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UNIVERSITI TEKNOLOGI PETRONAS

Synthesis of Biodiesel through In Situ Transesterification of *Jatropha curcas*

By

M. Surya Abadi Ginting

A THESIS
SUBMITTED TO THE POSTGRADUATE STUDIES PROGRAMME
AS A REQUIREMENT FOR
THE DEGREE OF MASTER OF SCIENCE
IN CHEMICAL ENGINEERING

BANDAR SERI ISKANDAR,
PERAK
MARCH 2009

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledge. I also declare that it has not been previously or concurrently submitted for any other degree at UTP or other institutions.

Signature : ______________________________

Name : M. SURYA ABADI GINTING

Date : ______________________________

ABSTRACT

Biodiesel is a renewable fuel synthesized through a chemical reaction of alcohol and vegetable or animal oils, fats or greases. Currently most of the biodiesel production is based on edible oils and use methanol and alkaline catalysts in two step transesterification process. The main limitation of biodiesel production is due to the high feedstock and production cost. The use of non edible oil sources, such as *Jatropha curcas*, can reduce the high feedstock cost since it does not compete with food supply and this leads to a cheaper feedstock source. Moreover, it is hoped that these problems can be counterbalanced by combining both extraction and reaction steps. This method is known as in situ transesterification.

The experiments were carried out in a batch reactor equipped with a reflux condenser, a magnetic stirrer and a thermometer. Effect such as types of base catalyst (KOH, NaOH and NaOMe), their concentrations (0.5, 1.0, 1.5, 2.0 and 2.5 (wt.%)), reaction time (2, 4 and 6 hours), reaction temperature (30, 40, 50, 60 and 70^{o}C), stirrer speed (100, 200, 400 and 600 rpm) and types of alcohol such as methanol, ethanol and mixture of methanol-ethanol (50% : 50%) (v/v) were studied. The kinetics of transesterification of *Jatropha curcas* seeds were also investigated.

The liquid products which consist of methyl ester, ethyl ester or mixtures of both were analyzed using Thin Layer Chromatography (TLC) and Gas Chromatography (GC). TLC was used to determine the content of the alkyl ester in the biodiesel sample qualitatively. However, it can not be used to quantify the amount of the alkyl ester in the biodiesel sample. Therefore, GC was used to determine the amount of the fatty acid alkyl ester in the biodiesel sample. The analysis of the biodiesel samples was conducted based on ASTM D 6854 – 00. It was found that the highest yield of the alkyl ester (99.97%) was obtained at 30°C, with 2.00 wt.% sodium methoxide concentration and stirrer speed of 600 rpm for 2 hours of reaction time.

However, the methanolysis in situ transesterification of the *Jatropha curcas* seed was unsuccessful because the yield of the biodiesel was only 39.42%. At the optimum conditions, the acid value, viscosity and total glycerin were 0.04 mg KOH/g of sample, 5.5 mm^2/s and 0.003 (wt.%), respectively. At 30^{o}C, the reaction order and reaction rate constant was found to be 1.24 and 0.009 liter$^{0.24}$/mol$^{0.24}$.s, respectively. The mechanism of the biodiesel production through in situ transesterification of *Jatropha curcas* seed was determined by solid-liquid kinetics. Then, it was found that the reaction rate was most probably ash diffusion controlled.

ABSTRAK

Biodiesel adalah minyak yang boleh diperbaharui melalui tindak balas kimia di antara alkohol dan minyak sayuran, haiwan atau lemak. Buat masa ini, kebanyakan penghasilan biodiesel adalah berdasarkan penggunaan minyak yang boleh dimakan dan penggunaan methanol dan penggalak alkali di dalam dua langkah proses transesterifikasi. Faktor utama yang boleh menghalang penghasilan biodiesel adalah kos bahan mentah dan kos pembuatan yang tinggi. Penggunaan minyak yang tidak boleh dimakan seperti *Jatropha curcas* boleh digunakan untuk mengurangkan kos bahan mentah kerana ia tidak perlu bersaing dengan makanan mengakibatkan pengurangan kos bahan mentah. Masalah ini juga boleh diatasi dengan menggabungkan kedua-dua langkah pengeluaran dan tindak balas. Kaedah ini dinamakan sebagai transesterifikasi in situ.

Uji kaji telah dijalankan di dalam reaktor batch dilengkapi dengan condenser reflux, pengaduk magnetik dan termometer. Kesan penggunaan penggalak alkali yang berbeza seperti : KOH, NaOH and NaOMe berserta dengan kepekatan yang berbeza iaitu : 0.5, 1.0, 1.5, 2.0 dan 2.5 (% berat), masa tindak balas iaitu 2, 4 dan 6 jam, suhu tindak balas iaitu 30, 40, 50, 60 dan 70^{o}C, kelajuan pengaduk iaitu 100, 200, 400 dan 600 rpm beserta jenis alkohol seperti metanol, etanol dan campuran metanol-etanol (50% : 50%) (v/v) telah dijalankan. Kinetik transesterifikasi biji *Jatropha curcas* juga telah dilakukan.

Produk dalam bentuk cecair seperti metil ester, etil ester dan campuran kedua-dua metil dan etil ester telah dianalisis menggunakan Thin Layer Chromatography (TLC) dan Gas Chromatography (GC). TLC digunakan untuk mengenal pasti kandungan alkyl ester di dalam sampel biodiesel. Tetapi ia tidak boleh digunakan untuk mengira bilangan alkyl ester yang wujud di dalam sampel biodiesel. Oleh itu, GC digunakan untuk menentukan bilangan asid lemak alkyl ester di dalam sampel biodiesel. Analisis sampel biodiesel telah dijalankan berdasarkan kaedah ASTM D 6854 – 00. Setelah analisis dijalankan, didapati kandungan alkyl ester yang tertinggi (99.97%) telah dihasilkan pada suhu 30oC dengan kepekatan 2 wt.% sodium metoksida dan kelajuan pengaduk pada 600 rpm selama 2 jam.

Namun, metanolisis proses transesterifikasi in situ menggunakan biji *Jatropha curcas* adalah kurang berhasil. Penggalak sodium metoksida dapat menghasilkan tindak balas yang lebih menggalakkan berbanding NaOH dan KOH. Pada keadaan optimum, nilai asid, kepekatan dan glicerin keseluruhan masing-masing adalah 0.04 mg KOH/g, 5.5 mm^2/s dan 0.003 (% berat). Pada suhu 30^oC, reaksi order dan bilangan kadar tindak balas masing-masing adalah 1.24 dan 0.009 $liter^{0.24}/mol^{0.24}.s$. Mekanisme penghasilan biodiesel melalui proses transesterifikasi in situ menggunakan biji *Jatropha curcas* telah ditentukan menggunakan kaedah kinetik pepejal-cecair. Kajian lebih lanjut menunjukkan bahwa kadar tindak balas adalah dikawal oleh ash difussion.

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ABBREVIATION

FFA	free fatty acid, %
THF	tetrahydrofuran
$\mathcal{D}e$	effective diffusion coefficient,
X	conversion, %
gpy	gallon per year
G	mass percentage of glycerin in sample
Ag	peak area of glycerin
A_{is1}	peak area of internal standard1
W_{is1}	weight of internal standard 1, mg
W	weight of sample, mg
a_g	slope of the calibration function
b_g	intercept of the calibration function
Gl_i	mass percentage of individual glycerides in sample
A_{gli}	peak area of individual glyceride
A_{is2}	peak area of internal standard 2
W_{is2}	weight of internal standard 2, mg
a_{o1}	slope of the calibration function for mono-, di- or triolein
b_{o1}	intercept of the calibration function for mono-, di- or triolein
k	reaction rate constant
ko	frequency or pro-exponential factor
E	activation energy, J/mol
R	gas constant, 8.314 J/mol.K
T	absolute temperature, K
A	KOH solution required for titration of the sample, ml
B	KOH solution required for titration of the blank, ml
M	molarity of the KOH solution, mol/l

CHAPTER 1

INTRODUCTION

1.1 Background

Energy is one of the most crucial issues in the world nowadays. This phenomenon can be caused by the escalation of energy demand, depletion of fossil oil resources and environmental concern. To figure out this issue, many countries in the world have been investigating a new energy sources to substitute or to replace the petroleum-derived diesel fuel. An alternative fuel must be technically feasible, economically competitive, environmentally friendly and readily available.

A number of investigations have shown that vegetable oil has a great opportunity as an alternative fuel for diesel engine [1 – 5]. The usage of vegetable oil as an alternative fuel has been tested by Rudolf Diesel in his compression ignition engine in the year of 1900 [6]. However, there are many problems associated with the use of vegetable oil directly in diesel engine such as carbon deposit, oil ring sticking, coking and trumpet formation on the injector, high viscosity (typical vegetable oil's viscosity is 8–10 higher than diesel's viscosity) [1, 7] and low volatility that causes the formation of deposit in engine because of incomplete combustion [8].

These problems can be avoided either by modifying the engine or chemical modification of the vegetable oil through processes such as pyrolysis, emulsification and transesterification. Among these processes, transesterification is the most viable approach [9–12].

Transesterification, also known as alcoholysis, is a reaction of triglyceride either from vegetable oil, animal fat or waste cooking oil with monohydroxy alcohol such as methanol or ethanol in the presence of alkaline or acidic catalyst. This will produce alkyl ester which is known as biodiesel and glycerol as a by product. This process has been widely employed to reduce the high viscosity of the vegetable oil. Biodiesel has demonstrated a number of promising characteristics including sulphur content, lubricity, cetane number and flash point [13–17]. Therefore, biodiesel can be used as an alternative fuel for diesel engines either to replace or to blend with the petroleum-based diesel fuel.

The transesterification reaction is described as follows:

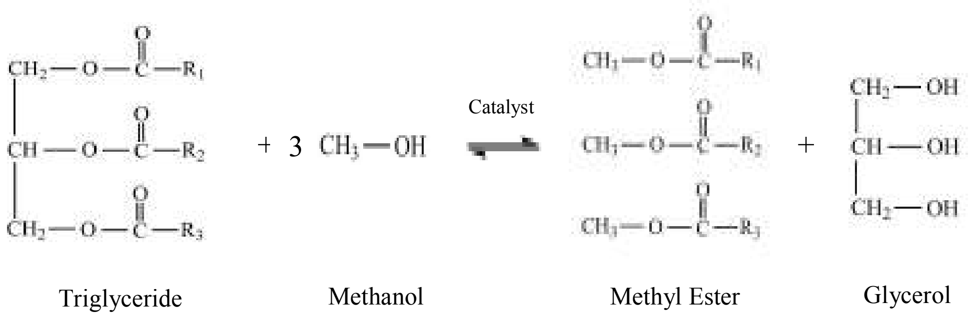


Figure 1.1 Conversion of triglyceride into methyl ester and glycerol

There are many resources which are being used as feedstock especially edible oil for producing this alternative fuel at industrial scale. Examples of which are palm oil, sunflower, soybean and rapeseed [18–21]. However, the use of the edible feedstocks in producing biodiesel will increase its price since it competes with food. As a result, the cost of biodiesel production will increase. Therefore, the non-edible oil sources are recommended to be applied as feedstock, *Jatropha curcas* for instance [22–23]. Other sources of fuel that have been investigated include distillers dried grains with solubles, meat and bone meal (MBM), rice bran, waste cooking oil, canola oil, *Pongamia pinnata* oil, tallow, lard and algae. These are all potential sources of feedstock for biodiesel production [24].

One of the most attractive non edible oil feedstock that has been investigated in details is *Jatropha curcas*. Plantation of *Jatropha curcas* has been developed in many countries including India, Africa, South-East Asia and Central and South America [23]. The use of *Jatropha curcas* seed as a feedstock for biodiesel has advantages such as being able to be planted in sandy, saline soils or even in desert climate [25]. Moreover, it has high content of oil which contains triglyceride that can be converted into biodiesel. The oil content of the *Jatropha* seed (dehulled seed on mass basis) is higher than that in rapeseed and sunflower with the amount of 52 – 54%, 40% and 45 – 50% respectively [21, 26].

Biodiesel has advantages in comparison with petroleum-based diesel fuel such as it is a renewable fuel, biodegradable, non-toxic and able to reduce the emissions of particulate matter (40%), carbon monoxide (44%) and unburned hydrocarbon (68%) since it is made from vegetable oils or animal fats [27]. In addition, its sulphur content is lower than that of petroleum-based diesel engine fuel, thus, reducing sulphur emissions to the environment. Its lubricant property is also better than that of petrodiesel-based fuel, therefore, it can improve the life time of the engines.

Moreover, having a higher flash point makes it safer to handle, use and store. *Jatropha* biodiesel's flash point is 135^{o}C and diesel's fuel flash point is 68^{o}C [7]. The combustion of biodiesel does not significantly contribute to the net atmospheric carbon level because of its closed carbon cycle. This reduction of green house gas emission due to biodiesel is in line with Kyoto Protocol agreement [28–31].

In the course of time, the biodiesel production demonstrates significant annual growth. Due to vast advantages of biodiesel, many countries are concerned in the research and development of the biodiesel for larger scale production. In 2003, more than 2.7 million tons biodiesel was produced in Europe and it was predicted that the biodiesel production will achieve up to 8 – 10 million tons in 2010 [32].

Meanwhile, in USA, the total biodiesel production was 221,000 tons in 2002 and it will be expected to reach 1.15 million tons in 2011 [32]. Moreover, China introduced biofuel technology development project in 2004 and one year later, it started the agricultural and forestry biomass development program. With this project, it is expected that China will be producing biodiesel to approximately 2 million tons in 2010 and 12 million tons in 2020 [27, 32].

In Malaysia, the production of biodiesel from crude palm oil was achieving 196,363 tons during period of August 2006 until March 2008 [33]. This biodiesel production will be increased with a total production capacity of 10.2 million tons per year since 91% of the total biodiesel projects have been approved by the government [33]. Among these projects, 12 plants have been operating with a production capacity of 1 million tons per year and the constructions of 2 other plants have been completed but have not yet start to operate. The total production capacity of the two plants is expected to be 160,000 tons per year [33].

However, the rising price of the feedstock, which is crude palm oil, makes the biodiesel production cost sharply increase. In 2006, the average cost of crude palm oil was RM1,502.50 per ton and it has reached up to RM2,516.50 per ton in 2007 [33]. Its cost would still be raise up to RM 3,433.50 per ton during period of January 2008 to March 2008 [33]. On the other hand, the cost of producing biodiesel from the crude palm oil was RM4,330 per ton on march 2008 [33].

Meanwhile, at the same period of time, the biodiesel fuel price in the market was only RM2,632 per ton [33]. As a consequence, many biodiesel plants have temporarily stopped their operating due to high production cost compared to selling price of the biodiesel in the market. Thus, the government is looking at the possibility of using non edible oil, *Jatropha curcas* oil for example, to replace the crude palm oil which is being used as feedstock. Because of this, the *Jatropha curcas* has been planted in Sabah, East Malaysia [33].

In a good agreement with Malaysian minister of plantation industries and comodities statement, Martyanov and Sayari, (2008) and Meng X et al., (2008) stated that the relatively high cost of biodiesel production presents a limitation factor which can inhibit the development of this alternative fuel. By replacing the refined edible vegetable oils with low cost feedstock such as waste cooking oil or non edible oil like *Jatropha* oil and substitution of homogeneous catalyst with heterogeneous catalyst would reduce the biodiesel production cost since the heterogeneous catalyst can be recovered and reused after the transesterification reaction [34–37].

However, the relatively higher amount of free fatty acid in waste cooking oil may result in the formation of soap if an alkali catalyst is applied in the production of the biodiesel. Furthermore, the low conversion of triglyceride to the desired product makes the heterogeneous catalyst rarely used to produce biodiesel [35–37].

