalyzed transesterification reaction.

3.1 Experimental methodology

Figure 3.1 shows the flow chart methodology of biodiesel production in scaling up. The process started with small scale or bench scale, followed by large scale or pilot plant scale and analyze by GC analysis and yield of production.

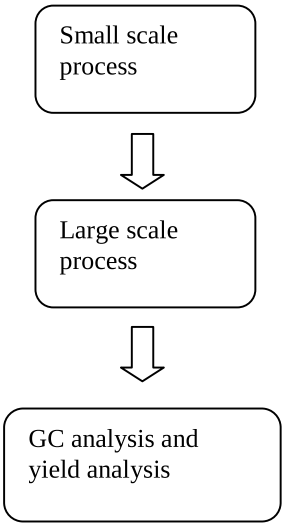


Figure 3.1: Flow chart methodology of biodiesel production in scaling up

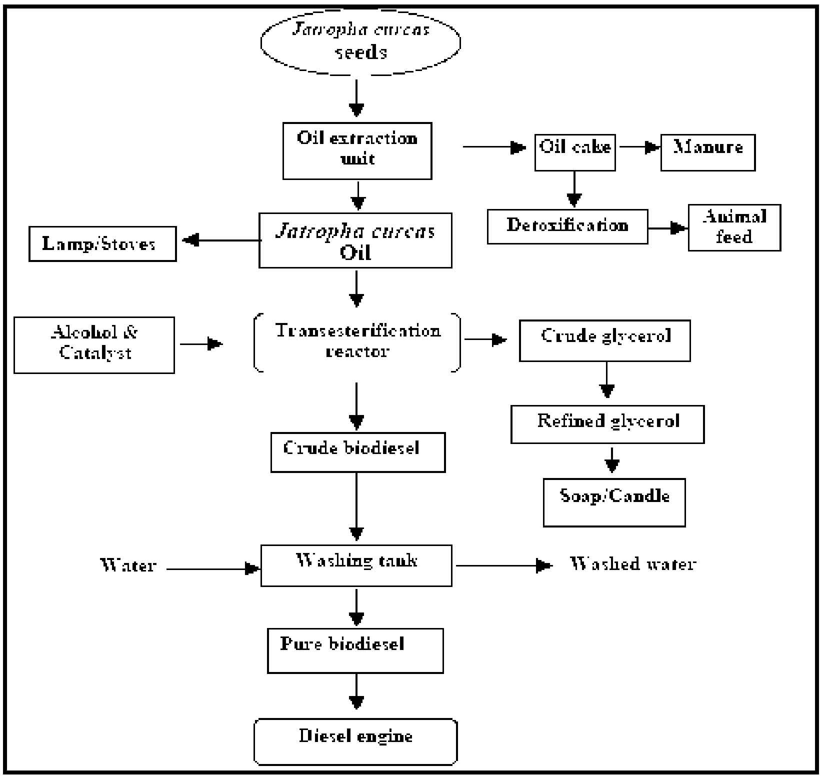


Figure 3.2: The overall process of the production biodiesel

3.1.1 Lab Scale

Esterification process.

50g of J.curcas oil was poured in the round bottom flask equipped with reflux condenser and heated at 65°C. The solution of concentration H_2SO_4 acid (1.0% based on the oil weight) in methanol was heated at 65°C and then added into the reaction flask once the oil achieve the desired temperature. The solution was heated and stirred to 2 hours reaction in 65 °C.

Base catalyzed transesterification

Firstly, the oil product that has been treated from the first step was poured into the reaction flask and heated at 65^oC. The solution of KOH and methanol were heated to 65^oC prior to addition and then added to the heated oil. The reaction mixture was heated and stirred again at 65^oC for 2h.

Recovery process

The solution was recovered by using rotary evaporator. The temperature was set on maximum which is below than 100 ^oC. The methanol and the water can be removed from the solution. The solution was formed in 2 layers which on the top is biodiesel and on the bottom is glycerol.

