SCALE UP STUDY ON PRODUCTION OF BIODIESEL FROM JATROPHA CRUDE OIL

MOHD TAUFIQ BIN RASDI

UNIVERSITI MALAYSIA PAHANG

MOHD TAUFIQ BIN RASDI BACHELOR OF CHEMICAL ENGINEERING 2013 UMP

SCALE UP STUDY ON PRODUCTION OF BIODIESEL FROM JATROPHA CRUDE OIL

MOHD TAUFIQ BIN RASDI

A Thesis submitted in fulfilment of the requirements for the award of the degree of Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering UNIVERSITI MALAYSIA PAHANG

FEBRUARY 2013

"I 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	:
Name	: PROF. DATO' IR. DR. BADHRULHISHAM BIN ABDUL AZIZ
Date	:

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 in citied 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	: MOHD TAUFIQ BIN RASDI
Date	:

Special Dedication of This Grateful Feeling to...

My family, my supervisor, my fellow colleague and all faculty members

For All Your Care, Support, Best Wishes and Believe in Me.

ACKNOWLEDGEMENTS

Alhamdulillah, praise to Allah with His utmost love and blessings for giving me the guidance in accomplishing this Undergraduate Research Project. I would like to forward my sincere appreciation to my research project supervisor, Professor Dato' Ir. Dr. Badhrulhisham bin Abdul Aziz for his guidance and support eventhough he is Deputy Vice Chancellorof Universiti Malaysia Pahang, he still can do his work as a good supervisor. For my academic advisor, Madam Nor Khonisah binti Daud, your concern and faith in me during my studies is deeply appreciated.

Special thanks to my beloved campus, University Malaysia Pahang, especially to Faculty of Chemical & Natural Resources Engineering, for facilities provided during the execution of this research project. Thank you to all supporting staffs of the faculty and laboratory assistants especially to Mr. Zainal Abidin as Engineer Instructor that taught me in handling biodiesel production.

My appreciation also goes to all my fellow colleagues and friends, who have been here through all these years. Thanks for all point of views shared, and helping hands offered in this research project. Our moments and experiences will always be something sentimental to be remembered. Last but not least, to my family and friends. Thank you.

SCALE UP STUDY ON PRODUCTION OF BIODIESEL FROM JATROPHA CRUDE OIL

ABSTRACT

Scale up is a very important activity in designing new industrial plants especially in specialty or fine chemicals production. The purposes of this study is to study on different between laboratory scale production and pilot plant production of biodiesel from Jatropha crude oil and to establish correlations between laboratory scale and pilot plant scale for construction of commercial plant. Transesterification process used KOH as a catalyst. The optimum quantity of methanol, catalyst KOH, reaction temperature and reaction time required for the transesterification of Jatropha oil were conducted by varying them. Then, the optimized conditions from laboratory scale were used in pilot plant scale. From this study, it was found that for laboratory scale and pilot plant scale, there are some differences in the value of the final yield. The difference of value of yield between the laboratory scale and pilot plant run was caused by several factors such as handling, operating conditions and others.

KAJIAN MENAIK SKALA MENGENAI PENGHASILAN BIODIESEL DARIPADA MINYAK JARAK

ABSTRAK

Menaik skala adalah satu aktiviti yang sangat penting dalam membina kilang industri baru terutama dalam pengeluaran bahan kimia khusus atau kecil. Tujuan kajian ini adalah untuk mengkaji perbezaan antara pengeluaran berskala makmal dan pengeluaran berskala pilot plant dalam pengeluaran biodiesel daripada minyak mentah Jatropha dan untuk mewujudkan hubungan antara skala makmal dan skala pilot plant bagi pembinaan kilang komersial. Proses pengtranesteran menggunakan KOH sebagai pemangkin. Kuantiti optimum untuk metanol, pemangkin KOH, suhu tindak balas dan masa tindak balas yang diperlukan untuk pengtranesteran minyak Jatropha telah dijalankan dengan mengubah kuantiti dan keaadaan parameter tersebut. Kemudian, keadaan yang telah dioptimumkan dari skala makmal telah digunakan dalam skala pilot plant. Daripada kajian ini, didapati bahawa untuk skala makmal dan skala loji perintis, terdapat beberapa perbezaan dalam nilai hasil akhir.Perbezaan nilai hasil antara skala makmal dan skala pilot plant adalah disebabkan oleh beberapa faktor seperti pengendalian, keadaan operasi dan lain-lain.

TABLE OF CONTENTS

	DECLARATION	ii
	DEDICATION	iv
	ACKNOWLEDGEMENT	v
	ABSTRACT	vi
	ABSTRAK	vii
	TABLE OF CONTENT	xi
	LIST OF TABLES	xii
	LIST OF FIGURES	xiii
	LIST SYMBOLS	XV
	LIST OF ABBREVIATIONS	xvi
CHAPTER 1	INTRODUCTION	1
	1.1 Research Background	1
	1.2 Problem Statement	4
	1.3 Research Objectives	5
	1.4 Scope of Study	5
	1.5 Significance of Study	6
CHAPTER 2	LITERATURE REVIEW	7
	2.1 Scale Up On Chemical Process	7
	2.1.1 Laboratory Studies	9
	2.1.2 Pilot Plant Studies	9
	2.2 Vegetable Oils as a Diesel Substitute	12

		2.2.1	Jatropha Curcas Linnaeus	12
	2.3	Biodie	esel and Its Properties	16
		2.3.1	Background of Biodiesel	16
		2.3.2	Free Fatty Acids (FFAs)	18
		2.3.3	Alcohols	19
		2.3.4	Catalysts	19
	2.4	Chem	ical Reactions	20
		2.4.1	Pretreatment of Free Fatty Acids	20
		2.4.2	Transesterification	22
			2.4.2.1 Mechanism of Transesterification	23
			2.4.2.2 Alkali Catalysed Transesterification	25
			2.4.2.3 Acid Catalysed Transesterification	28
	2.5	Main	Factors Affecting Yield of Biodiesel	31
		2.5.1	Mole Ratio of Alcohol To Oil	31
		2.5.2	Concentration of Catalyst	32
		2.5.3	Reaction Temperature	33
		2.5.4	Reaction Time	34
	2.6	Econo	mic Aspect of Biodiesel	35
	2.7	Enviro	onmental Consideration	37
CHAPTER 3	ME	THOD	OLOGY	39
	3.1	Resea	rch Design	39
	3.2	Chem	icals	39
	3.3	Equip	ments	40
		3.3.1	Laboratory Scale	40
		3.3.2	Pilot Plant Scale	41
		3.3.3	Rotary Evaporator	42
			=	

		3.3.4	Gas Chromatography	43
	3.4	Gener	al Flow of Methodology	44
	3.5	Labor	atory Scale Procedure	46
		3.5.1	Pretreatment	46
		3.5.2	Transesterification	46
		3.5.3	Separation	47
		3.5.4	Purification	47
	3.6	Pilot I	Plant Scale Procedure	48
		3.6.1	Pretreatment	48
		3.6.2	Transesterification	49
		3.6.3	Separation	49
		3.6.4	Purification	50
	3.7	Produ	ct Analysis	50
		3.7.1	Gas chromatography	50
		3.7.2	Yield Calculation	51
CHAPTER 4	RE	SULT A	AND DISCUSSION	52
	4.1	Introd	uction	52
	4.2	Labor	atory Scale	53
		4.2.1	Effect of Methanol Amount	53
		4.2.2	Effect of KOH Concentration	55
		4.2.3	Effect of Reaction Temperature	57
		4.2.4	Effect of Reaction Time	59
	4.3	Pilot I	Plant Scale	61
CHAPTER5	CO	NCLUS	SION AND RECOMMENDATIONS	62
	5.1	Concl	usion	62
	5.2	Recor	nmendations	63

RE	FERENCES	64
AP	PENDIX	68

LIST OF TABLES

PAGE

TABLE 2.1	Fatty acid composition for different vegetable oils	14	
TABLE 2.2	Oil content and production of non-edible oil seeds	14	
TABLE 2.3	Composition and characteristics of Jatropha curcas oil	15	
TABLE 2.4	Fuel properties of methyl esters from different oils	17	
	Alkali-catalysed transesterification of Jatropha curcas oil	20	
TADLE 2.5	with optimized reaction variables	28	
TABLE26	Acid-catalysed transesterification of Jatropha curcas oil	31	
TABLE 2.0	with optimized reaction variables	51	
TABLE 2.7	Emission comparison of biodiesel and diesel	38	
TABLE 4.1	Variation on methanol and biodiesel yield percentage	53	
ΤΑΡΙΕΛΟ	Variation in KOH concentration and biodiesel yield	55	
TADLE 4.2	percentage		
TABLE 13	Variation in reaction temperature and biodiesel yield	57	
TADLE 4.5	percentage	51	
TABLE 4.4	Variation in reaction time and biodiesel yield percentage	59	
ΤΔΒΙΕΛ5	Optimized condition and biodiesel yield percentage in pilot	61	
TADLE 4.J	plant scale		