Nowadays, the high cost of biodiesel production is a major obstacle to its commercialization. It is estimated that the production cost of biodiesel from rapeseed oil is higher than the production of diesel from fossil fuel for advanced processes. The cost is \$0.80/liter and \$0.22/liter, respectively [38]. The high cost of it is mainly due to the cost of the feedstock [39]. This is illustrated in the Figure 1.2. Figure 1.2 shows that the feedstock contributes the highest cost to the total amount of biodiesel production cost. The feedstock cost reaches up to 75.41% of total amount of the biodiesel production cost.

For the capacity of 30 million gallon per year (mm gpy) plant size, the percentage of distribution biodiesel production cost due to feedstock, chemical, energy, labor, depreciation, and overhead and maintenance percentage will be 80.8; 11; 1.2; 1.2; 3; 2.9%, respectively. In other words, the feedstock expense is the major contributor to the biodiesel production cost [32, 39–41]. The biggest contributing factors to the high cost of the feedstock are the extraction and refining of vegetable oils [41].

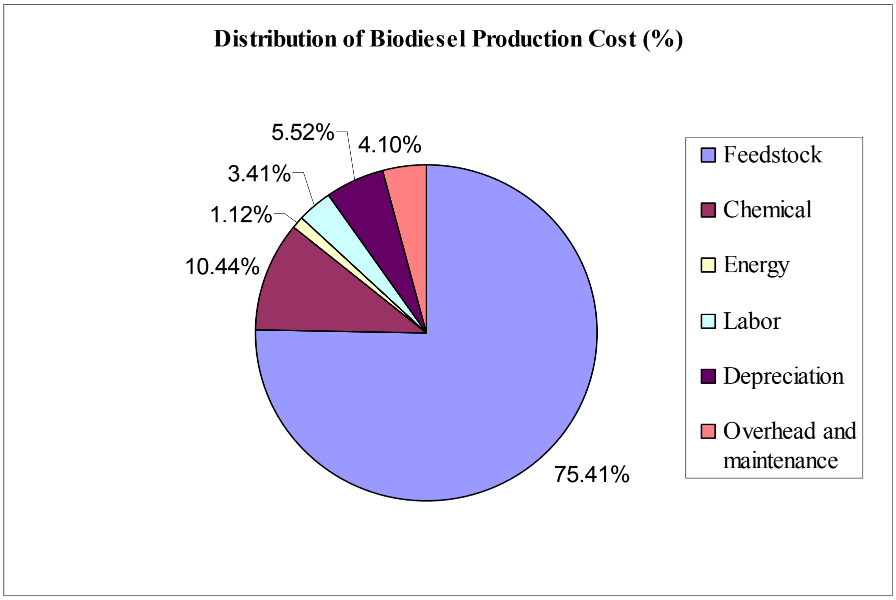


Figure 1.2 Distribution of biodiesel production cost for 5 mmgpy biodiesel plant source : CIRAS Iowa State University Extension [39]

The high cost of the biodiesel production makes the biodiesel as an alternative energy not competitive compare to petrodiesel-based fuel in the market. There are many ways how to cut-off the production cost. Integrating the extraction and reaction step into one process is an example. This process eliminates the extraction step such as the use of mechanical extractor or solvent extraction using hexane and refining of oil prior to be used in reaction. Eliminating the extraction and refining oil step could reduce the cost of biodiesel production until 45% [42].

Simplification of the oil production or processes and the use of non edible oil or low grade of feedstock are another way to reduce the biodiesel production cost. In this process, the alcohol acts as a solvent to extract the feedstock and also acts as a reactant by reacting with the oil which is being extracted to form biodiesel and glycerol as co-product.

Haas M J *et al.*, 2006 investigated a computer modelling approach to estimate the capital and production costs for synthesizing biodiesel from crude degummed of soybean oil in the presence of a 1.78% (w/w) solution of sodium methoxide as a catalyst [41]. Based on their analysis, raw materials costs contribute the greatest component to the overall production costs in which soybean oil feedstock cost is the biggest contributing factor which reaches up to 88% of the overall production cost [41]. On the other hand, recovery of the co-product, glycerol, which is generated during the transesterification reaction with concentration of 80% (w/w), is suitable for sale. This income is able to reduce the production cost by 6% [41].

Moreover, Zhang Y *et al.*, 2003 reported that a higher percentage contribution up to 10% of this valuable co-product, glycerol, could reduce the total manufacturing cost of biodiesel [40]. Thus, it is expected that using *Jatropha curcas* seeds as a source of the non-edible feedstock and integration of the oil extraction and reaction steps into single step, the overall production cost can be reduced and the products will become more competitive in the market.

1.2 Problem Statement

Due to high demand in alternative fuel, many researchers try to investigate the best way to produce biodiesel. As described previously, the most common processes to produce biodiesel is through alkali–catalyzed transesterification. However, this process requires refined vegetable oil with free fatty acid content of 0.5% [43–44]. Thus, the biodiesel production cost will still be high since the extraction and refining of the vegetable oil is the biggest contributor to the total cost of feedstock [41].

Therefore, in this research, the in situ transesterification is introduced as an alternative processes to produce biodiesel in which the transesterification reaction occurs on its raw material. The *Jatropha curcas* kernel has not been treated to release the lipid components from it.

1.3 Objective of Research

Either alkali-catalyzed or acid-catalyzed transesterification of *Jatropha curcas* has been widely investigated by numerous researchers world wide but none of them has studied it by in situ transesterification process either using homogeneous or heterogeneous catalyst. The use of homogeneous catalyst is more effective compared to heterogeneous catalyst in terms of biodiesel yield obtained [35–37, 45]. Thus, this catalyst has been chosen in this research. Alkali-catalyzed process is preferred to be used rather than acid-catalyzed since the acid value of the *Jatropha curcas* oil used is found to be 1.391 mg of KOH/g which indicates that the amount of the free fatty acid is very low (0.69%). Thus, by applying this process to produce biodiesel, it is believed that the process can reach the equilibrium conditions where maximum yield of fatty acid alkyl ester can be obtained at a faster rate.

The current practice of producing biodiesel is by extracting the oil from the seeds/oil bearing material, refine it and further react it with short chain of alcohols such as methanol or ethanol. These alcohols have a good extraction capacity and thus, it is believed that by contacting the alcohol directly in the oil bearing material and in the presence of alkaline catalyst, the oil will be simultaneously extracted and reacted to produce biodiesel. This process is known as in situ transesterification process. This process has been applied to produce fatty acid alkyl ester from sunflower, soybean and rice brand oil using acid catalyst [46–49].

In addition, a number of researchers have identified the important variables that affect the transesterification reaction either in term of biodiesel yield or conversion percentage such as reaction time, reaction temperature, type of catalysts and their concentration, molar ratio of alcohol to oil, stirrer speed and type of alcohol [7, 19–21, 26]. Zeng S *et al.*, 2006 concluded that the biodiesel yield was affected by the oil : methanol : acid molar ratio and the reaction temperature. Considering the above parameters, this research investigates the effectiveness of the in situ alkaline transesterification method to produce biodiesel from *Jatropha curcas* seeds and enhancement of the biodiesel yield by using different types of alcohol, catalysts and their concentration, reaction time, stirrer speed and reaction temperature.

1.4 Scope of Research

Biodiesel that was produced through in situ transesterification of *Jatropha* seeds with an alcohol and a base catalyst either hydroxide or alkoxides metal was analyzed by Gas Chromatography (GC) and Thin Layer Chromatography (TLC). The resulting product may contain not only the desired fatty acid alkyl esters but also unreacted triglyceride, the remaining alcohol and catalyst. In addition, the glycerol which is a by product of the transesterification reaction may also exist in the biodiesel even though it has been separated from the biodiesel. Other contaminants which can also be found in the biodiesel product are both monoglyceride and diglyceride [19, 25, 46, 50, 51]. The presence of these contaminants in the biodiesel could be caused by the incomplete transesterification reaction and insufficient purification. It can lead to serious engine problems and hazardous emissions when the biodiesel is applied as automotive diesel fuel.

Thus, to avoid engine problems, the amount of these contaminants must be less or equal to the amount which has been stated in the ASTM D-6751 [52] for example total glycerine is limited to 0.24 wt.%. Laboratory analysis, GC, must be carried out to identify and quantify the amount of these contaminants present in the alkyl esters to meet the requirement of the standard, ASTM D-6751 [52].

In this study, the synthesis of biodiesel through the in situ transesterification process from *Jatropha curcas* seeds has been investigated. The effects of temperature, reaction time, stirrer speed, type and concentration of the catalysts and type of the short chain alcohol have been studied to optimize the condition of the reaction. To meet the requirement of the biodiesel standard either Euro standard (EN 14214) or American standard (ASTM D-6751), the products have been analyzed using Gas Chromatography (GC). Other testings have also been conducted following the ASTM D-6751 method, for instances : flash point, kinematic viscosity, density, acid number, free glycerine and total glycerin.

1.5 Thesis Outline

This thesis is designed into several chapters which consist of :

1. Chapter 1, Introduction, includes background, objective and scope of research as well as thesis outline.
2. Chapter 2, Literature Review, discusses about definition of biodiesel, methods which were used to produce biodiesel and parameters that affect the yield of biodiesel.
3. Chapter 3, Research Methodology, consists of the sequential processes to produce biodiesel through in situ transesterification process, product analysis using gas chromatography (GC) and thin layer chromatography (TLC).
4. Chapter 4, Result and Discussion, designed into 2 sections : 1st section discusses about the yield of biodiesel and parameters that affect the result as well as the reaction kinetics and 2nd sections describes the quality of biodiesel obtained
5. Chapter 5, Conclusions and Recommendations, summaries the data obtained and recommendation for future work.

It is hoped that these results will give significant information regarding the in situ alkaline transesterification of *Jatropha curcas* seeds and can be used as a base study for larger scale of production.

CHAPTER 2

LITERATURE REVIEW

This chapter illustrates a process to produce biodiesel, raw material that can be applied to produce biodiesel, parameters that affect the conversion of triglyceride to fatty acid alkyl ester, thus enhance the yield of biodiesel and the summary of the literatures cited.

2.1 Definition of Biodiesel

According to the American Standard for Testing Material for biodiesel (ASTM D 6751 – 07a), biodiesel has been defined as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats [52]. Biodiesel is a renewable energy which can be produced either from vegetable oils or animal fats and reacted with alcohol such as methanol or ethanol in the presence of a catalyst to yield alkyl esters and glycerol as a co-product. There are at least 5 routes to produce biodiesel either from vegetable oils, animal fats or waste cooking oil as namely as follow :

1. Alkali – catalyzed transesterification
2. Direct acid – catalyzed transesterification
3. Acid catalysis followed by alkali – catalysis
4. Enzyme – catalyzed transesterification
5. Non – catalyzed process

As mentioned previously in Chapter 1, transesterification is the most common process applied to reduce the viscosity of the vegetable oil to meet the standard of diesel fuel. The overall transesterification reaction is shown as below [9, 23, 51, 53, 54]:

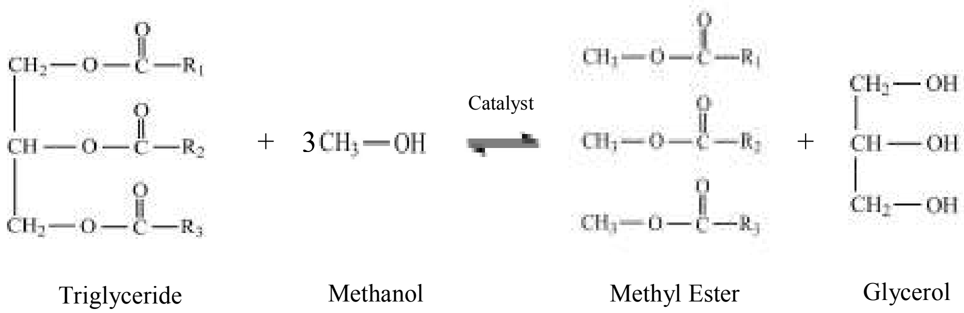


Figure 2.1 Formation of methyl ester and glycerol from triglyceride and methanol

where R_1, R_2 and R_3 indicate the fatty acid chains associated with the feedstock sources such as oils, fats or waste cooking oil in which palmitic, oleic and linoleic acids are the predominant component of the fatty acids, sometimes accompanied by stearic acid and linolenic acid [55]. According to the gas chromatography analysis, the fatty acid composition of the *Jatropha curcas* oil used is listed as follows :

Table 2.1 Fatty acid composition of *Jatropha curcas* oil

Fatty Acid	wt.%	wt.%[4]	wt.%[22]	Structure[1]	Formula	Molecular Weight
Myristic	0.12	0	0.37	14 : 0	$C_{14}H_{28}O_2$	228.376
Palmitic	19.5	14.1	13.34	16 : 0	$C_{16}H_{32}O_2$	256.428
Stearic	6.8	6.7	4.91	18 : 0	$C_{18}H_{36}O_2$	284.481
Oleic	41.3	47	32.03	18 : 1	$C_{18}H_{34}O_2$	282.465
Linoleic	31.4	31.6	45.05	18 : 2	$C_{18}H_{32}O_2$	280.450
Linolenic	0.2	-	0.23	18 : 3	$C_{18}H_{30}O_2$	278.434

[1] *xx : y indicates that xx is carbon in the fatty acid chain with y represents double bonds*

As can be observed in the Table 2.1, the fatty acids vary in their carbon chain length and in the number of double bonds. The major components of fatty acids present in the *Jatropha curcas* oil are the unsaturated fatty acids (oleic and linoleic acid). The fatty acid compositions in other sources of vegetable oil and animal fat are listed in Table 2.2 below:

Table 2.2 Fatty acid composition of vegetable oils and animal fats

Raw Material	Fatty acid composition, % by weight						
	12:0	14:0	16:0	18:0	18:1	18:2	18:3
Soybean[37]	0	0	12.3	5.8	26.5	49.8	5.9
Palm[48]	0.2	1.1	44.1	4.12	39.2	10.10	0.21
Rapeseed[56]	0	0	6	1	58	24	11
Coconut[9]	46.5	19.2	9.8	3.0	6.9	2.2	0
Cottonseed[57]	-	0.7	21.6	2.6	18.6	54.4	0.7
Sunflower[55]	-	-	6	5	20	60	-
Jatropha	-	-	19.5	6.8	41.3	31.4	-
Tallow[9]	0.1	2.8	23.3	19.4	42.4	2.9	0.9
WCO[32]	-	-	16	5.21	34.28	40.76	-

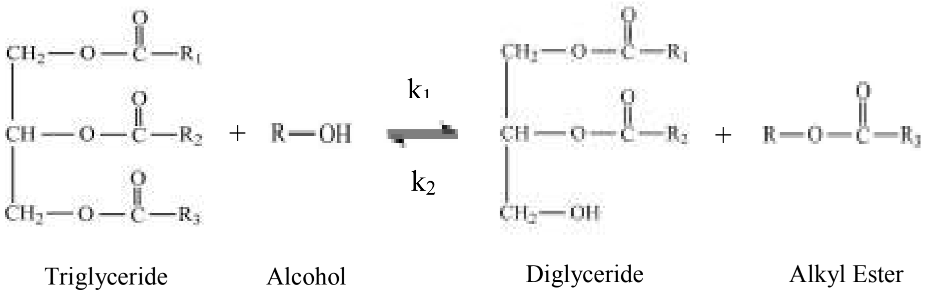
The different fatty acid composition of these vegetable oils can be caused by climate conditions, soil type, growing season, plant maturity, plant health, microbiological seed location within the flower and the genetic variation of the plant [58]. Composition of the fatty acid especially the type and amount of the unsaturated fatty acid affect the stability of the oil. Oleic acid is the most stable unsaturated fatty acid compared to linoleic and linolenic acid since its oxidation rate is lower than that of linoleic and linolenic acid which is 1, 12 and 25 respectively [58]. Thus, this characteristic makes *Jatropha* oil is suitable as biodiesel feedstock. The higher the saturated fatty acids percentage, the higher the cloud point of the biodiesel [59].