3.1.2 Pilot plant scale

Esterification process

15L of J.curcas oil was prepared and added into the reactor by using vacuum pump. The cooling water has to open, to operate the vacuum pump. J.curcas oil was heated in the reactor until 65 ^oC. The temperature was controlled on the reactor jacket temperature. 34L of Methanol and 1.5% of H2SO4 were prepared. When J.curcas oil was achieved 65 ^oC, the methanol and H2SO4 were added into the reactor by using vacuum pump to mix up with J.curcas oil. The stirrer was switched on to mix up well. The reaction was taking about 2 hours and the temperature 65 ^oC was controlled of the reactor jacket temperature.

Transesterification process

The first solution was heated until 65 ^{o}C. 34L of Methanol and 1.5% of Potassium hydroxide (KOH) were prepared. The mixture was added into the reactor by using vacuum pump. The stirrer was switched on and the solution was stirred until 2 hours in 65 ^{o}C. After 2 hours reaction, the stirrer was stopped and the temperature of jacket reactor was stopped after 30mins to settle down the solution by gravity.

Recovery process

The solution was entered into the recovery reactor. The temperature was set at 100 ^{o}C to separate the Methanol and water from the oil. After the process, there was 2 layers formed, on the top is biodiesel while on the bottom is glycerol.

3.2 Product analysis

3.2.1 Gas chromatography (GC/FID)

GC/FID was used to analyze the production of biodiesel in batch scale and in pilot plant scale product. A 30m x 250mm x 0.25μm.DB-Wax column was used for analyzing FAME in the product. Methyl palmitate and methyl stearate were used as the standard. 0.004g, 0.008g, 0.012g, 0.016g, and 0.020 of every standard and 10mL of Hexane were prepared for the standard. 0.015g of biodiesel production of every scale and 10mL of Hexane were prepared for analyzing the product. The oven of GC was held at the initial temperature 50^{o}C for 1min then ramped to the final temperature of 370^{o}C at a rate of 15^{o}C/min to 180^{o}C held for 1 min, 7^{o}C/min to 230^{o}C held for 0min, 10^{o}C/min to 370^{o}C held for 5 min, with total run time is of 35.81 min.

Fig. 1 Gas Chromatography (GC/FID)

3.2.2 Yield calculation

Yield calculation was determined by analyze the GC result. To find the conversion is:

$$\text{Conversion} = \frac{(\Sigma A - Aei)}{Aei} \times \left\{ \frac{(C_2 \times V)}{m} \times 100 \right\} \times \left[\frac{\Sigma\, m}{\Sigma V} \times 100 \right]$$

A = Area total (Pa.s)
Aei = Area sample (Pa.s)

$$\left\{ \frac{(C_2 \times V)}{\text{Mass}} \times 100 \right\} = \text{sample}$$

$$\left[\frac{\Sigma\, m}{\Sigma V} \times 100 \right] = \text{standard}$$

CHAPTER IV

Results and Discussion

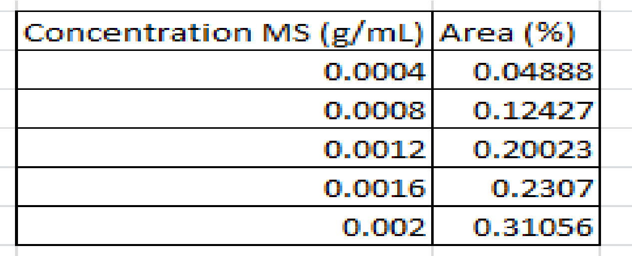
4.1 Introduction

This chapter presents the results of the production in bench scale and in pilot plant scale. The production of biodiesel was analyzed by using GC/FID analysis and also by calculating the yield. The parameters in bench scale process and in pilot plant scale process were same. The temperature 65 ^{o}C, the pressure 1atm, the ratio of methanol and oil is 2:1. From here, the difference between bench scale production and pilot plant scale production can be seen on the results formed.