LIST OF FIGURES

PAGE

FIGURE 2.1	The major steps in process development for scale up	8	
FIGURE 2.2	Jatropha curcas Linnaeus	12	
FIGURE 2.3	Mechanism of alkali-catalysed transesterification	25	
FIGURE 2 4	Mechanism of acid-catalysed transesterification of	30	
1100KE 2.4	vegetables oils	50	
FIGURE 2.5	General cost breakdown of biodiesel prediction	35	
FIGURE 3.1	Biodiesel laboratory scale reactor	40	
FIGURE 3.2	Biodiesel pilot plant reactor	41	
FIGURE 3.3	Lab scale rotary evaporator	42	
FIGURE 3.4	Gas chromatography	43	
FIGURE 3.5	Flow chart methodology of biodiesel production in	11	
1100KE 3.3	scaling up	44	
FIGURE 3.6	Simplified process flow chart of alkali-catalyzed	45	
1100KE 3.0	biodiesel production	45	
FIGURE 4.1	Variation in methanol amount vs. biodiesel yield	53	
1100KL 4.1	percentage	55	
FIGURE 4 2	Variation in KOH concentration vs. biodiesel yield	55	
1100101 1.2	percentage	55	

FIGURE 4.3	Variation in reaction temperature vs. biodiesel yield		
	percentage	57	
FIGURE 4.4	Variation in reaction time vs. biodiesel yield	50	
	percentage	57	
FIGURE A.1	Samples with various of parameters	68	
FIGURE A.2	Samples after transesterification	69	
FIGURE A.3	Failed and successful sample after water washing	69	

LIST OF SYMBOLS

A	Area Total
Aei	Area Sample
L	Liter
V	Volume
g	Gram
kg	Kilogram
min	Minute
h	Hour
°C	Degree Celsius

LIST OF ABBREVIATIONS

AR	Analytical Reagent
B100	Pure Biodiesel
CCRD	Central Composite Rotatable Design
FFA	Free Fatty Acid
GC	Gas Chromatography
H_2SO_4	Sulphuric Acid
КОН	Potassium Hydroxide
РАН	Polycyclic Aromatic Hydrocarbons
RSM	Response Surface Methodology

CHAPTER 1

INTRODUCTION

1.1 Research Background

During the research and development of a new chemical process, one of the problems is that merits close attention and often proves to be problematic is the scaling up the reactors. This is especially true of the biodiesel industry, which is characterized by unique gigantism that enables to produce and place products on market at relatively low prices, environmental friendly and without or less competition. The focus here is specifically on the chemical process found in the biodiesel industry. However, the problems are similar for material conversion processes, and the methodology presented can therefore apply equally well to the chemical and biodiesel industries.(Lu et al., 2009; Tiwari, et al., 2007)

Biodiesel is of recent growing interest recently and has been strongly recommended as a substitute for petroleum diesel. Biodiesel can be blended with petroleum diesel as it has similar characteristics with lower hazardous exhaust emissions

Biodiesel is able biological sources such as vegetable oils and animal fats. The oils from vegetable crops and animal fats are extracted or processed to obtain the crude oil. It usually contains free fatty acids, phospholipids, sterols, water, odorants and other impurities. The free fatty acids and water contents have significant negative effects during the transesterification reaction of glycerides with alcohols using alkali or acid catalysts since they causes soap formation, consume catalysts and reduce its effectiveness and result in a lower conversion (Shuit, Lee, Kamaruddin, & Yusup, 2010).

The most important aspects of biodiesel production to ensure trouble free operation in diesel engines are: Complete transesterification reaction, removal of glycerin, removal of catalyst, removal of alcohol, and removal of free fatty acids. These parameters are all specified through the biodiesel standard, ASTM D 6751. This standard identifies the parameters the pure biodiesel (B100) must meet before being used as a pure fuel or being blended with petroleum based diesel fuel. Biodiesel, B100, specifications (ASTM D 6751–02 requirements).

Many researchers have been undertaken on vegetable oils as a source for diesel fuel which includes palm oil, soybean oil, sunflower oil, coconut oil, and so on. Jatropha curcas, a non-edible oil-bearing and drought-hardy shrub with ecological advantages, belonging to the Euphorbiaceae family, was found to be the most appropriate renewable alternative source of biodiesel.

A catalyst is usually used to improve and enhance the reaction rate so that the reaction can be completed in a shorter reaction time. Alkali-catalysed is preferred in industrial process. Transesterification of vegetable oils using methanol and alkali-catalysed has the advantages such as short reaction time and relatively low temperature can be used with only small amount of catalyst and with little darkening of colour of the oil.

According to, biodiesel production from high free fatty acid oil needs a two-step transesterification process which is acid esterification followed by alkali transesterification to get high biodiesel yield. The most important variables which influence the transesterification reaction are reaction temperature, ratio of alcohol to vegetable oil, catalyst mixing intensity and purity off reactant. Yield of biodiesel is affected by molar ratio, moisture and water content, reaction temperature, stirring specific gravity and so on.

1.2 Problem Statement

The starting point generally consists of laboratory results that concern a chemical transformation whose translation into economic gain appears viable. Tons or millions of tons of raw materials industrially are treated in process production development 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. To achieve the neraest conversions, yields and selectivity in production of biodiesel from Jatropha oil is the problem to reproduce the laboratory results on a large scale. In some cases, it possibly improves 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 operation in producing biodiesel from Jatropha oil. The price of biodiesel is much higher compare to conventional diesel makes it is less chosen by the customer. Thus the aim of this study is to produce biodiesel as diesel substitute with minimum cost with potential to be commercialized.

1.2 Research Objectives

The main objective of this study is to study on different between laboratory scale production and pilot plant production of biodiesel from Jatropha oil. In addition, to establish correlations between laboratory scale and pilot plant scale for construction of commercial plant.

1.3 Scope of Study

- I. Study the effect of ratio of alcohol to vegetable oil on biodiesel yield.
- II. Study the effect of concentration of catalyst and reaction time on biodiesel yield.
- III. Study the effect of reaction temperature on biodiesel yield.

1.4 Significance of Study

Scale up is a very important activity in designing new industrial plants especially in specialty or fine chemicals production. From this study, a pilot plant of biodiesel production can be design based on the parameters and the important variables that used on bench or laboratory scale in order get the maximum biodiesel yield. The optimum conditions can be used in large-scale or pilot plant production to reduce the cost of production.

CHAPTER 2

LITERATURE REVIEW

2.1 Scale Up on Chemical Process

One of the job in which chemical engineer's is involved is the scale-up of laboratory experiment to pilot plant operation or to full-scale production. In the past, a pilot plant would be designed based on laboratory data. However, owing the high cost of a pilot plant-study, this is step is beginning to be surpassed in many instances by designing a full scale plant from the operation of laboratory-bench-scale unit called microplant. To make this jump successfully requires a thorough understanding of the chemical kinetics and transport limitations. 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). Figure 2.1 shows the procedure described and identifies the major steps in process development for scale up.



Figure 2.1 The major steps in process development for scale up.

2.1.1 Laboratory Studies

In laboratory-type experiments, in which 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 the laboratory, a series of measurement can be taken concerning all the mechanisms that are independent of size. This applies in particular to everything related to thermodynamics and chemical kinetics. Moreover, a good number of physical quantities involved in the model, such as densities, specific heats, phase equilibrium, viscosities and more, must be measured through the interval of operating conditions of the process.

2.1.2 Pilot Plant Studies

A pilot plant is an experimental rig, at least part of which displays operations representative of the part corresponding to it in the industrial plant. Representative operation implies operation that is identical or transposable by using a mathematical model of this part of unit. 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.

The pilot plant can often be small, because this is not where the scale up data is sought. Hence, its size can be selected both in accordance with certain material constraints and to minimize the total cost of the operation. At this stage, note that the term "scale up" does not correspond exclusively to a change in size of the equipment achieved by multiplying characteristics dimensions by factor greater than one.

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 byproducts 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.

A pilot plant must 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 pointed out, the success of a scale up depends on this first prospective phase. 2.2 Vegetable Oils as a Diesel Substitute

2.2.1 Jatropha Curcas Linnaeus



Figure 2.2 Jatropha curcas Linnaeus

Jatropha curcas is a drought-resistant tree belongs to the Euphorbiaceae family, which is cultivated in Central and South America, South-east Asia, India and Africa. It is easy to establish, grows almost everywhere even on gravelly, sandy and saline soils. It produces seeds for 50 years with a high oil content of about 37% or more. Among

various oil bearing seeds, Jatropha curcas has been found more suitable for biodiesel production as it has been developed scientifically to give better yield and productivity (Jain & Sharma, 2010). This non-edible oil is explored as a source for biodiesel production without compromising the food industry (Divakara, Upadhyaya, Wani, & Gowda, 2010).