The transesterification process can be catalyzed by both homogeneous and heterogeneous catalysts. Homogeneous catalysts consist of alkalis and acids. Among those catalysts, alkali-catalyzed transesterification of vegetable oil or animal fat in the presence of a simple monohydroxy alcohol such as methanol or ethanol, is the predominant process used in commercial biodiesel production since the reaction converge at faster rate and it can be optimized at mild conditions (60°C and atmospheric pressure) [43]. The most common used alkali catalysts in producing biodiesel are sodium hydroxide, potassium hydroxide and sodium methoxide as well as potassium methoxide [60].

In addition, other approaches have also been proposed such as acid catalysis, acid catalysis followed by alkali catalysis, supercritical alcohol and enzymes [34, 61-63]. Acid catalysts are usually used to convert the high free fatty acid content in raw material to esters effectively however the reaction rates for converting triglyceride to alkyl esters are too slow [43]. The biodiesel can also be produced through non catalytic process which is carried out at supercritical temperature of the alcohol. Despite the time needed to complete the reaction is much shorter than that of alkali process, this non catalytic process requires high temperature and pressure (350°C and 45MPa, respectively) [62].

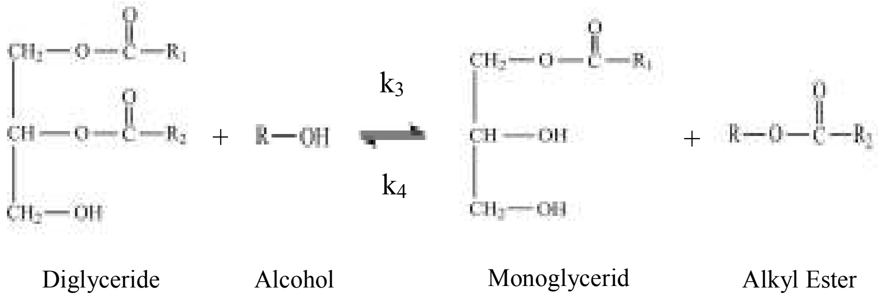
Transesterification reaction is a three-step reversible reaction which consists of a number of consecutive reversible reactions with intermediate formation of diglyceride and monoglyceride. The formation of the glycerol occurs at the third-reaction step and alkyl ester is formed in each step which is illustrated in the following paragraph [9, 12, 23, 51, 54]:

1. The formation of diglyceride



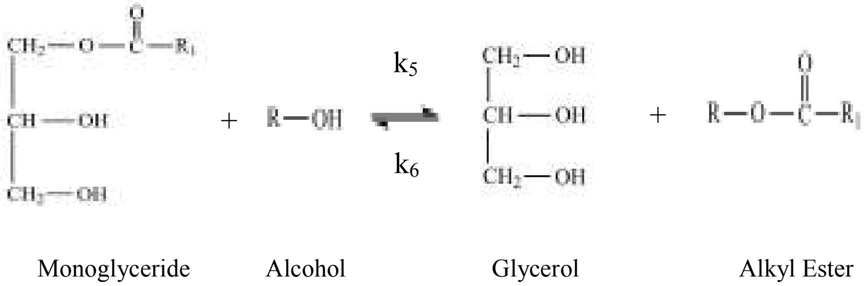
(2.1)

2. The formation of monoglyceride



(2.2)

3. The formation of glycerol



(2.3)

Each of these steps starts with an attack on the carbonyl carbon atom of the triglyceride, diglyceride or monoglyceride molecule by an alkoxide ion [9, 30, 64]. The alkoxide ion can be formed by dissolving hydroxide-base catalyst either sodium or potassium hydroxide in alcohol solution [30, 60, 65]. The amount of methoxide ion produced depends on the quantity of hydroxide ion and the alkali dissociation constant. The formation of an alkoxide ion is illustrated in the following reaction:

$$CH_3-OH \quad + \quad OH^- \quad \rightarrow \quad CH_3-\ddot{O}:^- \quad + \quad H_2O \qquad (2.4)$$

Methanol Hydroxide ion Methoxide ion Water

2.2 Transesterification Mechanism

The mechanism of the transesterification reaction in the presence of a methoxide ion, can be shown as follows [30]:

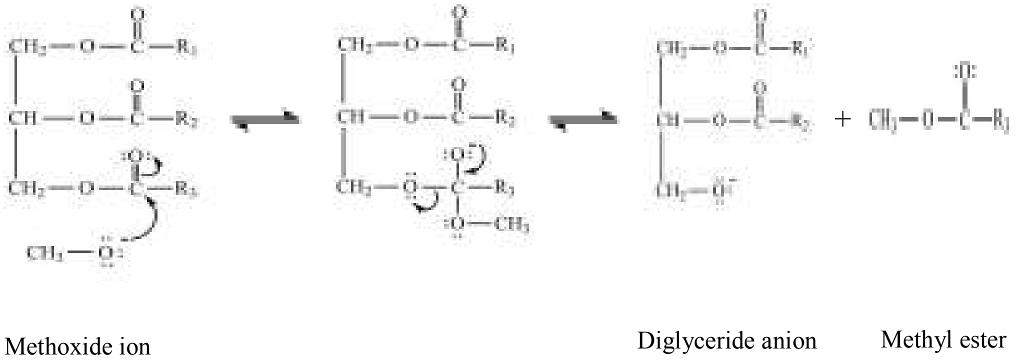


Figure 2.2 Alkali transesterification mechanism (a)

The resultant diglyceride anion equilibrates with the alcohol to produce more alkoxide ion. If the alcohol used is methanol, the alkoxide ion produced is known as methoxide ion. This can be observed through the following reaction, as shown in Figure 2.2 (b):

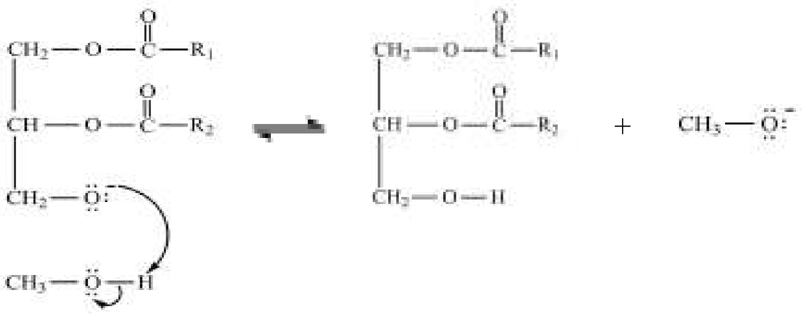


Figure 2.3 Alkali transesterification mechanism (b)

Then, diglyceride and monoglyceride are converted to alkyl esters and glycerol under the same mechanism.

2.3 Kinetics Transesterification of Vegetable Oil

The kinetics transesterification of vegetable oil have been extensively studied including the kinetics transesterification of soybean oil [51, 65], palm oil [54], monoglyceride of *Pongamia pinnata* oil [66] and rapeseed oil [67]. The kinetic is used to determine the reaction rate, reaction rate constant, reaction order and activation energy that involve in the transesterification reaction.

Kinetics of transesterification of soybean oil at various temperatures (30^oC, 40^oC, 50^oC, 60^oC and 70^oC) was investigated by Noureddini H and Zhu D, 1997 [51]. They reported that at Reynolds number of 3100, the higher the temperature, the shorter the time to achieve the mass transfer region. The experimental data appeared to be a good fit into a second-order kinetic mechanism. This is in accordance with the result reported by Doell R *et al*, 2008 [65].

In addition, the kinetics of palm oil transesterification in a batch reactor was studied by Darnoko D and Cheryan M, 2000 [54]. They concluded that the kinetic model appeared to be a pseudo second order at the initial stage of the reaction and the reaction rate constant increased as the temperature increased. Thus, the rate of transesterification increased. This result is in agreement with the value reported by Karmee *et al.,* 2004 [66] except at 30^{o}C.

Rate law or kinetic expression is an algebraic equation which relates rate of disappearance of a reactant to the species concentrations. The overall transesterification reaction is:

$$\text{Triglyceride} + 3CH_3OH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 3\text{FAME} + \text{Glycerol} \qquad (2.5)$$

It shows that for every mole of triglyceride that is consumed, 3 moles of FAME (Fatty Acid Alkyl Ester) appear. In other words, the rate of formation of FAME equals to ratio of stoichiometry coefficient of FAME to triglyceride multiply by the rate of disappearance of triglyceride ($-r_{\text{triglyceride}}$). It can be expressed as below:

$$\boxed{r_{\text{FAME}} = 3(-r_{\text{triglyceride}}) = -3r_{\text{triglyceride}}} \qquad (2.6)$$

Under the same scheme, the relationship between the rates of formation of FAME and glycerol is

$$\boxed{r_{\text{FAME}} = 1/3\ r_{\text{glycerol}}} \qquad (2.7)$$

Based on the stoichiometry coefficient, the relationship can be simplified as below,

$$\boxed{(-1/1)r_{\text{triglyceride}} = (-1/3)r_{\text{methanol}} = (1/3)r_{\text{FAME}} = (1/1)r_{\text{glycerol}}} \qquad (2.8)$$

According to equation 2.1; 2.2 and 2.3, for constant-volume batch reactor, the rate laws are expressed as follows [65]:

$$d[TG]/dt = - k_1[TG][R\text{-}OH] \tag{2.9}$$

$$d[DG]/dt = k_1[TG][R\text{-}OH] - k_3[DG][R\text{-}OH] \tag{2.10}$$

$$d[MG]/dt = k_3[DG][R\text{-}OH] - k_5[MG][R\text{-}OH] \tag{2.11}$$

The above formula (2.9; 2.10 and 2.11) will be used to calculate the reaction rate constant, reaction order and the rate of the transesterification for each of the three consecutive reactions.

The reaction rate constant is a temperature-dependent. It is expressed by Arrhenius' law [68] :

$$k = k_o e^{-E/RT} \tag{2.12}$$

where k_o is known as the frequency or pre-exponential factor and E is called the activation energy of the reaction.

2.4 Biodiesel's Feedstock

Vegetable oils, animal fats and waste cooking oils are the most common raw material employed in the production of biodiesel. Vegetable oils either from edible oil or non-edible oil could be utilized as a source to produce biodiesel. Depending on the climate and soil condition, different countries are looking into different source of raw material to produce biodiesel. A majority of biodiesel is obtained from edible oil such as soybean oil in USA [24, 50], rapeseed and sunflower oil in Europe [50, 69], canola oil in Canada, palm oil in Indonesia and Malaysia [54], coconut oil in the Philippines [27] and used cooking oil in China [70]. All of those sources are used as feedstocks for producing biodiesel.

Meanwhile, non-edible sources such as *Pongamia pinata* in India [71] and *Jatropha curcas* in South-East Asia, India and Africa are being developed as potential feedstocks for biodiesel production [23]. Animal fats although give much gain attention by researchers but it has not been commercialized yet in industry due to the availability of the feedstock for a sustainable process. Beef tallow is an example of animal fat sources with 50% total amount saturated fatty acid of the fatty acid components. Stearic and palmitic acids are the predominant saturated fatty acid in it which cause high melting point and viscosity [9]. Thus, it is not suitable to be used directly as an alternative fuel. Yellow grease is an another example of animal fats source with low quality feedstock in which it has a high free fatty acid content, which is up to 15 wt.% [72].

Using edible oil as a feedstock in producing biodiesel makes its production cost higher than that of petroleum-based diesel fuel due to the high cost of edible oil since it competes with food. It has been reported that the cost of the feedstock affect the total cost of production by 60–75% [30, 73]. Consequently, the price of biodiesel will not be competitive compared to petrodiesel-based fuel. To reduce the cost of the raw materials, either non-edible oil or waste cooking oil can be employed in producing biodiesel since both of these sources will not compete with food and this leads to a cheaper feedstock source.

The sources of feedstocks from waste cooking oil and animal fats have the amount of free fatty acid higher than those of vegetable oils [32, 55]. Prior to its use in producing biodiesel, these feedstocks which contain contaminants such as free fatty acid and water must be treated. The purpose of the pre-treatment is to remove or reduce the contaminants in order to give the high yield of biodiesel, to separate the esters from glycerol easily and to select the optimum process which will be involved in the production of biodiesel. Consequently, the pre-treatment step will increase the biodiesel production cost [40, 74].

The free fatty acid content in the oil should be less than 5% if the oil is subjected to transesterify through alkali process which is known as the most effective process to produce biodiesel [75]. *Jatropha curcas* oil usually has low level of free fatty acid (less than 3%) and its fatty acid composition is dominated by unsaturated fatty acids (70 – 85%) especially oleic and linoleic acid [76, 77]. Compare to palm kernel oil in which palmitic acid is the predominant component of the fatty acid, the oil can not be used at room temperature due to the high pour point, thus the oil will become gel [77].

In addition, the use of the *Jatropha curcas* as the raw material has many advantages as compared to other sources such as it can be grown in marginal soil and it has a lifespan of 30 years [78]. After 5 years the yield per hectare is 1.1 to 2.75 tonnes and 5.25 to 12.5 tonnes for growing *Jatropha* without irrigation and with irrigation, respectively [78]. In addition, it has higher yield of oil per hectare than that of soybean oil and also rapeseed oil [79]. The mature seed yield per ha per year depends on the site characteristics (rainfall 250 – 3000 mm per annum, soil type and soil fertility), genetics, plant age, and management such as propagation method, fertilizing and irrigation [25, 78].

In addition, it can be successfully cultivated in arid and semi-arid condition. It is believed to prevent and control soil erosion or able to be used as a living fence or to reclaim wasteland [25]. Moreover, it can also grow very well under low fertility and moisture conditions [4, 80]. *Jatropha* oil has low acidity and good oxidation stability than that of soybean oil. Its viscosity is lower than that of castor oil and also it has better cold properties as compared to palm oil [4, 23].

2.5 Type of Catalysts

A catalyst is usually used to improve the reaction rate and yield of the desired product. There are several types of catalysts which can be used to produce biodiesel either homogeneous catalysts or heterogeneous catalysts. The homogeneous catalysts consist of either acid or base catalyst. Sulphuric acid (H_2SO_4), hydrochloric acid (HCl) and sulfonic acid are the examples of the acid catalysts. Currently, the most common used catalysts are base catalysts such as sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium methoxide (NaOMe) and potassium methoxide (KOMe). The choice of acid or base catalyst to be used in producing biodiesel depends on the quality of the feedstock such as the amount of free fatty acids or water content of the feedstock.

If the percentage of free fatty acid is higher than 0.5%, the more suitable catalyst to be involved in producing biodiesel is acid catalyst instead of base catalyst. On the other hand, if the amount of the free fatty acid is equal or lesser than 0.5%, base catalyst is preferred [43]. Meanwhile, the base catalysts can still be used to accelerate the reaction until the free fatty acid content of the feedstock is 5%. But an additional amount of the base catalyst must be used to compensate the catalyst lost to soap formation [75].

2.5.1 Homogeneous Catalysts

2.5.1.1 Acid Catalysts

Acid-catalyzed alcoholysis of vegetable oil, animal fat or waste cooking oil has benefits compare to base-catalyzed processes. It can be used to catalyze a feedstock which has high free fatty acids (FFA) where esterification of the FFA and alcoholysis of the triglyceride occur simultaneously. Thus, the amount of the acid catalyst used is lower than that of base catalyst since the FFA do not neutralize the catalyst [81]. This low quality feedstock such as waste cooking oil or yellow grease significantly reduces the biodiesel production cost since its cost is cheaper than those of refined vegetable oils. However the high free fatty acid level requires a pre-treatment to reduce its FFA content. As a result, the total cost of biodiesel production will increase [40, 74].