4.2 GC/FID Analysis

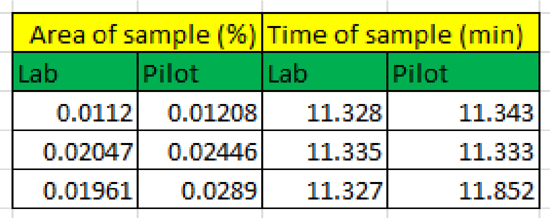
4.2.1 Methyl Stearate analysis

In Methyl Stearate analysis, the concentrations of the standard are 0.0004mg/mL, 0.0008mg/ml, 0.0012mg/ml, 0.0016mg/ml, and 0.0020mg/ml. The concentration of the sample is 0.0015mg/mL. From the peak of GC result, the Methyl stearate is around 11.3mins. From the sample result, we can determine the amount of every sample in methyl stearate standard. Table 4.1a shows the concentration of the standard and the area from GC analysis. Table 4.1b shows the area and time retention for every sample from GC result. Figure 4.1 shows the area of the standard and the sample versus the concentration of the standard graph.



Concentration MS (g/mL)	Area (%)
0.0004	0.04888
0.0008	0.12427
0.0012	0.20023
0.0016	0.2307
0.002	0.31056

Table 4.1a: Value of concentration and Area of Methyl Stearate



Area of sample (%)		Time of sample (min)	
Lab	Pilot	Lab	Pilot
0.0112	0.01208	11.328	11.343
0.02047	0.02446	11.335	11.333
0.01961	0.0289	11.327	11.852

Table 4.1b: Value of Area and Time Retention for every sample

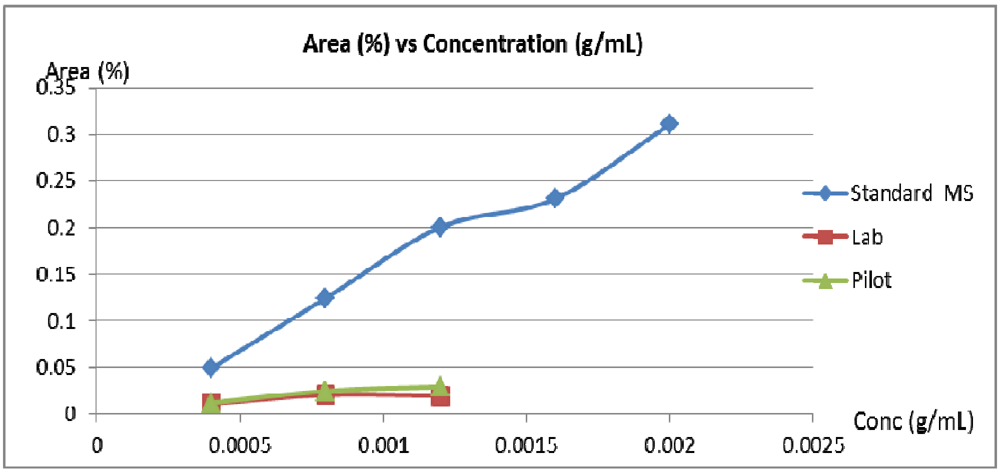
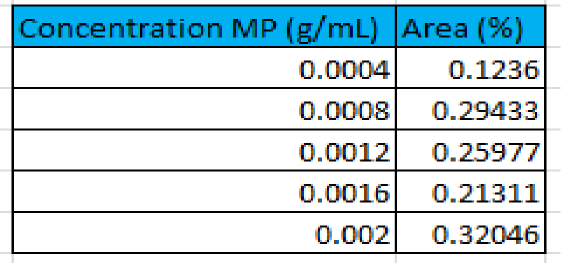