In addition, the oil percentage and the yield per hectare are important parameters in selecting the potential renewable source of fuel. Table 2.1 shows the fatty acid composition for different vegetable oils Production of non-edible oil seeds and the percentage of oil content are given in Table 2.2. Non-edible oils are not suitable for human consumption because of the presence of some toxic components in the oils. Therefore, Jatropha oil is considered a non-edible oil due to the presence of these toxic phorbol esters (Leung, Wu, & Leung, 2010; Shah & Gupta, 2007).

Fatty acid	Jatropha oil	Pongamia (Karanja oil)	Sunflower oil	Soybean oil	Palm oil
Lauric (C ₁₂ /0)	-	-	0.5	-	-
Myristic (C14/0)	-	-	0.2	0.1	-
Palmitic (C16/0)	14.2	9.8	4.8	11.0	40.3
Palmitoleic (C16/1)	1.4	-	0.8	0.1	
Stearic (C18/0)	6.9	6.2	5.7	4.0	3.1
Oleic (C18/1)	43.1	72.2	20.6	23.4	43.4
Linoleic (C18/2)	34.4	11.8	66.2	53.2	13.2
Linolenic (C18/3)		1	0.8	7.8	_
Arachidic (C20/0)	-	-	0.4	0.3	-
Behenic (C22/0)	-		-	0.1	
Saturates (%)	21.1	16.0	11.6	15.5	43.4
Unsaturates (%)	78.9	84.0	88.4	84,5	56,6

Table 2.1 Fatty acid composition for different vegetable oils(Source: Sarin, et al., 2007)

Table 2.2 Oil content and production of non-edible oil seeds(Source: Singh, et al., 2010)

Species	Oil fraction (%)	Seed yield (×10 ⁶ tones/year)	Oil yield (tones/ha/year) 2.0-3.0	
Jatropha	50-60	0.20		
Mahua	35-40	0.20	1.0-4.0	
Pongamia (Karanja)	30-40	0.06	2.0-4.0	
Castor	45-50	0.25	0.5-1.0	
Linseed	35-45	0.15	0.5-1.0	
Others	10-50	0.50	0.5-2.0	

The oil from the seeds has valuable properties such as a low acidity, good stability as compared to soybean oil, low viscosity as compared to castor oil and better cold properties as compared to palm oil. Besides, Jatropha oil has higher a cetane number compared to diesel which makes it a good alternative fuel with no modifications required in the engine (Tapanes, Aranda, Carneiro, & Antunes, 2008). However, most

non-edible oils contain a high level of free fatty acids (FFA) which is undesirable as it lowers the yield of biodiesel.

Since Jatropha oils consist of mainly oleic and linoleic acids which are unsaturated fatty acids, the biodiesel produced has desirable good low temperature properties. Although Jatropha oil also has high free fatty acid content, methods to overcome this high FFA are well developed. Thus, Jatropha curcas oil has been highlighted as a potential biodiesel feedstock among the nonedible oils. Table 2.3 tabulates the composition and characteristics of Jatropha curcas oil.

Characteristic	Range	
Specific gravity (g cm ⁻³)	0.860-0.933	
Calorific value (MJ kg ⁻¹)	37.83-42.05	
Pour point (°C)	-3	
Cloud point (°C)	2	
Flash point (°C)	210-240	
Cetane value	38.0-51.0	
Saponification number (mg g ⁻¹)	102.9-209.0	
Viscosity at 30 °C (cSt)	37.0-54.8	
Free fatty acids % (kg kg ^{-1} × 100)	0.18-3.40	
lodine number (mgl g ⁻¹)	92.0-112.0	
Acid number (mgKOH g ⁻¹)	0.92-6.16	

Table 2.3 Composition and characteristics of Jatropha curcas oil(Source: Achten, et al., 2008)

2.3 Biodiesel and Its Properties

2.3.1 Background of Bidiesel

One hundred years ago, Rudolf Diesel tested vegetable oil as fuel for his engine (Shay, 1993). With the advent of cheap petroleum, appropriate crude oil fractions were refined to serve as fuel and diesel fuels and diesel engines evolved together. In the 1930s and 1940s vegetable oils were used as diesel fuels from time to time, but usually only in emergency situations.

Biodiesel stands for a variety of ester based oxygenated fuels derived from renewable biological sources. In other words, biodiesel refers to a vegetable oil or animal fat-based diesel fuel consisting of long-chain alkyl (methyl, ethyl or propyl) esters or alkyl esters of fatty acids. It is a non-toxic, biodegradable and renewable fuel which can be used in compression ignition engines with little or no chemical modifications with significantly lower emissions than petroleum-based diesel when it is burned.

In addition, it does not contribute to the increase in carbon dioxide levels in the atmosphere and thus minimizes the intensity of the greenhouse effect. In addition, biodiesel is better than diesel fuel in terms of its properties such as sulphur content, flash point, aromatic content and biodegradability (Demirbas, 2005; Patil & Deng, 2009). Table 2.4 represents the fuel properties of methyl esters (biodiesel) from various plant based oils.

Properties	Jatropha methyl ester	Karanja methyl ester	Canola methyl ester	Corn methyl ester	Biodiesel standard ASTM D 6751-02
Specific gravity	0.86-0.88	0.88-0.89	0.88-0.90	0.88-0.89	0.87-0.90
Viscosity (mm ² /s)	2,35-2,47	5.52-5.79	2,56-2,84	2.45-2.56	1.9-6.0
Calorific value (MJ/kg)	39,65-41,63	37.8-39.69	44.65-44.93	44,92-45,06	-
Acid value (mg/KOH/g)	0.61-0.66	0.72-0.76	-	-	0.8 max
Cetane number	60,74-63.27	59,68-60,90	55.90-56.10	58.37-59.00	47 min
Pour point ("C)	-6 to 2	-3 to -1	4 to -1	-5 to -2	-15 to 10

Table 2.4 Fuel properties of methyl esters from different oils(Source: Patil, et al., 2009)

Although at present biodiesel cannot entirely replace petroleum-based diesel fuel, this alternative fuel is becoming increasingly important due to diminishing petroleum reserves that leads to a rise in petroleum prices and the environmental consequences of exhaust gases from the petroleum-fuelled engines (Berchmans & Hirata, 2008; Leung, et al., 2010).

2.3.2 Free Fatty Acids (FFAs)

A fatty acid is carboxylic acid with a long aliphatic tail (chain), which is either saturated or unsaturated. Fatty acid are usually derives from triglycerides or phospholipids. When they are not attached to others molecules, they are known as "free fatty acids".

The free fatty acids (FFAs) and moisture content have negative impacts on the transesterification of glycerides with alcohol when an alkali catalyst is used. High FFA content is unfavourable in an alkali-catalysed transesterification reaction because the FFA will react with the catalyst to form soap and the separation of products will be extremely difficult, resulting in a lower yield of biodiesel. The Jatropha curcas oil quality will deteriorate due to improper handling and storage. Improper handling and exposure of the oil to atmospheric air and sunlight contributes to a rise in FFA concentration (Berchmans & Hirata, 2008).

Crude Jatropha oil contains about 14% of FFA, which is far beyond the 1% limit for promoting transesterification reactions to occur using an alkaline catalyst (Tiwari, et al., 2007). It has been reported that transesterification will not occur if the FFA content in the oil is above 3% (Patil & Deng, 2009). Many pretreatment methods have been
proposed and applied, including steam distillation, extraction by alcohol and esterification by acid catalysts.

2.3.3 Alcohols

Alcohols are any organic compounds which have a hydroxyl functional group bonded to other carbons or hydrogen atoms having. Examples are methanol, ethanol, propanol and butanol. Methanol and ethanol are used most frequently. However, methanol is the most preferable because of its low cost and its physical and chemical advantages as polar and short chain alcohol (Demirbas, 2005). Methanol can also react with triglycerides quickly and easily dissolve the alkali catalyst.

2.3.4 Catalysts

A catalyst is usually used to improve and enhance the reaction rate so that the reaction can be completed in a shorter reaction time. Several catalysts have been investigated for the purpose of transesterification by many researchers. Examples are magnesium, calcium oxides and carbonates of basic and acidic macro-reticular organic resins, alkane alumina, phase transfer catalysts, sulphuric acids, p-toluene sulphonic acid

and dehydrating agents as a co-catalyst. However, basic catalysts are usually favored over acid catalysts because of the higher reactivity and the milder process conditions such as the lower temperature required (Georgogianni, Katsoulidis, Pomonis, Manos, & Kontominas, 2009).