In addition, the acid-catalyzed process requires a higher molar ratio of alcohol to oil and also longer hours of reaction duration to obtain high conversion of triglyceride to alkyl ester than that of base-catalyzed processes [43, 81]. A study on process design and technological assessment shown that the acid-catalyzed process with high level of free fatty acid of waste cooking oil as the feedstock to be a competitive alternative to alkali-catalyzed processes. However, if the non edible oil for example *Jatropha curcas* is applied as feedstock, alkali-catalyzed processes is more recommended than acid-catalyzed processes [74].

Soybean oil alcoholysis with different short chain of alcohol such as methanol, ethanol and buthanol in the presence of 1 wt.% H_2SO_4 with alcohol to oil molar ratio 30 : 1 was carried out at near the boiling point of each alcohols. The conversions of triglyceride to ester were satisfactory when the reaction time was 3, 22 and 69 hours, respectively, for butyl, ethyl and methyl ester. In addition, the conversion to fatty acid alkyl ester was similar for all of these alcohols when it was conducted at 65°C for 69 hours of reaction time [43].

The use of acid catalysts (1 wt.%) such as sulphuric, hydrochloric, formic, acetic and nitric acid on alcoholysis of refined soybean oil was conducted at 120°C with a 9 : 1 molar ratio methanol to triglyceride for more than 20 hours resulted that only sulphuric acid was effective (the conversion was higher than 99%). The other catalysts resulted in conversion of less than 0.7% [81]. Furthermore, solid acid catalyst such as Hβ–Zeolite, montmorillonite K–10 and ZnO was used to methanolysis the *Pongamia* oil at 120°C for 24 hours with a 10 : 1 molar ratio of alcohol to oil. They reported that the conversions of *Pongamia* oil to fatty acid methyl ester were 47%, 59% and 83%, respectively, for the Hβ–Zeolite, montmorillonite K–10 and ZnO as catalyst [82].

In addition, Zheng S *et al.*, 2006 [34] investigated the production of biodiesel from waste frying oil using acid catalyst. They reported that both the molar ratio of oil : methanol : acid and the reaction temperature were the most significant parameters which affecting the yield of biodiesel. In addition, there was no significant effect of stirring speed to the reaction rate or the yield of biodiesel obtained in the range of 100 to 600 rpm. Since all the above mixing speed is under the same turbulent region [34].

2.5.1.2 Base Catalysts

Base catalysts are the most common used catalyst to initiate the reaction in producing biodiesel commercially since the reaction conditions are moderate (60^{o}C and atmospheric pressure) and the process is faster than the acid-catalyzed transesterification [43]. Despite the fact that the base-catalyzed process is faster, the alcohol as well as the catalyst must be substantially anhydrous and the feedstock should have a low level of free fatty acid and water content. The presence of water may cause ester saponification under alkali process. Meanwhile, the free fatty acid will produce soap and water if it reacts with an alkali catalyst [9].

The saponification reaction is undesirable since it is not only consumes the catalyst but also forms soap which inhibits separation of biodiesel and glycerol due to emulsion formation during water washing step. Thus, the refined vegetable oils with low level of free fatty acid (1.0 %) and water content, anhydrous alcohol as well as catalyst are recommended to produce biodiesel through alkali-catalyzed processes [43, 60]. Sodium hydroxide (NaOH), sodium methoxide (NaOMe) and potassium hydroxide (KOH) are examples of base catalysts used in commercial biodiesel plant [21, 60].

Furthermore, the transesterification reaction can still be catalyzed with an alkali catalyst even the free fatty acid content of the feedstock reach up to 5%. Consequently, additional catalyst must be added to compensate for the catalyst lost to soap [75]. Sodium-based catalysts cost is lower than that of potassium-based catalyst. Thus, it is more frequently used than potassium-based catalysts.

Nevertheless, at the end of the reaction, the use of potassium hydroxide as catalyst can be neutralized by phosphoric acid. As a result, it will produce potassium phosphate which could be used as a fertilizer [60, 83].

Meanwhile, the use of hydroxide-based catalyst produces soap by neutralising the high free fatty acid content of oil and triglyceride saponification. Both of these soap formations are undesirable side reaction since it partially consumes catalyst and decreases the biodiesel yield. Although metal alkoxide solutions cost is higher than that of hydroxides but it is still used to produce biodiesel. It is safer, purer glycerol co-product is produced and more convenient to handle [21].

Freedman *et al.*, 1984 investigated base-catalyzed transesterification of sunflower oil with a 6 : 1 molar ratio of alcohol to oil and reaction temperature at 60^{o}C [43]. The use of 0.5 wt.% sodium methoxide in the reaction resulted in 99% yield of methyl ester in an hour. On the other hand, the yield of biodiesel was 98% after an hour when 1 wt.% sodium hydroxide was added into reactor. Methanolysis of refined sunflower oil at 65^{o}C with a 6 : 1 molar ratio of alcohol to oil and 1% of base catalyst based on weight of oil was investigated by Vicente *et al.*, 2004. They found that the yield of methyl ester was 99.33% and 86.71% for sodium methoxide and sodium hydroxide, respectively. It shows that at the optimum condition reaction, the methoxide catalyst is superior to the hydroxide catalyst [60].

Ethanolysis of refined soybean oil was studied by Kucek *et al.*, 2007 [20]. Soybean oil was transesterified using ethanol in the presence of base catalyst at 70^{o}C with a 12:1 molar ratio of alcohol to oil. Sodium hydroxide (0.3 wt.%) and potassium hydroxide (1 wt.%) were used to investigate the effect of alkali catalyst concentration to the yield of biodiesel. The yield of ethyl ester obtained was 97.2% and 95.6% for sodium hydroxide (0.3 wt.%) and potassium hydroxide (1.0wt.%), respectively [20].

Furthermore, used frying oil was catalyzed by base catalyst at reaction temperature of 70^{o}C with a 7.5 : 1 molar ratio of alcohol to oil [83]. They concluded that the use of 1.1 wt.% NaOH and 1.5 wt.% KOH resulted in 94 wt.% and 92.5 wt.% ester content, respectively, in an half hour of reaction time [83]. It shows that the required amount of sodium hydroxide is lesser than the amount of potassium hydroxide to produce biodiesel.

In addition, Rashid *et al.*, 2008 optimized the conditions to produce methyl ester by methanolysis of crude sunflower oil using alkali catalyst [26]. The optimum amount of methyl ester yield was achieved when the following reaction conditions were applied which is a 6 : 1 molar ratio of methanol to oil, 60^{o}C of reaction temperature and 1% (w/w) of NaOH concentration. The sunflower oil methyl ester yield reached up to 97.1% [26].

2.5.2 Heterogeneous Catalysts

As described previously, biodiesel is usually produced by alcoholysis of the vegetable oil using alkali homogeneous catalyst such as sodium hydroxide, sodium methoxide and potassium hydroxide [21, 60]. A number of investigators claimed that heterogeneous catalyst can be used to promote the transesterification reaction. The use of heterogeneous catalysts, KF/ZnO, KOH/NaX and Ba-ZnO for instances, showed that the conversion of the reaction could achieve up to 87% [35-37]. However, prior to its use in transesterification reaction, it has to be calcined at high temperature (873K) for 5 hours to obtain the best catalytic activity for the reaction [35, 36]. Furthermore, the conversion of the reaction is still small, thus the biodiesel obtained does not meet the requirement as fuel due to the presence of the unreacted mono-, di- and triglyceride.

Xie W and Huang X, 2006 applied KF/ZnO as a heterogeneous catalyst to produce biodiesel from soybean oil [35]. It was found that the amount of loaded KF and the calcination temperature to yield the highest basicity of 1.47 mmol/g and the best catalytic activity were at 15 wt.% and 873K, respectively. Later, the transesterification was carried out at methanol reflux temperature with a 10 : 1 molar ratio of methanol to oil in the presence of the 3% KF/ZnO catalyst in 9 hours. Under this condition, it was found that the conversion of soybean oil to biodiesel reached up to 87% [35].

Moreover, Xie *et al.*, 2007, also introduced another heterogeneous catalyst, NaX zeolite loaded with KOH, for the production of biodiesel from soybean oil [37]. NaX zeolite was loaded with 10% KOH, followed by heating at 393K for 3 hours. Then, the transesterification reactions were carried out at temperature of 338K with methanol to soybean oil molar ratio of 10 : 1 in 8 hours reaction time in the presence of catalyst with concentration varied from 1 wt.% to 6 wt.%. The conversion of soybean oil to fatty acid methyl esters reached up to 85.6% when the amount of the catalyst was 3 wt.%. Due to the economic reason, the used catalyst was regenerated by impregnating the catalyst in an aqueous solution of 5% KOH. Moreover, the conversion reached up to 84.3% [37].

In addition, Shumaker *et al.*, 2007 reported that methanolysis soybean oil using a calcined Li-Al layered double hydroxide as a catalyst resulted in high biodiesel yield at low catalyst loading (2 wt.%) and in a short reaction time (2 hours) [45]. At calcinations temperature of 450^{o}C, it showed that decomposition of the LDH to the mixed oxide without formation of less basic (and lower surface area) $LiAlO_2$ and $LiAl_5O_8$ phases. They also concluded that this catalyst still maintained a high level of activity over several cycles. However, the analysis showed that a small amount of lithium leached out from the catalyst [45].

2.5.3 Supercritical Alcohol

Biodiesel can also be produced through non-catalytic process, which is known as supercritical alcoholysis. In this non-catalytic process, the reaction time which required to convert all the triglyceride to alkyl ester is shorter than those of catalytic process either acids or alkalis catalysis. This process is also environmentally friendly because there is no waste water produced in post-treatment or washing process.

In addition, the purification of products is much simpler since there is no catalyst present in the products, only a removal of alcohol used is required. The possibility of this process to be used in producing biodiesel was investigated by several researchers. However, this approach requires a high temperature and pressure to carry out the transesterification reaction [56, 62, 85]. Consequently, the biodiesel production cost is very high. Therefore, this approach is not implemented yet in industrial scale.

Saka and Kusdiana, 2001 studied the transesterification reaction of rapeseed oil in supercritical methanol without using any catalyst [62]. This process was conducted in a vessel preheated at 350^{o}C and at a pressure of 45–65 MPa with a 1 : 42 molar ratio of oil to methanol and set interval time of supercritical treatment of methanol from 10 to 240 s. The results showed that in 240 s, this process was able to convert all the triglyceride to methyl ester. The yield of methyl ester obtained through this process was higher than the yield of biodiesel via base-catalyzed transesterification of rapeseed oil [62].

Furthermore, they also investigated the kinetics of transesterification of rapeseed oil to biodiesel as treated in supercritical methanol [67]. The experiments were conducted by varying the temperature, from 200^{o}C in subcritical to 500^{o}C in supercritical condition with different molar ratio of methanol to oil. They reported that the yield of methyl ester increased significantly in the supercritical state. The highest yield was obtained when the reaction was conducted at 350^{o}C with a 42:1 molar ratio of methanol to rapeseed oil [67].

This result is in accordance with the result reported by Song *et al.*, 2008 [85]. They studied a non-catalytic transesterification of RBD palm oil using supercritical methanol. The experiments were performed at various temperatures from 200 to 400°C and different methanol to RBD palm oil molar ratio of 45 and 60 at pressure of 40 MPa in 5 minutes reaction. The results showed that the highest content of methyl ester was obtained either with methanol to RBD palm oil molar ratio of 45 or 60 at 350°C reaction temperature [85].

2.6 Process Variables Affecting Yield of Biodiesel

Yield of biodiesel could be defined as the ratio of the actual amount alkyl esters produced to the amount of the alkyl ester produced theoretically [86]. The amount of this biodiesel yield depends on several parameters which affect the transesterification reaction such as type of catalyst and its concentration, molar ratio of alcohol to oil, reaction temperature, reaction time, free fatty acid and water content. All of those variables will be discussed in the following section.

2.6.1 Type of Catalysts and Their Concentration

Catalyst concentration and reaction time are the limiting conditions of the reaction to the amount of conversion [73]. Concentration of a catalyst is the main parameters affecting the yield of alkyl ester [20, 35, 50].

Akgun and Iscan, 2007 investigated the effects of process variables in producing biodiesel using response surface regression methodology with second-order polynomial equation [50]. The experiments were conducted at 65°C with an agitation speed of 1000 rpm using different kinds of catalysts (NaOH, KOH, $Ba(OH)_2$, wood ash and pyrolitic coke) and feedstocks (sunflower oil, corn oil, soybean oil, olive pomace oil, cottonseed oil). The results showed that the highest yield of biodiesel was obtained when a 1.3 wt.% NaOH was employed in an hour reaction time [50].

Factorial design and response surface methodology were used to optimize the alcoholysis of sunflower oil in the presence of potassium hydroxide as catalyst [87]. The catalyst concentration was varied from 0.5 to 1.5 wt.%. They reported that the catalyst concentration is the most important factor affecting the biodiesel yield followed by reaction temperature [87]. The highest yield of biodiesel was achieved at 25°C with KOH concentration of 1.3 wt.% and a 6:1 molar ratio of methanol to sunflower oil [87].

Karanja oil methanolysis with a 6 : 1 methanol to oil molar ratio and stirring speed of 600 rpm was carried out at 65°C for two hours in the presence of various concentration of potassium hydroxide [71]. It was reported that by varying the catalyst concentration from 0.25 wt.% to 1.5 wt.% with increment of 0.25, the highest methyl ester yield (96%) was obtained when the concentration of the catalyst was 1 wt.%. This result is known to be in a good agreement with the result reported by Darnoko and Cheryan, 2000 [18]. The optimal catalyst concentration used to yield the highest conversion of palm oil to methyl ester using a 6 : 1 molar ratio of methanol to oil at 60°C in 90 min reaction was 1wt.% KOH [18].

Rashid and Anwar, 2008 concluded that the optimum reaction conditions to achieve the highest sunflower oil methyl ester yield were : methanol to sunflower oil molar ratio of 6 : 1, reaction temperature at 60°C and NaOH concentration of 1 wt.%. The reaction was carried out at agitation rate of 600 rpm in 2 hours reaction time. Under these conditions, it was found that the biodiesel yield was 97.1% [21].

2.6.2 Molar Ratio of Alcohol to Oil

The most important factor affecting the yield of the biodiesel besides reaction temperature is the molar ratio of methanol to oil [88]. According to the transesterification reaction (Figure 2.1), the stoichiometry of the reaction shows that one mole of triglyceride requires three moles of the alcohol to produce 3 moles of fatty acid alkyl ester or biodiesel and one mole of glycerol. For the reason that the reaction is reversible, in order to drive the equilibrium towards biodiesel formation, it is necessary to use either an excess of alcohol or remove one of the products from the reaction mixture continuously. The higher the molar ratio of alcohol to oil, the faster the reactions to achieve equilibrium condition [20, 35, 43, 67, 71, 89].

Freedman *et al.*, 1984 studied the effect of molar ratio of alcohol to oil from 1 : 1 to 6 : 1 in the methanolysis of sunflower oil [43]. The reaction was carried out at 60^{o}C in an hour and catalyzed by sodium methoxide with concentration of 0.5 wt.%. The higher the molar ratio, the higher the biodiesel yield obtained. The conversion to methyl ester increased from 82% to 98% when the molar ratio was raised from 3:1 up to 6:1. The similar result was obtained while those parameters were implemented to methanolysis of soybean, peanut, and cottonseed oils. It showed that the highest conversions to esters were 93% – 98% when observed at the molar ratio of 6 : 1 [43].

On the other hand, in the alcoholysis of soybean oil with 1 wt.% H_2SO_4 as catalyst and molar ratio of 6 : 1 and 20 : 1, respectively, for 3 and 18 hours reaction time, conversions of triglyceride to ester were poor. It increased when the molar ratio was set higher to 30 : 1 for 3, 22 , and 69 hours reaction time for methanol, ethanol and buthanol, respectively which were conducted near to the boiling point of these alcohols [43].