Figure 4.1: Area (%) vs Concentration (g/mL) graph

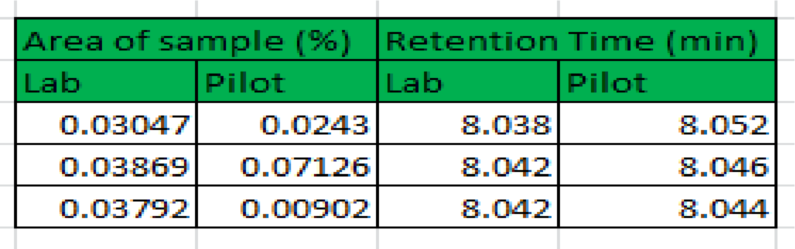
4.2.2 Methyl Palmitate analysis

In Methyl Palmitate analysis, the concentrations of the standard are 0.0004mg/mL, 0.0008mg/ml, 0.0012mg/ml, 0.0016mg/ml, and 0.0020mg/ml. The concentration of the sample is 0.0015mg/mL. From the peak of GC result, the retention time of Methyl palmitate is around 8mins. From the sample result, we can compare between the standard results. Table 4.2a shows the concentration of methyl palmitate and the area of the standard from the GC result. Table 4.2b shows the area and the retention time for every sample in bench scale and pilot plant scale. Figure 4.2 shows the area of the standard and the sample from the GC result versus the concentration of the standard graph.



Concentration MP (g/mL)	Area (%)
0.0004	0.1236
0.0008	0.29433
0.0012	0.25977
0.0016	0.21311
0.002	0.32046

Table 4.2a: Value of Concentration and Area of Methyl Palmitate



Area of sample (%)		Retention Time (min)	
Lab	Pilot	Lab	Pilot
0.03047	0.0243	8.038	8.052
0.03869	0.07126	8.042	8.046
0.03792	0.00902	8.042	8.044

Table 4.2b: Value of Area and Retention time for every sample

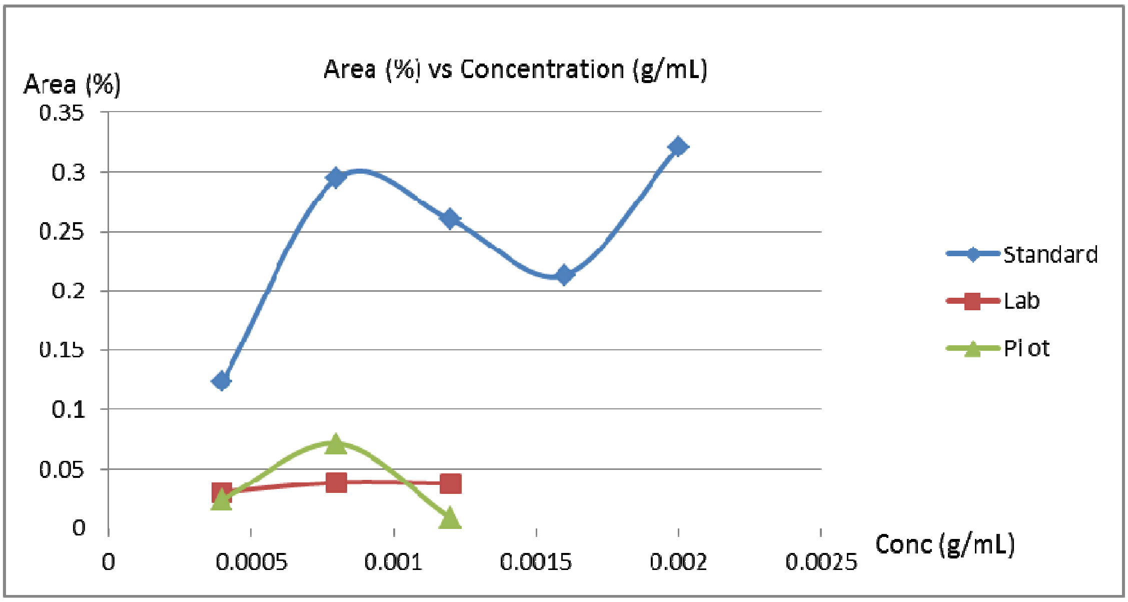


Figure 4.2: Area (%) vs Concentration (g/mL) graph.