2.4 Chemical Reactions

2.4.1 Pretreatment of Free Fatty acids

Pretreatment process called esterification of FFA with methanol in the presence of acidic catalysts is the most commonly applied method because the process is simple and acid catalysts will utilize the free fatty acids in the oil and convert into biodiesel (Leung, et al., 2010). Much research work has been reported for the successful pretreatment of the high FFA of Jatropha oil.

(Patil & Deng, 2009) have achieved a high yield of biodiesel from Jatropha curcas oil with pretreatment conditions using a methanol to oil ratio of 6:1, 0.5% (v/v) of H_2SO_4 at 40°C after 120 min. The FFA content of crude Jatropha oil was also reduced successfully to less than 1% with a 60% w/w methanol to oil ratio in the presence of

1% w/w of H₂SO₄ (based on weight of oil) as an acid catalyst in a 1 h reaction at 50°C (Berchmans & Hirata, 2008).

(Azhari, Faiz, Yunus, Ghazi, & Yaw, 2008) have conducted an optimization study to lower the FFA content of crude Jatropha oil via an esterification process using H_2SO_4 as a catalyst. The final FFA of the Jatropha oil was reduced from 25.3% to 0.5% at 60°C under atmospheric pressure, using a 60% w/w of methanol to oil ratio, a catalyst loading of 1% w/w (based on weight of oil) and 180 min of reaction time.

Further, (Tiwari, et al., 2007) utilized the central composite rotatable design (CCRD) arrangement of response surface methodology (RSM) to predict the optimized reaction variables for the pretreatment process. The optimum combination for reducing the FFA of Jatropha curcas oil from 14% to less than 1% was found to be 1.43% v/v of H_2SO_4 acid catalyst, a 28% v/v methanol to oil ratio and 88 min of reaction time at $60^{\circ}C$.

2.4.2 Transesterification

The molecular weight of Jatropha curcus oil with major chemical constituents was determined as 870 (Ramesh, 2003). Since the oil also contains other minor constituents, the approximate molecular weight of Jatropha curcus oil was taken as 900. As per the transesterification reaction, 3 moles of methanol were required to react with 1 mole of vegetable oil (Kavitha, 2003). The molecular weight of methanol is 32 and hence 96 g of methanol were required for the transesterification of 1 mole (or 900 g) of Jatropha curcus oil, which amounted to 10.67 % methanol.

Transesterification (alcoholysis) is the chemical reaction that involves triglycerides and alcohol in the presence of a catalyst to form esters and glycerol. This transesterification involving three consecutive reversible reactions, they are the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides. Glycerides are then converted into glycerol, giving one ester in each step.

Due to this transesterification being reversible, excess alcohol is used to shift the equilibrium towards the product. A successful transesterification reaction produces ester and crude glycerol. Though esters are the desired products of transesterification reactions, glycerin recovery is also important due to its numerous applications in daily products (Ramadhas, Jayaraj, & Muraleedharan, 2005). The transesterification reaction can be catalysed by alkalis, acids or enzymes (Demirbas, 2005). The overall transesterification reaction is given by three consecutive and reversible equations as shown.

Triglyceride (TG) + ROH
$$\leftrightarrow$$
 Diglyceride (DG) + RCOOR1(2.2)Diglyceride (DG) + ROH \leftrightarrow Monoglyceride (MG) + RCOOR2(2.3)Monoglyceride (MG) + ROH \leftrightarrow Glycerol + RCOOR3(2.4)

2.4.2.1 Mechanism of Transesterification

The esters of saturated and unsaturated monocarboxylic acids with the trihydric alcohol glyceride are named triglycerides. In a transesterification reaction, the triglyceride is converted stepwise to diglyceride, monoglyceride, and lastly to glycerol in the presence of a catalyst and alcohol. Usually, the alcohol preferred for producing biodiesel is methanol because of its low cost (Leung, et al., 2010).

To complete a transesterification stoichiometrically, 1 mol of triglyceride reacts with 3mol of alcohol to obtain 1 mol of fatty acid ester and 1mol of glycerol, shown in Eq. (2.5). In practice, this molar ratio of alcohol to triglyceride is often higher to drive the equilibrium to a maximum ester yield. The reaction can be catalysed by alkalis, acids and enzymes (Ma & Hanna, 1999).

The presence of free fatty acids and water always produces negative effects during the transesterification of vegetable oils and fats for biodiesel production, since an alkali catalyst will react with the FFA to form soap and reduce the catalyst effectiveness, which results in lower conversion. Water which originated from the oils and fats during the saponification reaction will retard the transesterification reaction through a hydrolysis reaction, shown in Eq. (2.6) because it can hydrolyse triglycerides to diglycerides and form more FFA (Demirbas, 2005; Leung, et al., 2010).

$H_2C = OCOR'$ HC = OCOR' + 3 ROH $H_2C = OCOR''$	catalyst	ROCOR' + ROCOR" + ROCOR"	$H_{2}C - OH$ $+ HC - OH$ $H_{2}C - OH$ $H_{2}C - OH$	
(inglycende) (alcono	1)	(giveerol)	(Tatty acid esters)	(2.5)
CH ₂ -O-CO-R ₁		CH2-OH		
1		1		
CH-O-CO-R ₂ + H ₂ C	» —— (CH-O-CO-F	$R_2 + R_1$ -COOH	
I		Ĩ.		
CH2-O-CO-R3		CH2-O-CO-	R,	
(triglyceride) (water	r)	(diglyceride)) (FFA)	(2.6)

2.4.2.2 Alkali Catalysed Transesterification

The alkali-catalysed transesterification of vegetable oils proceeds faster than the acid-catalysed reaction and the mechanism of this alkali-catalysed transesterification have been shown in Figure 2.3. The reaction mechanism is formulated in three steps. The first step is the reaction of the carbonyl carbon atom with the anion of the alcohol, forming a tetrahedral intermediate, from which the alkyl ester and corresponding anion of the diglycerides are formed. Another catalytic cycle is started when the catalyst reacts with a second molecule of alcohol. From there, diglycerides and monoglycerides are converted into alkyl esters and glycerol (Demirbas, 2005).



Figure 2.3 Mechanism of alkali-catalysed transesterification (Source: Demirbas, 2005)

(Tapanes, et al., 2008) have studied the reaction mechanism of the catalyst-based transesterification of Jatropha curcas oil and have proven the three step reaction mechanism. They reported that the reaction rate for Jatropha transesterification with ethanol is slightly lower than that with methanol as the stronger inductive effect of the ethyl group causes the breaking of the ethanol molecule to form an ethoxide anion which becomes more difficult than for the methoxide anion.

Many researchers have been using homogeneous alkali catalysts such as sodium hydroxide and potassium hydroxide to develop processes for the production of biodiesel from vegetable oils. Due to the low cost, both of these catalysts are most commonly used commercially (Leung, et al., 2010). The main concern in adopting alkali catalysts in biodiesel production is the FFA content of feedstock. A high FFA content of more than 1% w/w will enhance soap formation and the separation of end products will be hard, causing a low yield of biodiesel (Berchmans & Hirata, 2008). Therefore, the pretreatment of high FFA feedstock is required for effective alkali-catalysed transesterification to occur.

(Tiwari, et al., 2007) have reported biodiesel production from high free fatty acid (about 14%) of Jatropha curcas oil. After pretreatment to reduce the FFA to less than 1% using H_2SO_4 as a catalyst, the transesterification reaction took place with a molar ratio of methanol to oil of 5:1, and using 0.55% by weight of KOH as an alkaline catalyst.

Above 99% of Jatropha biodiesel which had properties satisfying the biodiesel standards was obtained after 24 min at a 60°C reaction temperature. This optimization study was carried out using a central composite rotatable design (CCRD). Complete conversion of Jatropha curcas oil to biodiesel can be achieved with a lower catalyst loading and a shorter reaction time possibly due to the assumption of the ideal reaction in quadratic polynomial models for the transesterification and the response surface methodology based on CCRD.

(Syam, et al., 2009) have also developed a two step process for generating biodiesel from Jatropha curcas oil which contains a very high level of free fatty acids. After a pretreatment process called esterification to reduce the FFA content to less than 1%, a transesterification reaction using KOH was conducted. The maximum yield of Jatropha methyl ester at 99% was achieved at a temperature of 65°C, a molar ratio of methanol to oil at 6:1, a catalyst loading of 1% (by weight of oil) and a reaction time of 60 min. Many researchers have investigated and studied the operating parameters that affecting transesterification reactions. Table 2.5 summarizes the optimized conditions for alkali catalysed transesterification of Jatropha curcas oil.

nce	Referen	Alkyl ester yield (%)	Optimum reaction condition	Catalyst amount (%wt of oil)	Catalyst	Molar ratio (alcohol to oil)	Alcohol
2010)	(Singh & Singh, 2	90 (5	65°C, 120 min	1.4	NaOH	<u>4.2:1</u>	Methanol
· Ma & Han	Demirbas 2005:	95	60°C, 120 min	2.0	КОН	9:1	Methanol
	(Denni bas, 2005,	99	65°C, 60 min	1.0	KOH	6:1	Methanol
mar, & Ran	1999; 11wari, Kui	93	66°C, 120 min	1.1	KOH	11:1	Methanol
	2007)	99 ²	60°C, 24 min	0.55	КОН	5:1	Methanol

Table 2.5: Alkali-catalysed transesterification of Jatropha curcas oil with optimized reaction variables.