Meanwhile, methanolysis of *Pongamia* oil at 45^{o}C in the presence of 1 wt.% KOH as catalyst with different molar ratio of methanol to oil such as 3 : 1 and 10 : 1, led to an outcome that the conversion of *Pongamia* oil to biodiesel was 80% and 83% in 1.5 hours of reaction time, respectively [82]. In addition, methanolysis of *Pongamia* oil in the presence of catalyst (1 wt.% KOH) was conducted at 65^{o}C with mixing speed of 600 rpm and molar ratio varied from 6 : 1 to 24 : 1. At a 6 :

1 molar ratio of methanol to oil, the yield of methyl esters was 97% for 3 hours reaction time and the same amount of biodiesel yield was obtained at molar ratio of 24 : 1 in 30 minutes of reaction time [71].

The effect of molar ratio of alcohol to oil was investigated using different feedstock between used frying oil (UFO) with acid value of 2.1 mg KOH/g and neat canola oil with the acid value of of <0.5 mg KOH/g . The transesterification was carried out at 70^{o}C with molar ratio varied from 3 : 1 to 11 : 1 in 15 min. The highest yield of biodiesel by transesterified neat canola oil and used frying oil was obtained at molar ratio 6 : 1 and 7 : 1 for the 1.0 wt.% NaOH and 1.1 wt.% NaOH, respectively. The yield of the biodiesel from the neat canola oil and the used frying oil was 90% and 87.5%, respectively [84].

The production of soybean oil methyl esters was conducted by methanolysis of the soybean oil in the presence of NaX loaded with KOH as heterogeneous catalyst. The optimum condition of molar ratio of alcohol to oil was studied by varying its value from 4 : 1 to 16 : 1 with increment of 2 when the reaction temperature (338K), reaction time (8 hrs) and catalysts' amount (3 wt.%) were kept constant. It showed that by increasing the molar ratio, the conversion of soybean oil would increase. But when the molar ratio is higher than 10 : 1, there was no significant effect to the conversion. Therefore, the maximum conversion of oil (85.6%) was achieved at the molar ratio of 10 : 1 [37].

2.6.3 Reaction Temperature

The most important parameter which affects the transesterification reaction based on the orthogonal test is the reaction temperature [32]. This is in accordance with the conclusion reported by Zheng [88]. The alcoholysis of the vegetable oil is recommended near at the boiling point of the alcohol used [26, 43]. On the other hand, Kucek *et al.*, 2007 concluded that the temperature has a negligible effect on the yield of ethyl ester [20].

Freedmad *et al.*, 1984 reported that for transesterification of refined soybean oil with a 6 : 1 molar ratio of methanol to oil and 1 wt.% sodium hydroxide which was conducted at three different reaction temperatures (60^{o}C, 45^{o}C and 32^{o}C) resulted the ester content to be 94%, 87%, 64%, respectively, after 0.1 hr. The percentage of the ester was identical for the reaction temperature at 60^{o}C and 45^{o}C, but slightly lower for 32^{o}C after 1 hour. After 4 hours, the formation of the ester was higher at 32^{o}C than those of others temperatures [43].

Temperature is an important parameter which can affect the reaction rate of biodiesel production. This was investigated by Doell *et al.*, 2008 on the transmethylation of soybean oil [65]. The experiments were carried out at four different reaction temperatures (23, 30, 40 and 50^{o}C) using 0.05 wt.% sodium methoxide as a catalyst with molar ratio of methanol to oil and THF to oil of 27:1 and 12 : 1, respectively. They reported that the higher the temperature, the larger the value of rate constant obtained for all of those reactions either in the formation of diglyceride, monoglyceride or glycerol [65].

The effect of temperature on the kinetics of palm oil transesterification was studied by Darnoko and Cheryan, 2000 [54]. The transesterification reaction was conducted at various temperatures which are 50, 55, 60 and 65^{o}C with KOH concentration of 1 wt.% and a methanol to oil molar ratio of 6 : 1 in 90 minutes of reaction time. The results showed that the conversion of tri-, di- and mono-glyceride appeared to be a pseudo second-order for the initial stages of the reaction (up to 30 min). The value of rate constant of those reactions increased at higher temperatures. In another word, it could be stated that the higher the temperature, the higher the conversion of triglyceride to methyl ester obtained [54].

Moreover, the effect of reaction temperature on the kinetics of the transesterification of monoglyceride of *Pongamia* oil was studied by Karmee *et* *al.*, 2004 [66]. Experiments were performed at four different temperatures such as 30, 45, 55 and 60^{o}C using 1 wt. % KOH with a 10 : 1 molar ratio of alcohol to monoglyceride in 150 minutes. They reported that the kinetics of the reaction followed a reversible second-order model, with a good fit obtained at all temperatures except for 30^{o}C. Their results showed that the higher the temperature, the higher conversion to methyl ester obtained in a short time which is in 30 minutes. After 30 minutes, there was no significant difference of the conversion obtained between those at 55 and 60^{o}C [66].

Kucek *et al.*, 2007 reported that reaction temperature has no significant effect to the ethyl ester obtained from ethanolysis of refined soybean oil [20]. The transesterification reaction was carried out at 30^{o}C and 70^{o}C with alcohol oil molar ratio of 12 : 1 in an hour. When NaOH concentration applied was 0.3 wt.% based on oil mass, the ethyl ester yield obtained was 96.8% and 97.2% at reaction temperature of 30^{o}C and 70^{o}C, respectively. Under the same reaction conditions applied for NaOH, the concentration of KOH used was 1 wt.%. It was found that with KOH as catalyst, the ethyl ester yield was 95.1% and 95.6% at 30^{o}C and 70^{o}C, consecutively [20].

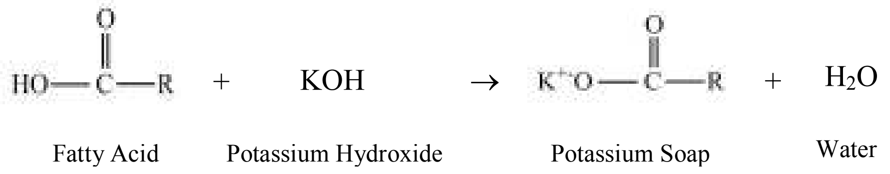
2.6.4 Reaction Time

In a batch system, the conversion efficiency of feedstock to alkyl ester is rapidly increased with increase in reaction time and it will be constant when the reactions reach an equilibrium condition [32, 90].

Darnoko and Munir, 2000 studied the effect of residence time in the production of palm methyl esters in a CSTR using a 6 :1 molar ratio of methanol to oil and 1 wt.% KOH as catalyst at 60^{o}C [18]. The results showed that the higher the residence time, the lower the concentration of methyl esters obtained due to a shift of the reaction equilibrium to the left. The optimum condition of the residence time to yield the highest methyl esters was 60 minutes [18].

2.6.5 Free Fatty Acid (FFA)

The oils or fats which are used as feedstock usually contain a small amount of water and free fatty acid. The feedstocks which have high level of free fatty acid require special processes to be involved in producing biodiesel. Alkali catalyst which is usually used to promote the reaction should not be applied since it will react with the acid and form soap. The maximum amount of free fatty acid content in the feedstock which can still be catalyzed by alkali catalyst is 1.0% [9]. An additional amount of alkali catalyst should be added into reaction if the amount of free fatty acid reaches 5% [75]. This additional amount of alkali catalyst is generally used to compensate the catalyst that loses to form soap. The formation of the soap can be seen in the following reaction when the catalyst applied is potassium hydroxide [72]:



$$HO-\overset{\overset{\displaystyle O}{\|}}{C}-R \quad + \quad KOH \quad \rightarrow \quad K^{+}\,{}^{-}O-\overset{\overset{\displaystyle O}{\|}}{C}-R \quad + \quad H_2O \qquad (2.13)$$

The soap that is formed during reaction will promote emulsification that causes the separation of ester and glycerol phase to be difficult. The free fatty acid content affects the process which will be used to produce biodiesel.

The amount of free fatty acid of mahua oil was reduced by esterification process with methanol (0.32 v/v) and an acid catalyst (1.24% w/v H_2SO_4) from 17% to 1% [91]. It showed that by increasing the reaction time, it had no significant effect to reduce the acid value. It could be caused by water that was produced during the esterification process. The more FFAs were esterified by methanol and an acid catalyst, the more water would be produced with increasing the time [91].

If the free fatty acid content of feedstock is higher than 5%, the feedstock should not be catalyzed by alkali-based because the biodiesel yield will be low. The following methods can be used to produce biodiesel if the free fatty acid is higher than 5% [72] :

1. Enzymatic method

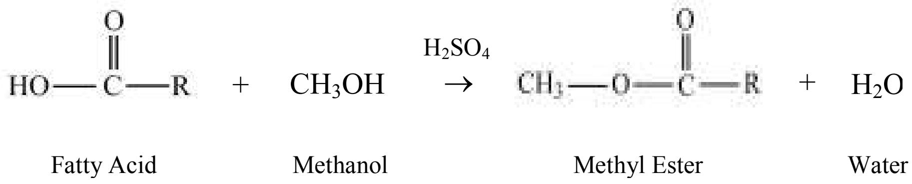
   This method appears to be less affected by water. On the other hand, the cost of enzymes is very expensive. It makes enzymes rarely to be used in biodiesel production on large scale [10].
2. Glycerolysis method

   Glycerolysis means that glycerol will be reacted with free fatty acid in the presence of ZnCl as catalyst to form monoglyceride and water. The reaction should be done at high temperature such as 200^{o}C for 2 until 3 hours. As a result, the free fatty acid content in the raw material will decrease less then 1%, and then based-catalyzed transesterification can be used for further process [72].
3. Acid catalysis method

   Acid catalyst is used to catalyze free fatty acid, whereas with an alcohol it will form an alkyl ester and water. This method should be carried out at high temperature and high pressure to complete the reaction in a short time. If the reaction is conducted at 60^{o}C and atmospheric pressure, the reaction will be completed in several hours and sometime it takes a few days [43].

4. Acid catalysis followed by alkali catalysis

   This two steps process is more effective compared to either single step acid catalysis or base catalysis if the free fatty acid content of feedstock is high (>5%). This process is used as a pre-treatment to convert the high level of free fatty acid of the feedstock to methyl ester. Thus, the free fatty acid content of the feedstock will decrease. The reaction is described as [72]:



$$HO-\overset{\overset{O}{\|}}{C}-R + CH_3OH \xrightarrow{H_2SO_4} CH_3-O-\overset{\overset{O}{\|}}{C}-R + H_2O \quad (2.14)$$

Ghadge and Raheman, (2006) investigated this approach using madhuca indica which had initial free fatty acid about 17 ± 0.5% as a feedstock [91]. This high free fatty acid level would be reduced in a pre-treatment step using acid catalyst prior to alcoholysis in the presence of base catalyst to produce biodiesel. The process was conducted under optimum conditions which were a 0.32% v/v methanol to oil ratio, 1.24% v/v H_2SO_4 as catalyst and 76 minutes of reaction time at 60°C. After the pre-treatment, the mixture of water and alcohol was removed by settling in a separator funnel for an hour and the product was subjected to transesterification. The base-catalyzed transesterification of madhuca indica was carried out at 60°C for half an hour with a 0.25 v/v ratio of methanol to oil in the presence of 0.7% w/v KOH and resulted in biodiesel yield to be 98% [91].

This method seems to be effective to produce biodiesel from *Jatropha curcas* with high free fatty acids content. It was applied by Tiwari *et al.*, 2007 using response surface methodology based on central composite rotatable design in order to optimize this process [7]. It was found that the optimum combinations to reduce the free fatty acid content from 14±0.5% to less than 1% in pre-treatment process were 1.43 v/v % H_2SO_4 as a catalyst and 0.28 v/v methanol to oil ratio in 88 minutes reaction time at 60°C. Then, after the second process using alkali catalyst, 0.55 w/v % KOH, it was found that the yield of biodiesel achieved was more than 99% [7].

In addition, this process was also used by Berchmans and Hirata (2008) to produce biodiesel from crude *Jatropha curcas* seed oil which has a high content of free fatty acids (15%) [61]. These free fatty acids were esterified at the first step using 1 w/w % H_2SO_4 as a catalyst with a 0.6 w/w ratio of alcohol to oil in 1 hour reaction at 50°C. After one hour of reaction, the mixture was allowed to settle in a separator funnel for 2 hours. Then, the mixture of methanol and water at the top layer was removed and to be subjected to the second step which was a base-catalyzed transesterification. This base–catalyzed transesterification was carried out at 60°C with ratio of alcohol to oil and ratio of NaOH to oil of 0.24 w/w and 1.4 w/w, respectively in a two hours reaction. The maximum yield of biodiesel achieved was 90% under the above conditions. It was higher than those obtained by single step base catalysis in which the yield of biodiesel was only 55% [61].

2.7 In Situ Transesterification

In situ transesterification is a process to produce biodiesel by transesterifying a raw material that contains the lipid-linked fatty acids with an alcohol and in the presence of catalyst [42]. Raw materials which can be used to form fatty acid alkyl ester are soy bean, rapeseed, palm, sunflower, rice bran, *Jatropha curcas* or mixtures thereof and in which the feedstock has not been treated to release the lipid components of the feedstock. This process, in situ transesterification, integrates the oil extraction and the transesterification reaction into single step process which could be reducing the cost of biodiesel production due to the elimination of extraction and refining oil processes.

Moreover, there are many reasons that can be considered in using the in situ method such as :

1. Lipid losses can be reduced because imperfect hull-kernel separation. Since whole seeds are subjected to esterification process, the overall yield of esters could be considered coming from the lipid content of the hull itself.
2. Transesterification in situ of sunflower seed oil resulted in higher yield of biodiesel compared to the yield that is obtained by treatment of the pre-extracted oil [53].

In addition, Siler-Marinkovic and Tomasevic, 1998 reported that yield of methyl esters obtained from acid-catalyzed transesterification of sunflower oil in situ is higher than that of conventional method [46]. The experiments were designed to determine the effect of molar ratio of methanol to oil, amount of acid catalyst, reaction time and reaction temperature to the yield and properties of methyl ester. The highest yield of methyl ester was obtained when 300 : 1 molar ratio of alcohol to oil was employed with reaction time and reaction temperature are 4 hours and 64.5^{o}C, respectively. However, the reaction was essentially complete in an hour when the molar ratio (300 : 1) was used [46].

Yucel and Turkay, 2003 studied the effect of free fatty acid content of rice bran oil, water content of ethanol and various monohydroxy alcohols to the yield of monoalkyl ester obtained [49]. They concluded that the higher free fatty acid content of feedstock, the higher ethyl ester content of crude ester produced due to higher fatty acid selectivity. Decreasing water content of ethanol will increase the amount of ethyl ester not only because of the equilibrium condition but also because of decreasing the solubility of neutral oil in ethanol. The highest ester content was obtained when the methanol was employed as a reagent instead of others alcohols [49].

In contrast, methanol is a poor solvent since the oil dissolved in it is less than those of others alcohols such as ethanol, n-propanol and n-butanol (Kildiran *et al.*, 1996) [47]. They investigated parameters that affecting the yield and purity of biodiesel through in situ alcoholysis of soybean oil using sulphuric acid as catalyst. It was reported that the oil which dissolved in the methanol after in situ process was approximately 20% of the total oil and the amount of the methyl ester was only 42%. On the other hand, the use of ethanol resulted the oil dissolved was 80.9% of the total oil. The solubility of triglyceride will increase in alcohol if the alcohol chain-length is increased. As a result, the amount of oil dissolved in the alcohol would also increase. Another important parameter which affecting the amount of ester obtained is the particle size of feedstock. By decreasing the particle size, the rate of extraction will increase. Consequently, the amount of ester produced is higher [47].