4.3 Yield analysis

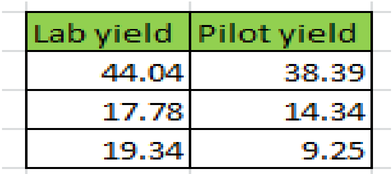
Yield analysis is to determine the conversion of the sample. To determine the yield, it is also from the GC analysis. From GC result, we can determine the conversion by using:

$$\text{Conversion} = \frac{(\Sigma A - Aei)}{Aei} \times \left\{ \frac{(C_2 \times V)}{m} \times 100 \right\} \times \left[\frac{\Sigma m}{\Sigma V} \times 100 \right] \qquad \text{(eq 4.1)}$$

A = Area total (Pa.s)
Aei = Area sample (Pa.s)
$\left\{ \frac{(C_2 \times V)}{\text{Mass}} \times 100 \right\}$ = sample

$\left[\frac{\Sigma m}{\Sigma V} \times 100 \right]$ = standard

From this equation, the yield for the lab and pilot plant can be determined. Table 4.3 shows the yield value of the production in lab scale and pilot plant scale. Figure 4.3 shows the graph of lab versus pilot yield.



Lab yield	Pilot yield
44.04	38.39
17.78	14.34
19.34	9.25

Table 4.3: Yield value of the production

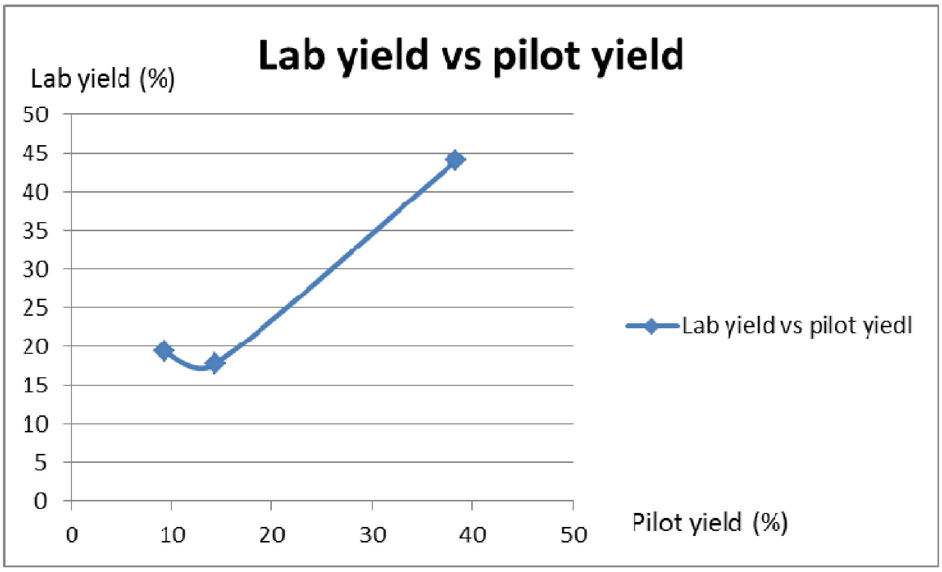


Figure 4.3: Lab scale yield (%) vs Pilot plant scale yield (%) graph

CHAPTER V

Conclusions and Recommendations

5.0 Introduction

The conclusions and recommendations are based on the experiment and the study. The conclusions are based on the objective of the project. The recommendations are to improve the conversion of the product and also to improve the process.

5.1 Conclusions

There are difference between lab scale production and pilot plant scale production and yield production because of the difference of the condition. In the lab scale the condition of temperature and reaction can be controlled but in the pilot plant scale, the temperature of the reaction hard to control. In the pilot plant scale, there are piping, vacuum pump, and valve to operate the reaction. In lab scale, there are no piping, vacuum pump and valve to operate the reaction. There are difference because of the condition in lab scale and pilot plant scale.

5.2 Recommendations

In scale up study should be more research, it is very important to commercial the chemical production. There are a lot of things that have to study such as the dimension, the design, the conversion of production in scale up, and others.

More detailed study should be carried out. The process of producing biodiesel in pilot plant should in continuous process, the conversion of the product will be high than the production in batch process.

Other alternative processes should be explored such as supercritical process. The supercritical methanol process is non-catalytic, simpler purification, has a lower reaction time and lower energy use. Therefore, the supercritical methanol method should be more effective and efficient than the common commercial process (Kusdiana and Saka,2004).

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