2.4.2.3 Acid Catalysed Transesterification

The acid-catalysed transesterification process has slower reaction rate and the high methanol to oil molar ratio requirement compared to alkali-catalysed transesterification. In addition, an acid-catalyst has a lower activity and the transesterification reaction occurs at a higher process temperature than for the alkali-catalysed reaction (Georgogianni, et al., 2009). Besides, a long reaction time makes the process impractical and uneconomical (Miao, Li, & Yao, 2009).

On the other hand, the advantage of using an acid-catalysed transesterification is the tolerance towards the presence of high FFAs in the feedstock. Acid catalysts can directly produce biodiesel from low-cost lipid feedstock with an FFA greater than 6% (Vyas, Verma, & Subrahmanyam, 2010). Liquid acid catalysts such as sulphuric acid have a tolerance and less sensitive to FFA and can simultaneously conduct esterification and transesterification by giving a high yield in esters (Miao, et al., 2009). Other acid catalysts included sulphonic acid, phosphoric acid, hydrochloric acid, Lewis acids (AlCl₃ or ZnCl₂) and more (Georgogianni, et al., 2009).

The mechanism of acid-catalysed transesterification of vegetable oil is shown in Figure 2.4. The protonation of the carbonyl group of the ester promotes the formation of carbocation, which after a nucleophilic attack of the alcohol produces a tetrahedral intermediate. This intermediate will eliminate glycerol to form a new ester and to regenerate the catalyst. Acid-catalysed transesterification should be carried out in the absence of water (Demirbas, 2005).



Figure 2.4 Mechanism of acid-catalysed transesterification of vegetables oils (Source: Meher, et al., 2006)

When focusing on Jatropha curcas oil as the feedstock to synthesis Jatropha biodiesel, acid-catalysed transesterification is hardly performed or proposed by other researchers as an alkali-catalyst is considered as the most favourable. (Shuit, et al., 2010) have reported on the reactive extraction using an acidic catalyst to produce biodiesel from J. curcas L. seeds. Concentrated sulphuric acid was used as a catalyst since the crude Jatropha curcas oil contains a high FFA at about 15%. About 99.8% of Jatropha methyl ester was obtained by using a size of the Jatropha seed of less than 0.355mm and using n-hexane as a co-solvent, a reaction temperature of 60°C, a reaction period of 24 h, a methanol to seed ratio of 7.5 ml/g (approximate ratio of 5.9:1) and 15

wt% of H_2SO_4 (by weight of Jatropha seed). Table 2.6 tabulates the optimized conditions for acid catalysed transesterification of Jatropha curcas oil.

Alcohol	Molar ratio (alcohol to seed)	Catalyst	Catalyst amount (%wt of seed)	Optimum reaction condition	Alkyl ester yield (%)	Reference
Methanol	5.9:1	H ₂ SO ₄	15.0	60°C, 24 h	99.8	(Euzen, Trambouze,

 Table 2.6 Acid-catalysed transesterification of Jatropha curcas oil with optimized reaction variables.

2.5 Main Factors Affecting Yield of Biodiesel

2.5.1 Mole Ratio of Alcohol to Oil

The stoichiometric ratio for the transesterification reaction involves 3 mol of alcohol and 1 mol of triglyceride to produce 3 mol of fatty acid ester and 1mol of glycerol. Excess alcohol is used during transesterification to ensure that the oils will be completely converted to ester due to the forward reaction being more favorable. Furthermore, a higher alcohol to triglyceride ratio can result in a greater ester conversion in a shorter time. The molar ratio is associated closely with the type of catalyst used. The percentage of free fatty acids in oils is high, a molar ratio as high as 20:1 or 24:1 is

needed when using acid-catalysed transesterification (Miao, et al., 2009; Soriano, Venditti, & Argyropoulos, 2009). For alkali-catalysed transesterification where the free fatty acids are less than 1% after pretreatment, a molar ratio of methanol to oil of 5:1 or 6:1 is sufficient to convert Jatropha oil to biodiesel (Chitra, Venkatachalam, & Sampathrajan, 2005; Lu et al., 2009; Tiwari, et al., 2007).

2.5.2 Concentration of Catalyst

Catalyst concentration can affect the yield of the biodiesel produced. As mentioned earlier, basic catalysts are usually preferred to acid catalysts because of the higher reactivity and the lower process temperature required (Georgogianni, et al., 2009). Sodium methoxide was more effective than sodium hydroxide because of the reduced amount of water produced upon mixing sodium hydroxide with methanol (Freedman, Pryde, & Mounts, 1984).

As the catalyst concentration increases, the conversion of triglycerides and the yield of biodiesel also increased. However, the yield of biodiesel was reduced if the alkali catalysts were added above their optimum concentration as this causes more soap formation (Leung, et al., 2010). A concentration of NaOH in the range of 1.0–1.4% (w/w) has been found to produce 90–98% conversion from Jatropha oil to methyl ester

(Berchmans & Hirata, 2008; Chitra, et al., 2005). As for the concentration of KOH ranging from 0.55 to 2.0% (w/w), 95–99% of Jatropha biodiesel has been obtained (Lu, et al., 2009; Patil & Deng, 2009; Tiwari, et al., 2007).

2.5.3 Reaction Temperature

The rate of reaction is strongly affected by the reaction temperature. A higher reaction temperature can decrease the viscosities of oils and result in an increase in reaction rate as more energy is being supplied for the reaction to occur. Thus the yield of the biodiesel product is improved. However, the reaction temperature must be less than the boiling point of alcohol (boiling point of methanol is at 60–70°C at atmospheric pressure) to ensure the alcohol will not be lost through vaporization. Also, the yield of biodiesel decreases if the reaction temperature goes beyond its optimum level because a higher reaction temperature will accelerate the saponification reaction which results in a lower yield. Depending on the types of oil, the maximum yield is obtained at temperatures ranging from 60 to 80 °C (Barnwal & Sharma, 2005; Leung, et al., 2010).

2.5.4 Reaction Time

The conversion rate increases with reaction time. Initially the reaction was slow due to the mixing and dispersion of alcohol into the oil as reported. After some time, the reaction proceeds faster until maximum yield is reached (Freedman, et al., 1984). For alkali-catalysed transesterification, the yield of biodiesel reaches maximum at a reaction time of 120 min or less (Berchmans & Hirata, 2008; Sahoo & Das, 2009). Acidcatalysed transesterification requires an even longer reaction time than the alkalicatalysed reaction because alkali catalysts are usually exhibit a higher reactivity than acid catalysts (Georgogianni, et al., 2009). The reaction time needed during the conversion of triglycerides to biodiesel may range from 18 to 24 h as investigated in previous work (Shuit, et al., 2010; Soriano, et al., 2009). However, an excess reaction time will lead to a reduction in the product yield due to the backward reaction of transesterification, causing more fatty acids to form soaps (Leung, et al., 2010)

2.6 Economic Aspect of Biodiesel

The relatively high cost of vegetable oils (about four times the cost of diesel in India) has made biodiesel not economically feasible as the methyl ester produced from these edible oils is much more expensive and cannot compete economically with diesel fuels. The cost of raw materials accounts for 60–75% of the total cost of biodiesel fuel (Demirbas, 2005; Singh & Singh, 2010). (Lim & Teong, 2010) also determined that the price of the feedstock alone accounts for more than 75% of the overall cost of biodiesel production which is shown in Figure 2.5. With the recent increase in the petroleum prices and the uncertainties of petroleum availability due to depletion, biodiesel is still gaining interest.



Figure 2.5 General cost breakdown of biodiesel prediction (Source: Lim, et al., 2010)

Therefore there is a need to explore alternative feedstock to lower the cost of biodiesel production. The selection of the best feedstock selection is essential to ensure and keep the biodiesel production cost low. In terms of production cost, there are two aspects, the transesterification process and glycerol recovery. A continuous transesterification process with a shorter reaction time and a greater production capacity can lower the production cost. In addition, the cost of biodiesel fuel can be lowered if a biodiesel plant has its own glycerol recovery facility (Singh & Singh, 2010). (Leduc, Natarajan, Dotzauer, McCallum, & Obersteiner, 2009) have also studied the factors involved in producing biodiesel from Jatropha curcas at a competitive cost and to minimize the overall costs in order to fulfill the demand as a potential diesel substitute.