Furthermore, Ozgul-Yucel and Turkay, 2002 studied the variables affecting the yield of methyl esters derived from in situ esterification of rice bran oil [92]. They reported that either by increasing the initial amount of free fatty acid of rice bran oil or the reaction temperature, it will increase the methyl esters content. Meanwhile, the amount of methyl esters only slightly increased (2.16% – 3.22%) not only because of the longer duration of reaction time but also due to the more amount of catalyst. Moisture content of the rice bran oil had a little effect to yield of methyl ester. On the other hand, increasing the amount of methanol from 200ml to 250ml had no effect to the amount of methyl ester obtained [92].

Haas *et al.*, 2004 investigated an effective reaction condition to produce fatty acid alkyl ester from vegetable oil using in situ alkaline transesterification [93]. The experiments were designed using statistical experimental design methods and response surface regression analysis to optimize reaction conditions. As a result, the highest yield of biodiesel was obtained at a molar ratio of methanol/AG/NaOH of 226 : 1 : 1.6 and 60^{o}C reaction temperature in 8 hours incubation. In addition, in 8 hours incubation, the yield of methyl ester at room temperature (23^{o}C) is higher than that obtained at 60^{o}C but the molar ratio methanol/AG/NaOH used was 543 : 1 : 2 [93].

There are many sources which can be used as a feedstock for biodiesel production. Haas *et al.*, 2007 studied the applicability of lipid-bearing materials to be used in this process, known as in situ transesterification [24]. They reported that distillers dried grains with solubles (DDGS, which is co-product of the production of ethanol from corn), and meat and bone meal (MBM, which is a product of animal rendering) have a potential to be used as feedstock to convert it to fatty acid alkyl ester since it has a low economic value and contain 5–10%

lipid. The experiments were designed similar to the approach that they previously used, Haas *et al.*, 2004. This approach successfully converted both the DDGS and MBM to methyl ester in high yield of biodiesel [24].

Georgogianni *et al.*, 2007 have reported a comparison of the biodiesel yield which is produced by conventional and in situ transesterification methods, both of mechanical stirrer (600 rpm) and low frequency ultrasonicator (24 kHz) effect [94]. A higher yield of biodiesel on conventional method by methanolysis of sunflower seed oil either on mechanical stirrer or ultrasonication was reported when the higher concentration of catalyst (sodium hydroxide, 2.0 wt%) was employed. For the in situ transesterification process, the biodiesel yield was similar for both mechanical stirrer and ultrasonication effect for methanolysis of sunflower seed. On the other hand, ethanolysis of sunflower seed by ultrasonication was more effective in term of reaction time needed to complete the reaction in comparison with mechanical stirrer [94].

2.8 Summary

According to the above literature review, it can be stated that biodiesel can be produced through catalysis or non-catalysis process. The catalysis process consists of conventional and in situ transesterification processes which can be catalyzed either by acids or alkalis. Although acid catalyst can be applied to transesterify the low cost feedstocks which have high level of free fatty acid but the reaction conditions require high temperature, high molar ratio of alcohol to oil and longer reaction time to complete the reaction [43]. Thus, this approach is rarely applied in a large scale since its operating cost is higher than base-catalyzed transesterification using non edible oil for example *Jatropha curcas* as a feedstock [74].

Meanwhile, non-catalysis process can also be used to produce biodiesel. This process requires shorter time to complete the reaction. However, the reaction must be carried out at high temperature and pressure [62, 85, 89]. Consequently, this method can not be commercialized in industrial scale due to high production cost.

Using non edible oil as feedstock can reduce the total production cost of biodiesel since the greatest contributor to this value is the cost of the feedstock [39, 41, 44]. The biggest contributing factors to the high cost of the feedstock are the extraction and refining of vegetable oils. Thus, producing biodiesel directly on its raw material wherein it has not been treated to remove the lipid components of the feedstock will have a great opportunity to be applied in industrial scale since its production cost will be considerably reduced. Therefore, this method will be investigated in this study to produce biodiesel from *Jatropha curcas* and alcohol in the presence of alkali catalyst since its acid value is 1.391 mg of KOH/g. Table 2.3 summarizes the maximum biodiesel yield produced through the various methods discussed in the literature review section.

Table 2.3 Yield of biodiesel through different methods

Method	Max. Yield (%)	Catalyst (wt.%)	Temp. (^oC)	Time (min)	Alcohol oil molar ratio	Ref.
Alkali-Catalyzed Transesterification						
KOH – RBD Palm Oil	97.3	1	60	60	6 : 1	[18]
KOH – sunflower oil	96	0.28	70	-	3 : 1	[19]
NaOH – Soybean Oil	97.2	0.3	70	60	12 : 1	[20]
KOH – Soybean Oil	95.6	1	70	60	12 : 1	[20]
KOH – Rapeseed Oil	96	1	65	120	6 : 1	[21]

NaOH – Sunflower Oil	97.1	1	60	120	6 : 1	[26]
NaOH – WCO	89.8	1	50	90	6 : 1	[32]
KOH – RBD Palm Oil	90	1	60	90	6 : 1	[54]
KOH – Sunflower Oil	91.67	1	65	240	6 : 1	[60]
NaOH – Sunflower Oil	86.71	1	65	240	6 : 1	[60]
NaOMe – Sunflower Oil	99.33	1	65	240	6 : 1	[60]
KOH – Karanja Oil	97-98	1	65	120	6 : 1	[71]
KOH – Crude *Pongamia* Oil	92	1	60	90	10 : 1	[82]
KOH – Sunflower Oil	98.4	1.3	25	60	6 : 1	[87]
KOH – Mahua Oil	98	0.7w/v	60	30	6 : 1	[91]
Acid Catalyzed Transesterification						
H_2SO_4 - WFO	99±1	-	70	240	Oil:methanol:acid (1:245:3.8)	[34]
H_2SO_4 – Soybean Oil	92	1	65	4140	30 : 1	[43]
H_2SO_4 – Soybean Oil	99	0.5	100	480	9 : 1	[81]
Heterogeneous – Catalyzed Transesterification						
KF/ZnO – Soybean Oil	87[a]	3	na[b]	540	10 : 1	[35]

Ba/ZnO – Soybean Oil	95.2^a	6	65	60	12 : 1	[36]
KOH/NaX – Soybean Oil	85.6^a	3	65	480	10 : 1	[37]
$[Al_2Li(OH)_6]$ $(CO_3)_{0.5}$.mH2O – Soybean Oil	94±2	2	65	120	15 : 1	[45]
In Situ Transesterification						
H_2SO_4 – Sunflower	98.2	100%*	64.5	240	300 : 1	[46]
H_2SO_4 – Oil Palm	96–97	5.488	68	720	9.9 : 0.2816	[48]
H_2SO_4 – Rice bran oil	85.8	5 ml	65	60	200 ml : 50 gr seed	[49]
NaOH – Soy flake	940mg	0.09N	60	480	543 : 1	[93]
NaOH – Sunflower	98	2%	80	40	215 ml : 20 gr	[94]
Non-Catalysis Process						
Supercritical Methanol – RBD Palm Oil	93.33	-	350	5	45 : 1	[85]
Supercritical Methanol, nano – MgO	99.04	3	250	12	36 : 1	[89]

a conversion

na^b at reflux of methanol

* on oil basis

CHAPTER 3

RESEARCH METHODOLOGY

Experiment to synthesize biodiesel from *Jatropha curcas* seed using in situ technique were designed to determine the effect of process variations such as reaction time, reaction temperature, types of base catalysts and their concentration and variation of short chain alcohol such as methanol and ethanol that could affect the yield of fatty acid alkyl ester.

3.1 Materials and Chemicals

The raw material used in this work is *Jatropha curcas* and was purchased from CV. Tanah Karo Simalem, Lausolu, Indonesia. The following chemicals used in this research were supplied by Merck (Malaysia). These include pro analysis methanol (CH_3OH, with purity > 99.9%), pro analysis hexane ($CH_3(CH_2)_4CH_3$, with purity > 99.9), pro analysis sodium hydroxide (NaOH, with purity > 99%) and pro analysis isopropanol ($CH_3CH(OH)CH_3$, with purity > 99.8%). Meanwhile, sodium methoxide 30 wt.% solution in methanol (CH_3NaO) was purchased from Acros Organics (Malaysia). The other chemicals were purchased from GENE Chemical (Malaysia) which are analytical grade potassium hydroxide (KOH, with purity > 85%), ethanol absolute (C_2H_5OH, with purity > 99.7%) and sodium sulphate anhydrous (Na_2SO_4, with purity > 98%).

The reference standards for fatty acid methyl ester with gas chromatography grade were purchased from Supelco, USA. These standards consist of methyl laurate, methyl myristate, methyl palmitate, methyl stearate, methyl oleat, methyl linoleat, monoolein, diolein, triolein, 1,2,4 butanetriol and tricaprin. Meanwhile, N-Methyl-N-trimethylsilyltriflouroacetamide (MSTFA), pyridine (with purity 99%), glycerine and n-heptane were purchased from Sigma Aldrich (Malaysia).

The standards for fatty acid ethyl ester with chromatography grade were supplied by Sigma Aldrich (Malaysia). These include ethyl laurate (99%), ethyl myristate (98%), ethyl palmitate, ethyl stearate (95%), ethyl oleat (98%) and ethyl linoleat (99%).

The raw material and chemical that were used for synthesizing the biodiesel in this research are listed in Table 3.1 below:

Table 3.1 Raw material and chemical

No	Raw Material and Chemicals	Description
1	*Jatropha curcas* seeds	Its oil acid value is 1.391 mg of KOH/g
2	Methanol	With purity 99.9%
3	Ethanol absolute	With purity 99.7%
4	Hexane	With purity 99.9%
5	Sodium Hydroxide	With purity 99%
6	Potassium Hydroxide	With purity 85%
7	Sodium Methoxide	30 wt.% solution in methanol
8	Sodium Sulphate anhydrous	With purity 98%

3.2 Experimental Approach

The experiment is divided into two sections consisting of preliminary and main experiment. The preliminary experiment involves preparation of the *Jatropha* seeds through physical treatment including dehulling of the seeds, grinding, sieving and drying. In this case, moisture and oil content as well as acid value had to be determined prior to do the main experiment in which the in situ transesterification process would be carried out to produce biodiesel either as methyl ester, ethyl ester or mixture of both. The following paragraphs elaborate in details the physical treatment stage and the main experimental work consecutively.

3.2.1 *Jatropha* Seed Preparation

Prior to being subjected to in situ transesterification process, *Jatropha curcas* seed must be dehulled and ground in order to increase the efficiency of the extraction. Using a grinder, *Jatropha curcas* seeds were ground to the particle size of 500µm. For homogeneous and accurate particle size of the *Jatropha* seeds, sieve trays were used with size fractions from 100µm to 500µm mesh size. Figure 3.1 shows the prepared sample sizing of *Jatropha curcas* seeds.

Figure 3.1 *Jatropha curcas* seeds sizing

After the sizing process, the seed was then placed in the oven to eliminate any presence of moisture. The oven was set at 100°C for 2 hours. The moisture content of the seeds was measured using Mettler Toledo moisture analyzer [95]. 15g seed were placed in the sample pan. Prior to start calculating the sample's moisture content, ramp time (3 minutes) must be set, followed by setting the desired temperature of 100°C. The reading of the moisture content started when the temperature reached 100°C and it was continued until the reading was constant. It was found that the moisture content of the seeds were 1.51% ± 0.15. Figure 3.2 shows the moisture analyzer used.


(a) (b)

Figure 3.2 Determination of moisture content
(a) weighing the *Jatropha* seed (b) analyzing process

3.2.2 Oil Extraction

There are at least two common processes to extract oil from the seeds namely mechanical extraction and chemical extraction. Prior to be subjected to extraction process, the *Jatropha* seed was dried in the oven at 100^oC to reduce its moisture content. Using mechanical method to extract the oil, either whole seeds, kernels or both can be fed into the process. However, only kernels can be applied into the process if chemical extraction is used because the efficiency of the extraction will decrease in the presence of the hull [25].

3.2.2.1 Mechanical Expeller

To extract the oil from the seed mechanically, either a manual ram press or an engine driven screw press can be used. These mechanical expellers can extract the oil from the seed up to 60 – 65% and 75 – 80% of the available oil either using the manual ram press or engine driven screw press, respectively (Henning RK, 2000) [96].

3.2.2.2 Chemical Extraction

The oil can also be extracted chemically. The most common chemical used for extracting oil from the seeds is hexane since it can extract the oil up to 99% of the total amount of the oil available in the seed [25]. This solvent extraction will only be economical if it is applied in a large-scale production of biodiesel of more than 50 tons per day [25]. It is recommended to use solvent extraction if the mass flow rate is more than 300,000 kg/day [72].

In this work, chemical extraction is used to determine the oil content of the *Jatropha* seed using soxhlet extractor and hexane as a solvent. Either 10g, 20g or 30g of *Jatropha* seed were accurately weighed and placed in the thimble. Meanwhile, 140 ml of hexane with 99.9% purity was poured into the round bottom flask. The extraction time started when the temperature reached the boiling point of hexane (68^{o}C) and stopped after 2, 4 or 6 hours.

To get more accurate data, this extraction process was varied from 2 hours to 6 hours with increment of 2 hours. The equipment set-up is as shown in Figure 3.3. Based on the soxhlet extraction, it was found that the average oil content of the *Jatropha* seeds is 53.92% ± 0.19 as shown in the Figure 4.1.

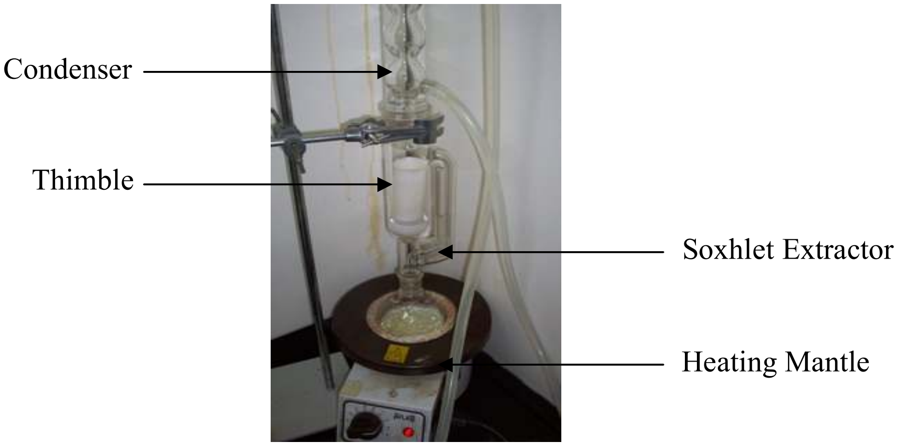


Figure 3.3 Soxhlet extraction

3.2.3 Acid Value Determination

According to American Standard for Testing Material (ASTM D 974–06), acid number is defined as the quantity of base, expressed in milligrams of potassium hydroxide per gram of sample that is required to titrate a sample to a specified end point. The formula to calculate the acid number based on ASTM D 974-06 is as follows [97] :

$$Acid\ number,\ mg\ of\ KOH/g = \frac{[(A-B)M \times 56.1]}{W} \tag{3.1}$$

where :

A = KOH solution required for titration of the sample, ml
B = KOH solution required for titration of the blank, ml
M = Molarity of the KOH solution
W = Sample used, g

Procedure to determine the acid number refers to ASTM D 974-06 [97]. 20g of *Jatropha* oils were dissolved in a mixture of toluene and isopropyl alcohol containing a small amount of water. Without any delay, the resulting single-phase solution was then titrated at a temperature below 30^{o}C with standard alcoholic base to the end point indicated by the colour change. To obtain more accurate data, determination of the acid number was randomly carried out in triplicates with deviation of 0.1. It was found that the acid number of the *Jatropha* oil was 1.391 ± 0.1 mg of KOH/g. Therefore, alkali catalysts were chosen to initiate the reaction. The acid value of the product was also determined to control the reaction time.