For biodiesel to be well established and accepted in the market, many factors and issues must be overcome. The key issues are the utilization of low cost feedstock such as non-edible vegetable oils or waste oils, improving the efficiency of the production process through optimum process variables and conditions and minimizing the cost of the catalysts used though the regeneration of catalysts

2.7 Environmental Consideration

Biodiesel is better for the environment because it is made from renewable resources and has <u>lower emissions</u> compared to petroleum diesel. It is less toxic than table salt and biodegrades as fast as sugar. Biodiesel has a higher cetane number than diesel because of its long chain fatty acids with 2–3 double bonds; it is without aromatics and contains 10–11% oxygen by weight. These characteristics of biodiesel reduce the emission of carbon dioxide (CO), hydrocarbon (HC) and particulate in the exhaust gas compared to diesel fuel (Graboski & McCormick, 1998).

The burning rate of biodiesel is reduced by about 11% compared to diesel (Rajesh, Raghavan, Shet, & Sundararajan, 2008). However, in view of the environmental impact through emissions, biodiesel has been reported to emit lesser pollutants compared to diesel. The comparison of biodiesel emission and conventional diesel is given in Table 2.7.

Emission type	B100 (%)	B20 (%)
Total unburned hydrocarbons	-67	-20
Carbon monoxide	-48	-12
Particulate	-47	-12
NOx	+10	+2 to -2
Sulphates	-100	-20
PAH (polycyclic aromatic hydrocarbons)	-80	-13
nPAH (nitrated PAH's)	-90	-50

Table 2.7 Emission comparison of biodiesel and diesel

Generally, all emissions associated with 100% pure biodiesel (B100) are lower than conventional diesel except for NO_x . The NO_x emissions from pure biodiesel increase on average by 10% depending on the combustion characteristics of the engine and the testing procedure. Moreover, sulphur emissions are essentially eliminated with pure biodiesel as compared to diesel. Besides, the exhaust emissions of total hydrocarbons, carbon monoxide and also particulates are lower on average by 67%, 48% and 47% respectively for biodiesel compared to diesel fuel. The level of polycyclic aromatic hydrocarbons (PAH) which have been identified as potential cancer causing compounds also shows a decrease of 80% in biodiesel emission.

CHAPTER 3

METHODOLOGY

3.1 Research Design

The important variables that are influence the transesterification reaction such as molar ratio of alcohol to oil, reaction temperature and concentration of catalyst are at their optimum condition in order to obtain maximum yield of biodiesel.

3.2 Chemicals

Jatropha crude oil, methanol (99.5%) and sulfuric acid (99% pure) are of analytical reagent (AR) grade. Potassium hydroxide, KOH in pellet as catalyst.

3.3 Equipments

3.3.1 Laboratory Scale

A 250 ml three-neck flask is equipped with a mechanical agitator and a reflux condenser, separator funnel and heated with a water bath to control the reaction temperature.



Figure 3.1 Biodiesel laboratory scale reactor

3.3.2 Pilot Plant Scale

A biodiesel pilot plant at FKKSA laboratory is used for pilot plant scale study.



Figure 3.2 Biodiesel pilot plant reactor

3.3.3 Rotary Evaporator

Rotary evaporator is used to remove water from methyl ester.



Figure 3.3 Lab scale rotary evaporator

3.3.4 Gas Chromatography (GC)

GC is used to analyze the yield of biodiesel in batch scale and in pilot plant scale product with the reference standard method.



Figure 3.4 Gas chromatography

3.4 General Flow of Methodology

Figure 3.5 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 then analyze by GC analysis and yield of production.



Figure 3.5 Flow chart methodology of biodiesel production in scaling up

The whole process for biodiesel production by transsterification reaction is simlplified as follows:



Figure 3.6 Simplified process flow chart of alkali-catalyzed biodiesel production (Source: Leung, et al., 2010)

3.5 Laboratory Scale Preocedure

3.5.1 Pretreatment

Jatropha oils must be heated above 100°C for 1 hour to remove the water and other impurities. The free fatty acid contents in the oils are determined by a standard titrimetry method. In acid esterification, 100 g of Jatropha crude oil is poured into the flask and heated to about 60°C. Then 28% w/w of methanol to oil ratio is added and stirred at low stirring speed for 88 min followed by 1.43% v/v of sulfuric acid. The reaction mixture is then poured into a separation funnel to remove excess alcohol, sulfuric acid and impurities. The acid values of the reaction mixtures are measured. The pretreated oil is used for the transesterification reaction.

3.5.2 Transesterification

100 g of Jatropha oil was poured into the three necked round-bottomed flask. The Jatropha oil was heated to the required temperature. In order to maintain the catalytic activity, the solution of potassium hydroxide in methanol (methoxide) was freshly prepared while the Jatropha oil was heated so that prolonged contact with the air would not diminish the effectiveness of the catalyst through interaction with moisture and carbon dioxide. The prepared methoxide solution was added to the preheated oil and it was mixed vigorously during the reaction. The mixture was stirred with speed of 700 rpm. When the required reaction period reached, the reaction was stopped. The mixture was allowed to settle under gravity for 24 hours in the separatory funnel.

3.5.3 Separation

After settling the mixture in the separatory funnel for 24 hours, it was separated into two layers. Two layers were formed: the upper layer consisted of methyl ester, methanol traces, residual catalyst, and other impurities, whereas the lower layer consisted of glycerin, excess methanol, catalyst, and other impurities.

3.5.4 Purification

After separation from the glycerin layer, the methyl ester layer was purified by washing with hot distilled water at 60°C until the washing water had a pH value similar to that of distilled water (pH 7). The hot distilled water-to-crude methyl ester ratio is 1:1. To prevent the possibility of losing the methyl ester due to emulsion formation, the washing was done gently. Next, any remaining water was removed from the methyl ester layer at 70°C by vacuum rotary evaporator. The end product, biodiesel was obtained as a clear amber-yellow liquid. Finally, the methyl ester content of the products was analyzed by using GC with the reference standard method.

3.6 Pilot Plant Scale Procedure

3.6.1 Pretreatment

Jatropha oils must be heated above 100°C for 1 hour to remove the water and other impurities. The free fatty acid contents in the oils are determined by a standard titrimetry method. In acid esterification, 10 kg of oil is added into the reactor by using vacuum pump and heated to about 60°C. Then 28% w/w of methanol to oil ratio is added by using vacuum pump and stirred at low stirring speed for 88 min followed by 1.43% v/v of sulfuric acid. The reaction mixture is then poured into a separation funnel to remove excess alcohol, sulfuric acid and impurities. The acid values of the reaction mixtures are measured. The pretreated oil is used for the transesterification reaction.

3.6.2 Transesterification

The main transesterification reaction took place in biodiesel pilot plant at FKKSA laboratory. The experiment was conducted with optimized conditions that got from laboratory scale experiment. 10 kg of Jatropha oil was weighted and poured into the reactor tank. Jatropha oil was heated to 60°C. While the Jatropha oil was heated, the solution of potassium hydroxide in methanol (methoxide) was prepared simultaneously by 1 kg of potassium hydroxide was added into 2 kg methanol. The prepared methoxide solution was introduced into the reactor and the mixture was stirred vigorously for required reaction time. The mixture was stirred with speed of 700 rpm. After that, the reaction was stopped and the mixture was allowed to settle in the separation tank for 24 hours.

3.6.3 Separation

After settling the mixture for 24 hours, it was separated into two layers. The upper layer consisted of methyl ester, methanol traces, residual catalyst, and other impurities, whereas the lower layer consisted of glycerin, excess methanol, catalyst, and other impurities. The lower glycerine layer was drawn off from the bottom of the settling tank.

3.6.4 Purification

The crude biodiesel was pumped into the washing tank. The crude biodiesel layer was needed to purify by washing with warm water. After neutralization process, the washing process of biodiesel was started. During the washing process, gentle agitation was required to avoid the emulsion. After 30 minutes, the wash water layer was drained off from the bottom of the washing tank. The washing process was repeated two to four times. After the washing process, it was required to measure the pH of the biodiesel layer. When the pH of the biodiesel layer reached 7, the washing process was completed. Next, any remaining water was removed from the methyl ester layer at 70°C by vacuum rotary evaporator. The end product, biodiesel was obtained as a clear amber-yellow liquid. Finally, the methyl ester content of the products was analyzed by using GC with the reference standard method.

3.7 Product Analysis

3.7.1 Gas Chromatography (GC)

GC is used to analyze the production of biodiesel in laboratory scale and in pilot plant scale product. A 30m x 250mm x 0.25µm.DB-Wax column is used for analyzing

fatty acid methyl ester (FAME) in the product. Methyl palmitate and methyl stearate are used as the standard. 0.004g, 0.008g, 0.012g, 0.016g, and 0.020 of every standard and 10mL of Hexane are prepared for the standard. 0.015g of biodiesel production of every scale and 10mL of Hexane are prepared for analyzing the product. The oven of GC is held at the initial temperature 50°C for 1min then ramped to the final temperature of 370° C at a rate of 15° C /min to 180° C held for 1 min, 7° C /min to 230° C held for 0min, 10° C /min to 370° C held for 5 min, with total run time is of 35.81 min.

3.7.2 Yield Calculation

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

Conversion =
$$\frac{(\Sigma A - Aei)}{A_{ei}} \times \left[\frac{C_2 V}{m} \times 100\right] \times \left[\frac{\Sigma m}{\Sigma V} \times 100\right]$$
 (3.1)

Where,

A = area total (Pa.s) Aei = area sample (Pa.s) $\left[\frac{C_2 V}{m} \times 100\right]$ = sample $\left[\frac{\Sigma m}{\Sigma V} \times 100\right]$ = standard

CHAPTER 4

RESULT AND DISCUSSION

4.1 Introduction

This chapter presents the results of the production in laboratory scale and pilot plant scale. The optimum conditions were optimized by determine the optimum quantity of methanol, catalyst KOH, reaction temperature and reaction time required for the transesterification of Jatropha oil were conducted by varying the concentration of methanol from 10 to 25 % of Jatropha oil weight, KOH concentration from 0.5 to 1.5 % of Jatropha oil weight, reaction temperature from 30 to 60°C and reaction time from 30 to 120 min. Then, the optimized conditions from laboratory scale were used in pilot plant scale.

4.2 Laboratory Scale

4.2.1 Effect of Methanol Amount

Table 4.1 Variation in methanol amount and biodiesel yield percentage

Experiment	Jatropha	Methanol	KOH	Reaction	Reaction	Biodiesel	Glycerol	Emulsion	Loss	Yield
	oil	(g)	(g)	Temperature	Time	(g)	(g)	(g)	(g)	(%)
	(g)			(°C)	(min)					
E1	100	10	1	60	90	29.17	69.83	9.50	2.50	29.17
E2	100	15	1	60	90	76.00	29.00	8.50	2.50	76.00
E3	100	20	1	60	90	98.00	16.17	3.83	3.00	98.00
E4	100	25	1	60	90	89.17	25.83	8.50	2.50	89.17



Figure 4.1 Variation in methanol amount vs. biodiesel yield percentage

The molar requirement of methanol was found to be 10.67%. Hence, to optimize the amount of methanol required for the reaction, experiments were conducted with 10%, 15%, 20% and 25% methanol. The concentration of KOH, reaction temperature and reaction time used with the methanol variations were constant at 1.0 wt%, 60°C and 90 min respectively. The results of this study are presented in Table 4.1. The results clearly indicate that the optimum concentration of methanol required for effective transesterification of Jatropha oil was 20 wt%. Moreover, it was found that when the concentration of methanol was increased above or decreased below the optimum, there was no significant increase in the biodiesel production, but the excess or short fall in concentration of methanol only contributed to the increased formation of glycerol and emulsion. The variation in methanol concentration versus ester yield percentage is shown in Figure 4.1. Figure 4.1 clearly shows that the maximum ester yield of 98 % was obtained using 20 wt% methanol.
4.2.2 Effect of KOH Concentration

Table 4.2 Variation in KOH concentration and biodiesel yield percentage

Experiment	Jatropha	Methanol	KOH	Reaction	Reaction	Biodiesel	Glycerol	Emulsion	Loss	Yield
	oil	(g)	(g)	Temperature	Time	(g)	(g)	(g)	(g)	(%)
	(g)			(°C)	(min)					
E5	100	20	0.5	60	90	92.17	18.67	7.17	2.49	92.17
E6	100	20	1	60	90	97.83	14.83	5.67	2.67	97.83
E7	100	20	1.5	60	90	75.17	37.33	7.50	1.50	75.17



Figure 4.2 Variation in KOH concentration vs. biodiesel yield percentage

The catalyst KOH concentration variations adopted in this study were 0.5%, 1.0% and 1.5% of Jatropha oil weight. The methanol concentration of 20 w% that gave the best ester yield, constant reaction temperature and reaction time of 60°C and 90 min respectively were used with KOH variations for the production of biodiesel from Jatropha oil. The results of this study are presented in Table 4.2. The results clearly indicate that the optimum concentration of KOH required for effective transesterification was 1.0 wt%. It was observed that, if the KOH concentration was decreased below or increased above the optimum, there was no significant increase in the biodiesel production, but there was increased formation of glycerol and emulsion. The variation in KOH concentration versus ester yield percentage is shown in Figure 4.2. It is seen clearly from Figure 4.2 that the maximum ester yield of 97.8 % was obtained using 1.0 wt% KOH concentration.

4.2.3 Effect of Reaction Temperature

Experiment	Jatropha	Methanol	KOH	Reaction	Reaction	Biodiesel	Glycerol	Emulsion	Loss	Yield
	oil	(g)	(g)	Temperature	Time	(g)	(g)	(g)	(g)	(%)
	(g)			(°C)	(min)					
E8	100	20	1	30	90	61.00	33.33	24.17	2.50	61.00
E9	100	20	1	45	90	79.33	24.67	14.83	2.17	79.33
E10	100	20	1	60	90	97.33	14.50	6.67	2.50	97.33

Table 4.3 Variation in reaction temperature and biodiesel yield percentage



Figure 4.3 Variation in reaction temperature vs. biodiesel yield percentage

The temperature variations adopted in this study were 30, 45 and 60°C. The constant reaction time of 90 min and the constant methanol and KOH concentrations of 20 wt% and 1.0 wt% respectively, which gave the best ester yield, were maintained with the temperature variations for the production of biodiesel from Jatropha oil. The results of this study are presented in Table 4.3. The results clearly indicate that the maximum ester yield was obtained at 60°C temperature. The variation in reaction temperature versus ester yield percentage is shown in Figure 4.3. It clearly shows that the ester yield proportionately increased with the increase in reaction temperature. The reaction temperature should always be below the boiling point (65°C) of methanol (Freedman, Pryde, & Mounts, 1984) and so the reaction temperature was fixed up to 60°C. The maximum ester yield of 97.3 % was obtained at 60°C as shown in Figure 4.3.

4.2.4 Effect of Reaction Time

Table 4.4 Variation in reaction time and biodiesel yield percentage

Experiment	Jatropha	Methanol	КОН	Reaction	Reaction	Biodiesel	Glycerol	Emulsion	Loss	Yield
	oil	(g)	(g)	Temperature	Time	(g)	(g)	(g)	(g)	(%)
	(g)			(°C)	(min)					
E11	100	20	1	60	30	89.33	22.33	8.17	1.17	89.33
E12	100	20	1	60	60	94.50	17.67	7.50	1.33	94.50
E13	100	20	1	60	90	98.00	15.83	5.67	1.50	98.00
E14	100	20	1	60	120	97.83	15.17	6.33	1.67	97.83



Figure 4.4 Variation in reaction time vs. biodiesel yield percentage

In order to optimize the reaction time, the different reaction times selected for this study were 30, 60, 90 and 120 min. The constant methanol concentration of 20 wt%, constant KOH concentration of 1.0 wt% and constant temperature of 60°C were maintained with reaction time variations. The results of this study are given in Table 4.4. The results clearly indicate that the biodiesel yield increased with the reaction time. The biodiesel yield was found to be more or less the same at 90 and 120 min of reaction time. The variation in reaction time versus biodiesel yield percentage is shown in Figure 5 and it clearly shows that the maximum ester yield of 98 % was obtained at 90 min of reaction time. The biodiesel yield percentage in alkali catalysed transesterification under different experiments for maximum biodiesel yield is shown in Figure 4.4. The experiment E13 with 20 wt% methanol concentration, 1.0 wt% KOH concentration at 60°C with reaction time of 90 min yielded 98 % of biodiesel as shown in Table 4.4 and in Figure 4.4.

4.3 Pilot Plant Scale

After having optimized the concentration of methanol, KOH, reaction temperature and the reaction time required for the transesterification of Jatropha oil, experimental study on large scale production of biodiesel from Jatropha curcus oil was carried out only 1 times due to the limitation of Jatropha oil amount. About 10 kg of Jatropha oil was transesterified using 2 kg of methanol and 0.1 kg of KOH, at a constant temperature of 60°C. The reaction time of 90 min was allowed in order to facilitate the completion of reaction.