3.3 In Situ Transesterification

Synthesizing biodiesel from *Jatropha curcas* seed was carried out in a batch process. The process applied will be explained in details as follows. Catalyst either sodium or potassium hydroxide was dissolved in the alcohol (methanol, ethanol or mixture of both) with various concentration such as 0.5 wt.%, 1.0 wt.%, 1.5 wt.%, 2.0 wt.% and 2.5 wt.% of the oil content and the resulting solution was then transferred into a two-neck round-bottom flask and heated at the required temperature of 30, 40, 50, 60 or 70°C.

Later, an accurately weighed of 20g seed were poured into the two-neck round bottom flask of which the alcohol and catalyst were mixed and heated. The two-neck round bottom flask was equipped with a magnetic stirrer, a reflux condenser and a thermometer. This set up equipment is shown in Figure 3.4 below:

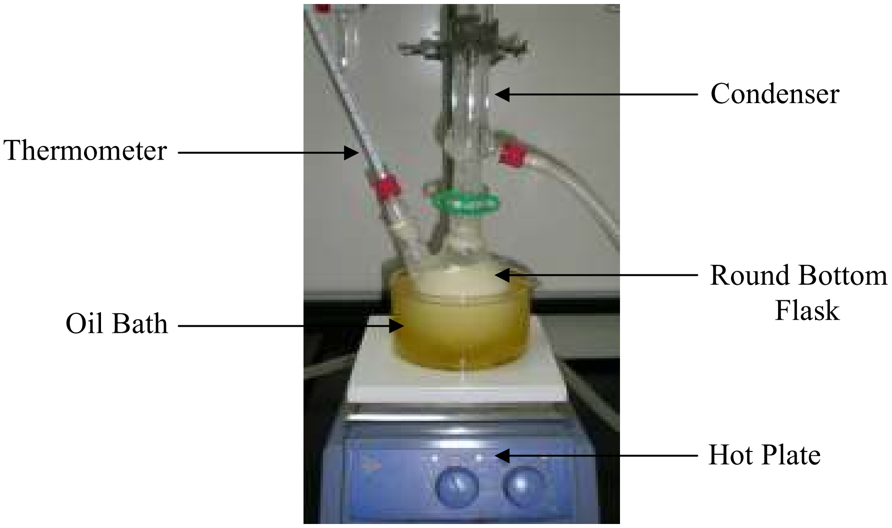
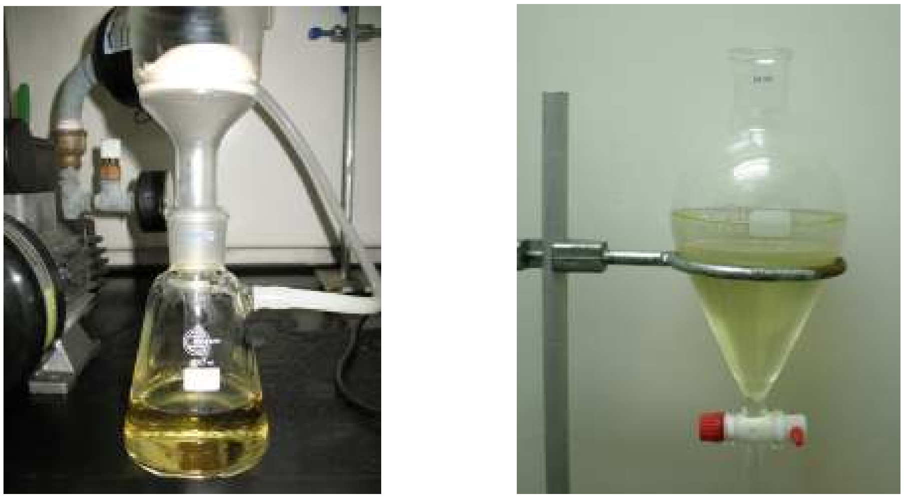


Figure 3.4 In situ transesterification processes

The reaction time was recorded when the reaction temperature reached the desired value of 30°C, 40°C, 50°C, 60°C or 70°C and stopped after 2, 4 or 6 hours. The reaction must be stopped to prevent the reverse reaction from occurring since transesterification is a reversible reaction. Then, the mixture was vacuum-filtered on a Buchner funnel to separate the solution from the cake. Thereafter, the filtrate obtained was transferred to a separator funnel and added with water and further extracted 3 times with hexane. This can be seen in Figure 3.5.



(a) (b)

Figure 3.5 Separation process (a) Filtration (b) Settling

Separation process would take up to 24 hours. There were two layers appeared in the separator as shown in Figure 3.5 (b). The top layer contained ester, a little bit of impurities such as unreacted triglyceride, catalyst, water and glycerol. The bottom layer contained alcohol, water, catalyst, glycerol and a little bit of ester. It was then separated by draining through the bottom of the settling funnel. Once the removal of bottom layer completed, the top layer was then poured into a beaker glass. The residual water however might still present in the top layer. Thus, the top layer was dried over sodium sulphate and the solution was filtered after 10 minutes to separate the solution from the sodium sulphate precipitate.

The solution was then evaporated using rotary evaporator which operated at 70^{o}C, 200 mmHg and 200 rpm to separate the alkyl ester from hexane. Next, the alkyl ester (biodiesel), was placed in a bottle and sealed. Thereby, the concentration of the product could be maintained prior to the analysis using Gas Chromatography according to ASTM D 6584 – 00 [98]. The separation process using rotary evaporator is shown in Figure 3.6.

Figure 3.6 Separation of hexane from biodiesel using rotary evaporator

3.4 Analytical Methods for Biodiesel

There are two types of analytical methods that were used in this research to analyze the composition of the biodiesel produced namely Thin Layer Chromatography (TLC) and Gas Chromatography (GC). Analyzing biodiesel is very important to ensure that the biodiesel produced is acceptable as fuel for use in compression–ignition (diesel) engines based on the ASTM D 6751[52]. Either the biodiesel could be used as a fuel or not depends on the level of impurities present in it.

These impurities include unreacted triglyceride, unseparated glycerol, free fatty acids, residual of both alcohol and catalyst and intermediate products such as mono- and di-glyceride. The presence of these contaminants in the biodiesel would have effect to engine performance due to operational problem such as filter clogging or engine deposit [14]. Thus, standards have been developed to limit the amount of the contaminants present in the biodiesel.

3.4.1 Thin Layer Chromatography (TLC)

Thin Layer Chromatography was used to identify the ester, free fatty acid, mono-, di- and triglyceride content in the samples qualitatively. Hexane, diethyl ether and acetic acid were used as solvents with percentage of 80, 20, 1 (vol%), respectively [42]. The sample was diluted in iso propanol with ratio of 1 : 4. Then, it was put on the silica plate with size of 2 cm x 10 cm and placed in a chamber in which the mixture of the solvent had been poured. Once the eluent reached the desired distance (7cm, represents as retention factor), the silica plate was moved into iodine chamber. 30 minutes later, it could be observed that there were many spots which represented the alkyl ester, triglyceride, free fatty acid, diglyceride and monoglyceride, from top to the bottom, respectively. This is illustrated in Figure 3.7 below.

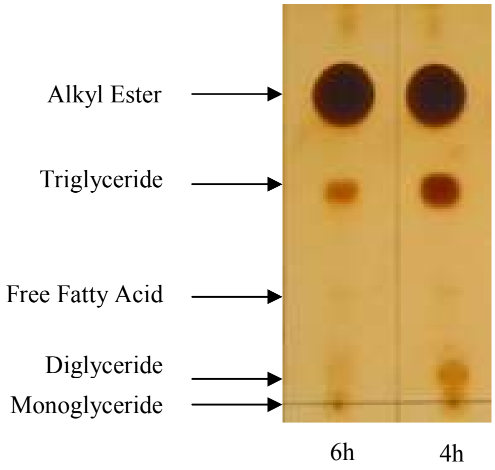


Figure 3.7 Thin layer chromatogram of ethyl ester for reaction time of 6 and 4 hours

3.4.2 Gas Chromatography (GC)

Gas Chromatography (GC) was used to determine the quantity of the biodiesel yield including the conversion of the triglyceride to biodiesel as main product. This method was conducted based on the ASTM D 6584–00 [98]. The biodiesel was analyzed using Gas Chromatography after silyating with N-methyl-Ntrimethylsilyltrifluoracetamide (MSTFA). The GC was equipped with an on-column injection and flame ionization detector (FID). The column used was HT-5 with a diameter, a film thickness and a length of 0.32mm, 0.1µm and 30m, respectively.

Its column temperature was set at initial temperature of 50°C for 1 minute. Then, it was increased to 180°C with rate of 15°C/min, followed by 7°C/min until 230°C, thereafter the rate was increased to 30°C/min until the temperature raise up to 380°C and it was held for 10 minutes. Moreover, The FID was set at 380°C and helium was used as carrier gas with flow rate of 3 ml/min.

Calibration curve was created by the use of two internal standards and four reference materials. Mono-, di- and triglyceride were determined by comparing to triolein, diolein and monoolein standards, respectively. After identification of the peaks from the chromatogram, the areas of the peaks identified as mono-, di- and triglyceride were measured. Based on the slope and y-intercept of the calibration functions, the individual glycerides can be calculated as follows [98] :

$$Gl_i = \left(a_o \times \frac{A_{gli}}{A_{is2}} + b_{o1} \right) \times W_{is2} \times \frac{100}{W} \tag{3.2}$$

where :

Gl_i = mass percentage of individual glycerides in sample

A_{gli} = peak area of individual glyceride

A_{is2} = peak area of internal standard 2

W_{is2} = weight of internal standard 2, mg

W = weight of sample, mg

A_{o1} = slope of the calibration function of mono-, di-, and triolein

B_{o1} = intercept of the calibration function of mono-, di-, and triolein

$$\textit{Total Glycerin} = \textit{Free Glycerin} + \textit{Bound Glycerin} \tag{3.3}$$

The amount of the free glycerine was determined by Gas Chromatography. Whereas the bound glycerine was calculated based on equation (3.4) [98] :

$$Bound\ Glycerin = \sum \left(Gl_M, Gl_D, Gl_T\right) \tag{3.4}$$

Where:

Gl_M = 0.2591 x Σ monoglyceride, mass % determined in equation 3.2
Gl_D = 0.1488 x Σ diglyceride, mass % determined in equation 3.2
Gl_T = 0.1044 x Σ triglyceride, mass % determined in equation 3.2

This analytical method was used to determine mono-, di- and triglyceride content in the final biodiesel samples. As a result, the yield of biodiesel can be calculated by the following formula [86] :

$$Yield\ of\ biodiesel\ (\%) = \frac{actual\ weigh\ of\ biodiesel}{theoretical\ weigh\ of\ biodiesel}\ x\ 100\% \tag{3.5}$$

Based on ASTM D 6751 – 07a [52], there are many parameters that must be fulfilled for an oil to be considered as a biodiesel (B100) before being used as a pure fuel or being blended with petrodiesel. The parameters are calcium and magnesium combined, flash point, methanol (alcohol) content, water and sediment, kinematic viscosity, sulphated ash, sulphur, copper strip corrosion, cetane number, cloud point, carbon residue, acid number, free glycerine, total glycerine, phosporus content, distillation temperature, sodium and potassium combined and oxidation stability. The limitation amount of those parameters is listed in the Table 3.2.

All of the above properties have its own test method such as flash point and cetane number refer to D93 and 613, respectively. As can be seen in the following Table 3.2:

Table 3.2 Detailed Requirements for Biodiesel (B100)

Property	Test Method[A]	Limits	Units
Calcium and Magnesium, combined	EN 14538	5 max	ppm (µg/g)
Flash point (closed cup)	D 93	93 min	°C
Alcohol control, one of the following must be met : 1. Methanol content 2. Flash point	 EN 14110 D 93	 0.2 max 130 min	 % volume °C
Water and sediment	D 2709	0.05 max	% volume
Kinematic viscosity, 40°C	D 445	1.9 – 6.0[B]	mm^2/s
Sulfated ash	D 874	0.02 max	% mass
Sulfur[C] Grade S 15 Grade S 500	 D 5453 D 5453	 0.0015 max* 0.05 max**	 % mass % mass
Cetane number	D 613	47 min	
Cloud point	D 2500	Report[D]	°C
Carbon residue[E]	D 4530	0.05 max	% mass
Acid number	D 664	0.5 max	mg KOH/g
Free glycerin	D 6584	0.02	% mass
Total glycerin	D 6584	0.24	% mass
Phosporus content	D 4951	0.001 max	% mass
Sodium and Potassium, combined	EN 14538	5 max	ppm (µg/g)
Oxidation Stability	EN 14112	3 min	hours

Source : ASTM D 6751 – 07a [52]

[A] The test methods indicated are the approved referee methods.

[B] The 6 mm2/s upper viscosity limit is higher than petroleum based diesel fuel and should be taken into consideration when blending.

[C] Other sulphur limits can apply in selected areas in the United States and in other countries.

[D] The cloud point of biodiesel is generally higher than petroleum based diesel fuel and should be taken into consideration when blending.

[E] Carbon residue shall be run on the 100% sample

* or 15 ppm and ** or 500 ppm

CHAPTER 4

RESULTS AND DISCUSSIONS

This chapter summarized results of the experiments and discussions. To provide reliable and precision data, the equipments were calibrated and the experiments as well as analysis of samples were repeated minimum of two times. The whole experiments were carried out in a batch reactor equipped with a reflux condenser, a magnetic stirrer and a thermometer as described in Chapter 3. All the samples produced in this work were analyzed using Gas Chromatography (GC Shimadzu 2010A) based on the American Standard for Testing Material for determination of free and total glycerine in B-100 biodiesel methyl esters (ASTM D-6584-00) [98].

Synthesis of biodiesel using alkali in situ transesterification of *Jatropha curcas* was studied with the following process variables as tabulated in Table 4.1.

Table 4.1 Process variables involved in the in situ transesterification of *Jatropha curcas*

No	Process Variables	Description
1	*Jatropha curcas* seed	20 gram
2	Alcohol	Methanol, ethanol and mixture of methanol-ethanol (50% : 50%)(v/v)
3	Catalyst	KOH, NaOH and NaOMe
4	Catalyst's conc.	0.5 wt.%, 1.0 wt%, 1.5 wt.%, 2.0 wt% and 2.5 wt.%
5	Time	2h, 4h, 6h, 12h* and 24h* (*methanol only)
6	Temperature	30°C, 40°C, 50°C, 60°C and 70°C
7	Stirrer speed (rpm)	200, 400 and 600
8	Ratio of methanol to *Jatropha* seed	4.67, 7 and 14 (vol/wt)

4.1 Properties Of *Jatropha curcas* Oil

Prior to synthesizing the biodiesel from *Jatropha curcas* using in situ method, the *Jatropha* seed was ground to particle size of 500 µm and dried in the oven at 100°C to remove the moisture content. The moisture content of the seeds was measured by Mettler Toledo moisture analyzer and was found to be 1.51% ± 0.15. To determine the oil content of the *Jatropha curcas* seed, the seed was extracted using hexane as a solvent in a soxhlet apparatus. It was found that the average of the oil content in the *Jatropha* seeds was 53.92 ± 0.19 %. The percentage of the oil content is presented in the following graph, Figure 4.1.