Table 4.5 Optimized condition and biodiesel yield percentage in pilot plant scale

Experiment	Jatropha	Methanol	KOH	Reaction	Reaction	Biodiesel	Glycerol	Emulsion	Yield
	oil	(kg)	(kg)	Temperature	Time	(kg)	(kg)	(kg)	(%)
	(kg)			(°C)	(min)				
E15	10	2	0.1	60	90	9.58	1.82	0.70	95.80

The results of large scale transesterification of Jatropha oil in the biodiesel pilot plant are presented in Table 4.5. The amount of water used for biodiesel washing was 10 kg. The biodiesel yield of 9.58 kg was obtained from 10 kg of Jatropha oil. The yield of 95.8 % (by weight of oil) was obtained. The amount of glycerol obtained as a byproduct from 10 kg of oil was 1.82 kg and the emulsion was 0.7 kg, during washing of crude biodiesel in order to obtain pure biodiesel.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Among all the experiment variations adopted, it was found that the maximum biodiesel yield of 98 % was obtained using 20 wt% methanol and 1.0 wt% KOH of Jatropha oil at 60°C reaction temperature. The minimum reaction time required for maximum biodiesel yield was found to be 90 min. The biodiesel yield from 10 kg of Jatropha oil was 9.58 kg (95.8 %) in pilot plant scale biodiesel production. There are difference between laboratory scale production and pilot plant scale production and yield production but the difference is not to large. These differences are due to the different operating and handling condition for both scales.

5.2 **Recommendations**

Scale up study on chemical process can be carry out by using simulations such as Aspen Plus, Hysis or Super Pro. This kind of simulation will give more detailed information and data effectively. 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. 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.

REFERENCES

- Achten, W. M. J., L.Verchot, Franken, Y. J., Mathijsd, E., Singh, V. P., Aertsa, R., et al. (2008). Jatropha bio-diesel production and use. *Biomass and Bioenergy*, 32, 1063-1084.
- Azhari, Faiz, M., Yunus, R., Ghazi, T. I. M., & Yaw, T. C. S. (2008). REDUCTION OF FREE FATTY ACIDS IN CRUDE JATROPHA CURCAS OIL VIA AN ESTERIFICATION PROCESS. International Journal of Engineering and Technology, 5, 92-98.
- Barnwal, B. K., & Sharma, M. P. (2005). Prospects of biodiesel production from vegetable oils in India. *Renewable and Sustainable Energy Reviews*, 9, 363-378.
- Berchmans, H. J., & Hirata, S. (2008). Biodiesel production from crude Jatropha curcas L. seed oil with a high content of free fatty acids. *Bioresource Technology*, 99, 1716-1721.
- Chitra, P., Venkatachalam, P., & Sampathrajan, A. (2005). Optimisation of experimental conditions for biodiesel production from alkali-catalysed transesterification of Jatropha curcus oil. *Energy for Sustainable Development*, 9, 13-18.
- Demirbas, A. (2005). Biodiesel production from vegetable oils via catalytic and noncatalytic supercritical methanol transesterification methods. *Progress in Energy and Combustion Science*, *31*, 466-487.
- Divakara, B. N., Upadhyaya, H. D., Wani, S. P., & Gowda, C. L. L. (2010). Biology and genetic improvement of Jatropha curcas L.: A review. *Applied Energy*, 87, 732-742.
- Euzen, J.-P., Trambouze, P., & Wauquier, J.-P. (Eds.). (1993). Scale-Up Methodology For Chemical Process. Paris: Editions TECHNIP.
- Freedman, B., Pryde, E. H., & Mounts, T. L. (1984). Variables affecting the yields of fatty esters from transesterified vegetable oils. *Journal of the American Oil Chemists Society*, 61, 1638-1643.

- Georgogianni, K. G., Katsoulidis, A. K., Pomonis, P. J., Manos, G., & Kontominas, M. G. (2009). Transesterification of rapeseed oil for the production of biodiesel using homogeneous and heterogeneous catalysis. *Fuel Processing Technology*, 90, 1016-1022.
- Graboski, M. S., & McCormick, R. L. (1998). Combustion of fat and vegetable oil derived fuels in diesel engines. *Progress in Energy and Combustion Science*, 24, 125-164.
- Jain, S., & Sharma, M. P. (2010). Prospects of biodiesel from Jatropha in India: A review. *Renewable and Sustainable Energy Reviews*, 14, 763-771.
- Kavitha, P. L. (2003). Studies on Transesterified Mahua Oil as an Alternative Fuel for Diesel Engines. Unpublished M.Sc. thesis, Anna University, Chennai, India.
- Leduc, S., Natarajan, K., Dotzauer, E., McCallum, I., & Obersteiner, M. (2009). Optimizing biodiesel production in India. *Applied Energy*(125-131).
- Leung, D. Y. C., Wu, X., & Leung, M. K. H. (2010). A review on biodiesel production using catalyzed transesterification. *Applied Energy*, 87, 1083-1095.
- Lim, S., & Teong, L. K. (2010). Recent trends, opportunities and challenges of biodiesel in Malaysia: An overview. *Renewable and Sustainable Energy Reviews*, 14, 938-954.
- Lu, H., Liu, Y., Zhou, H., Yang, Y., Chen, M., & Liang, B. (2009). Production of biodiesel from Jatropha curcas L. oil. *Computers and Chemical Engineering*, 33, 1091-1096.
- Ma, F., & Hanna, M. A. (1999). Biodiesel production: a review. *Bioresource Technology*, 70, 1-15.
- Meher, L. C., Sagar, D. V., & Naik, S. N. (2006). Technical aspects of biodiesel production by transesterification—a review. *Renewable and Sustainable Energy Reviews*, 10, 248-268.

- Miao, X., Li, R., & Yao, H. (2009). Effective acid-catalyzed transesterification for biodiesel production. *Energy Conversion and Management*, 50, 2680-2684.
- Patil, P. D., & Deng, S. (2009). Optimization of biodiesel production from edible and non-edible vegetable oils. *Fuel*, 88, 1302-1306.
- Rajesh, S., Raghavan, V., Shet, U. S. P., & Sundararajan, T. (2008). Analysis of quasisteady combustion of Jatropha bio-diesel. *International Communications in Heat* and Mass Transfer, 35, 1079-1083.
- Ramadhas, A. S., Jayaraj, S., & Muraleedharan, C. (2005). Biodiesel production from high FFA rubber seed oil. *Fuel*, 84, 335-340.
- Ramesh, D. (2003). Study on Production of Biodiesel from Selected Oil Bearing Nuts and Utilization in Engine. Unpublished Ph.D. thesis, Tamil Nadu Agricultural Uiniversity, Coimbatore, India.
- Sahoo, P. K., & Das, L. M. (2009). Process optimization for biodiesel production from Jatropha, Karanja and Polanga oils. *Fuel*, 88, 1588-1594.
- Sarin, R., Sharma, M., Sinharay, S., & Malhotra, R. K. (2007). Jatropha–Palm biodiesel blends: An optimum mix for Asia. *Fuel*, *86*, 1365-1371.
- Shah, S., & Gupta, M. N. (2007). Lipase catalyzed preparation of biodiesel from Jatropha oil in a solvent free system. *Process Biochemistry*, *42*, 409-414.
- Shay, E. G. (1993). Diesel fuel from vegetable oils: Status and opportunities. *Biomass and Bioenergy*, *4*, 227-242.
- Shuit, S. H., Lee, K. T., Kamaruddin, A. H., & Yusup, S. (2010). Reactive extraction and in situ esterification of Jatropha curcas L. seeds or the production of biodiesel. *Fuel*, 89, 527–530.
- Singh, S. P., & Singh, D. (2010). Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review. *Renewable and Sustainable Energy Reviews*, 14, 200-216.

- Soriano, J. N. U., Venditti, R., & Argyropoulos, D. S. (2009). Biodiesel synthesis via homogeneous Lewis acid-catalyzed transesterification. *Fuel*, *88*, 560-565.
- Syam, A. M., Yunus, R., Ghazi, T. I. M., & Yaw, T. C. S. (2009). Methanolysis of Jatropha Oil in The Presence of Potassium Hydroxide Catalyst. *Applied Sciences*, 17, 3161-3165.
- Tapanes, N. C. O., Aranda, D. A. G., Carneiro, J. W. d. M., & Antunes, O. A. C. (2008). Transesterification of Jatropha curcas oil glycerides: Theoretical and experimental studies of biodiesel reaction. *Fuel*, 87, 2286-2295.
- Tiwari, A. K., Kumar, A., & Raheman, H. (2007). Biodiesel production from jatropha oil (Jatropha curcas) with high freefatty acids: An optimized process. *Biomass* and Bioenergy, 31, 569-575.
- Vyas, A. P., Verma, J. L., & Subrahmanyam, N. (2010). A review on FAME production processes. *Fuel*, *89*, 1-9.

APPENDIX

Figures from the laboratory scale experiment:



Figure A.1 Samples with various of parameters



Figure A.2 Samples after transesterification



Figure A.3 Failed and successful sample after water washing