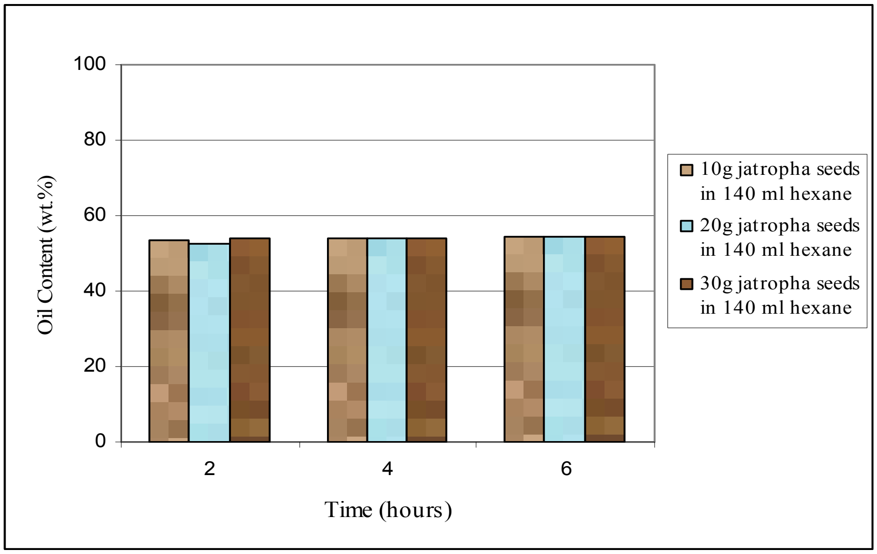


Figure 4.1 The oil content of *Jatropha curcas* seed

As shown in Figure 4.1, increasing the extraction time does not significantly affect the amount of extracted oil. Extending the extraction time from 2 to 6 hours, the percentage of extracted oil can be considered constant. It means that the oil content in the *Jatropha* seed can be completely extracted in about 2 hours using 140ml hexane. As the amount of the seed was increased from 10g to 30g, the percentage of extracted oil was also constant at constant volume of hexane

(140ml). The acid value of the oil was determined based on the ASTM D 974 – 06 [97] and was found to be 1.391 ± 0.1 mg of KOH/g.

Akintayo E T, (2004) reported that the oil content of the *Jatropha curcas* seed and acid value of the oil was 47.25 wt.% and 3.5 mg KOH/g, respectively. They used *Jatropha curcas* seed which was purchased from Ado-Ekiti, Nigeria [99]. They used hexane as solvent to extract the oil from the *Jatropha* seed in a soxhlet apparatus and determined the oil content in it. They determined the acid value of the oil based on the method described by the Association of Official Analytical Chemists (AOAC, 1984) [99].

The difference of the oil content and the acid value reported by Akintayo E T, (2004) and the results obtained in this work can be caused by the conditions of the *Jatropha* seed and the way to store the *Jatropha* seed before it is used. The highest oil content in the *Jatropha* seed will be obtained when it is in ripe condition. In addition, it has low acid value when it is keep in dry storage. If the seed is stored for a long time, the acid value will increase due to oxidation of the polyunsaturated fatty acid (linoleic acid). This phenomenon was observed during the experiment.

The other parameters that were tested to the *Jatropha* oil are tabulated as follows:

Table 4.2 Physical-chemical properties of *Jatropha curcas* oil

Parameter	*Jatropha* Oil*	*Jatropha* Oil[99]
Acid Value (mg KOH/g)	1.391 ± 0.1	3.5 ± 0.1
Free Fatty Acid (%)	0.698 ± 0.1	1.76 ± 0.1
Saponification Value (mg KOH/g)	200.23 ± 0.5	198.85 ± 1.4
Viscosity (30°C, 40°C), cP	(47.8, 45.9)	(17.1, -)**
Specific Gravity (20°C, 25°C)	(0.9159, 0.9136)	(0.9095[77] ,0.919)
Calorific Value (cal/g)	9358.32 ± 82.37	9036.1 ± 20.1[4]

** Jatropha oil used in this research*

*** cSt and ± means that standard deviation of triplicates determinations*

As shown in Table 4.2, the free fatty acid of the *Jatropha* oil used in this research work is 0.698%. It means that if the oil is used as a raw material to produce biodiesel, base catalysts can be applied to enhance the reaction. Base catalysts have advantages such as it can be used at room temperature and at atmospheric pressure and also the time which is required to complete the reaction is shorter than that of acid catalyst [43]. Table 4.2 also shows that the high gross heat value of the *Jatropha* oil (9358.32 cal/g) indicates that the *Jatropha curcas* may serve as an intermediate source of energy [4]. Therefore, both *Jatropha curcas* and base catalyst were applied in this work.

In order to achieve the optimum conditions for synthesizing biodiesel through in situ transesterification of *Jatropha curcas*; reaction time, catalyst concentration, reaction temperature and stirrer speed were manipulated. The effects of these parameters on the yield of biodiesel produced are discussed in the following sections. During the experiments, the quantity and the particle size of the *Jatropha* seeds were kept constant at about 20g and 500µm except for the in situ methanolysis of *Jatropha curcas*, a 10, 20 and 30g of the seeds were used. The catalyst concentration needed was calculated based on the mass of the oil content in the seed.

4.2 In Situ Methanolysis of *Jatropha* Seed

In this work, methanol was used as a solvent and as a reactant to extract the oil and react it simultaneously to produce biodiesel and glycerol. This process is also known as in situ transesterification. The process was conducted at different reaction time, type of catalysts and their concentration, stirrer speed and the amount of the *Jatropha* seed. Each experiment was carried out in duplicates to obtain an average data.

4.2.1 Effect of Reaction Time

The reaction was conducted at 60°C with stirrer speed of 100 rpm. The catalyst used was NaOH with 1 wt.% concentration and ratio of alcohol to *Jatropha* seed was 7 (vol/wt). Initially, the reaction time was varied from 1h, 2h and 3h with *Jatropha*'s weight of 20g. Due to less amount of biodiesel obtained under this range, the reaction time was then extended to 24 hours. Increasing the reaction time from 3 to 24 hours increased slightly the weight of the biodiesel. However, the amount of the biodiesel produced was less than that of expected. It was expected that the weight of the biodiesel could reach up to 8–10g.

After 24h, the amount of the biodiesel produced was only 3.45 ± 0.7g. This was probably due to low stirrer speed or solubility of the methanol. At lower stirrer speed, the contact between methanol and *Jatropha* seed would be less. As a consequence, some of the *Jatropha* seeds were suspended in the round bottom flask. It means that not all the oil in the seed was recovered by the methanol and converted to biodiesel. Moreover, the low solubility of the methanol can also affect the amount of oil that is extracted and reacted to form biodiesel. The yield of the biodiesel obtained is illustrated in Figure 4.2. The maximum biodiesel yield obtained was 34.5%.

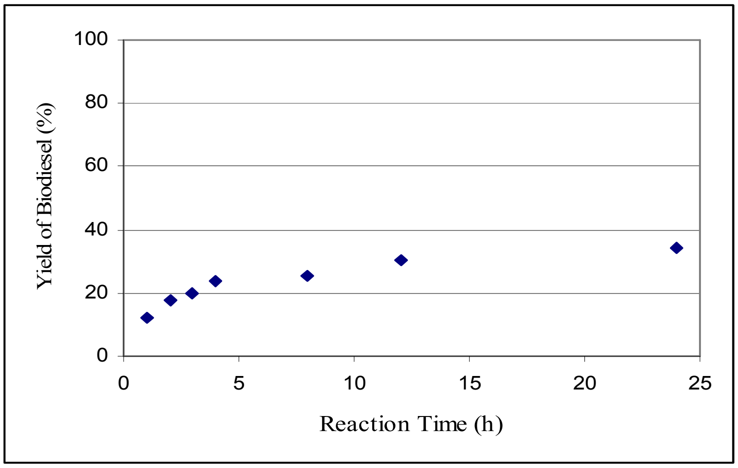


Figure 4.2 Yield of biodiesel produced in the in situ methanolysis of *Jatropha curcas* seed

4.2.2 Effect of Catalysts and Their Concentration

To investigate the effect of the base catalysts and their concentrations, both sodium and potassium hydroxide were used to catalyze the reaction with various concentrations of 0.5, 1.0, 1.5, 2.0 and 2.5 wt.%. The in situ methanolysis of *Jatropha* seed was carried out at 60^{o}C with stirrer speed and ratio of methanol to the seed of 100 rpm and 7 (vol/wt), respectively. The maximum yield of the biodiesel obtained when NaOH and KOH used was 41.12% and 28.57%, respectively.

The average weight of the biodiesel produced is shown in the Table 4.3. It showed that the amount of the biodiesel increased as the concentration of catalysts (NaOH and KOH) was increased from 0.5 to 1.5 wt.%. On the other hand, the weight of the biodiesel decreased when the catalyst concentration was increased from 1.5 to 2.5 wt.%. This occurred due to the formation of soap, which increased the viscosity of the reactants and as a result lowered the amount of the biodiesel. This was in accordance with the results reported by Meher *et al.* (2006) [71] and Dorado *et al.* (2004) [100].

Meher *et al.* (2006) investigated the effect of the concentration of KOH on methanolysis of Karanja oil [71]. The concentration of the KOH was varied from 0.25 to 1.5 wt.%. The reaction was conducted at 65^{o}C with 6 : 1 molar ratio of alcohol to oil and stirred at speed of 600 rpm for 2 hours. They concluded that the optimum amount of the catalyst to speed up the reaction to completion was 1 wt.% with a yield value of 96% [71]. However, the acid value of the oil that they used was 0.6 mg KOH/g, whereas the jatropha oil's acid value was 1.391 ± 0.1 mg of KOH/g. At low acid value, the saponification of the triglyceride and neutralization of the free fatty acid was negligible. Consequently, the concentration of the base catalyst needed to complete the reaction was low since there was no side reaction.

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Table 4.3 Average weight of biodiesel produced at various catalyst concentrations

Catalyst Concentration (wt.%)	Weight of Biodiesel (gram)	
	NaOH	KOH
0.5	3.33 ± 0.36	1.84 ± 0.35
1.0	3.45 ± 0.7	2.25 ± 0.24
1.5	4.03 ± 0.9	2.80 ± 0.3
2.0	3.59 ± 0.5	2.81 ± 0.2
2.5	-	-

4.2.3 Effect of Stirrer Speed

Mixing is very important for the in situ transesterification of *Jatropha curcas* since in the in situ method the extraction and reaction occur simultaneously on its raw material. The extraction rate can be increased either by reducing the size of the raw material or by increasing the stirrer speed. As the size of the feedstock decreased, its surface area would be bigger. Thus, the extraction rate would increase. Meanwhile, increasing the stirrer speed will improve the homogeneity of the seed and base-methanol solution. Therefore, the extracted oil will be higher than that when lower stirrer speed is used.

The influence of the stirrer speed on the in situ methanolysis of *Jatropha curcas* was investigated by varying the stirrer speed from 100, 200, 400 and 600 rpm. The ratio of methanol to the seed was kept constant at 7(v/w) with NaOH concentration and reaction time of 1 wt.% and 24h , respectively. The reaction was carried out at 60^{o}C in triplicates in order to obtain an accurate data. The weight of the biodiesel obtained is presented in Table 4.4.

As shown in Table 4.4, at higher stirrer speed, more biodiesel was produced. It might be caused by increasing the stirrer speed, more oil could be extracted from the seed and promoted the homogenization of the reactants. Without sufficient mixing, the reaction would only occur at the interface of the base-alcoholic solution and oil. Therefore, the reaction rate was considered too slow to be feasible [101].

Table 4.4 Weight of the biodiesel obtained at different stirrer speed

Stirrer Speed (rpm)	Weight of Biodiesel (gram)
100	3.45 ± 0.7
200	3.64 ± 0.8
400	3.75 ± 0.64
600	4.19 ± 0.53

In the in situ transesterification of *Jatropha curcas*, the amount of the biodiesel produced not only depends on the stirrer speed but also on the size of the *Jatropha* seed used. In this work, the size of the *Jatropha* seed was kept constant at 500µm. At higher stirrer speed, more base-alcoholic solution was dispersed in the oil. Under this condition, mass transfer occurred due to different concentration and this enhanced the rate of reaction. As a result, an increase in the weight of the biodiesel was observed as shown in Table 4.4.

4.2.4 Effect of Ratio of Methanol to *Jatropha* Seed

One of the most important variables that affect the alkyl ester formation is molar ratio of alcohol to oil. A 6 : 1 molar ratio of alcohol to oil is usually applied on alkali-catalyzed transesterification of vegetable oil [21, 71, 84]. The reaction will be faster at higher molar ratio and it will require longer reaction time to achieve the same conversion at lower molar ratio [71]. In situ method is different from conventional method since the alcohol acts both as a solvent and as a reactant to extract the oil and react with it to form biodiesel and glycerol. Therefore, the amount of the alcohol used in conventional method is lesser than that of in situ method.

In this work, for the in situ methanolysis of *Jatropha* seed, the ratio of methanol to *Jatropha* seed used was 140 : 10, 140 : 20 and 140 : 30 (vol/wt). The in situ process was carried out at 60^{o}C with stirrer speed of 600 rpm in the presence of 1 wt.% NaOH for 24h. The percentage of the biodiesel obtained is tabulated in Table 4.5. It can be seen that the lower the ratio of methanol to oil, the lower the percentage of the biodiesel obtained. It showed that as quantity of the *Jatropha* seed increased, the lower the capability of methanol to extract the oil from the seed.

Table 4.5 Percentage of biodiesel at different ratio of methanol to *Jatropha* seed

Ratio of Methanol to Seed (v/w)	Percentage of Biodiesel (wt.%)
140 : 10	40.23 ± 0.42
140 : 20	39.52 ± 0.51
140 : 30	23.48 ± 0.64

Siler-Marinkovic and Tomasevic (1998) investigated the effect of molar ratio of methanol to oil in the in situ transesterification of sunflower oil [46]. They concluded that in situ methanolysis with 300 : 1 molar ratio of methanol to oil was essentially complete in an hour [46]. They conducted the experiment at 64.5^{o}C by varying the molar ratio from 100 : 1 to 300 : 1. They found that the composition of the products derived from in situ process was similar to the conventional method and this was in accordance with the results obtained in this work. However, the in situ of *Jatropha curcas* seed using methanol was unsuccessful in terms of the biodiesel yield produced. The highest percentage of the biodiesel obtained was 40.23%.

The formation of biodiesel could be affected by the solubility of the alcohol [76]. As mentioned earlier, methanol acted as solvent to extract the oil from the raw material and also behaved as a reactant to react with the oil to produce biodiesel. If the capacity of the methanol to extract the oil was poor, the biodiesel produced would be low. Even though parameter such as particle size, stirrer speed and reaction time were manipulated at their optimum conditions, the biodiesel production gave unsatisfactory result. Thus, it can be concluded that this occurred due to the low solubility of the methanol. This was in accordance with the results reported by Kildiran *et al.* (1996) [47].

Kildiran *et al.* (1996) reported that methanol was a poor solvent for soybean oil [47]. As a result, the amount of oil dissolved in methanol and converted to biodiesel was low after in situ process. They used soybean with particle size of 0.5 mm in the presence of 6ml concentrated sulphuric acid. The in situ alcoholysis was conducted at 65^{o}C for 3h reaction time. After in situ alcoholysis, the oil dissolved in the methanol was 19.8% (wt/wt) of the total oil and the fatty acid methyl ester content of this dissolved oil was 42% (wt/wt) [47].

In this work, even though the in situ transesterification was conducted for 24h, the yield of the biodiesel was still unsatisfactory. This followed the results reported by Kildiran *et al.* (1996) [47]. However, Siler-Marinkovic and Tomasevic (1998) found that in situ methanolysis of sunflower was successful in an hour. This might be caused by the particle size and the stirrer speed that they used in their research. However, this information is not stated in their paper.

4.3 In Situ Ethanolysis of *Jatropha* Seed

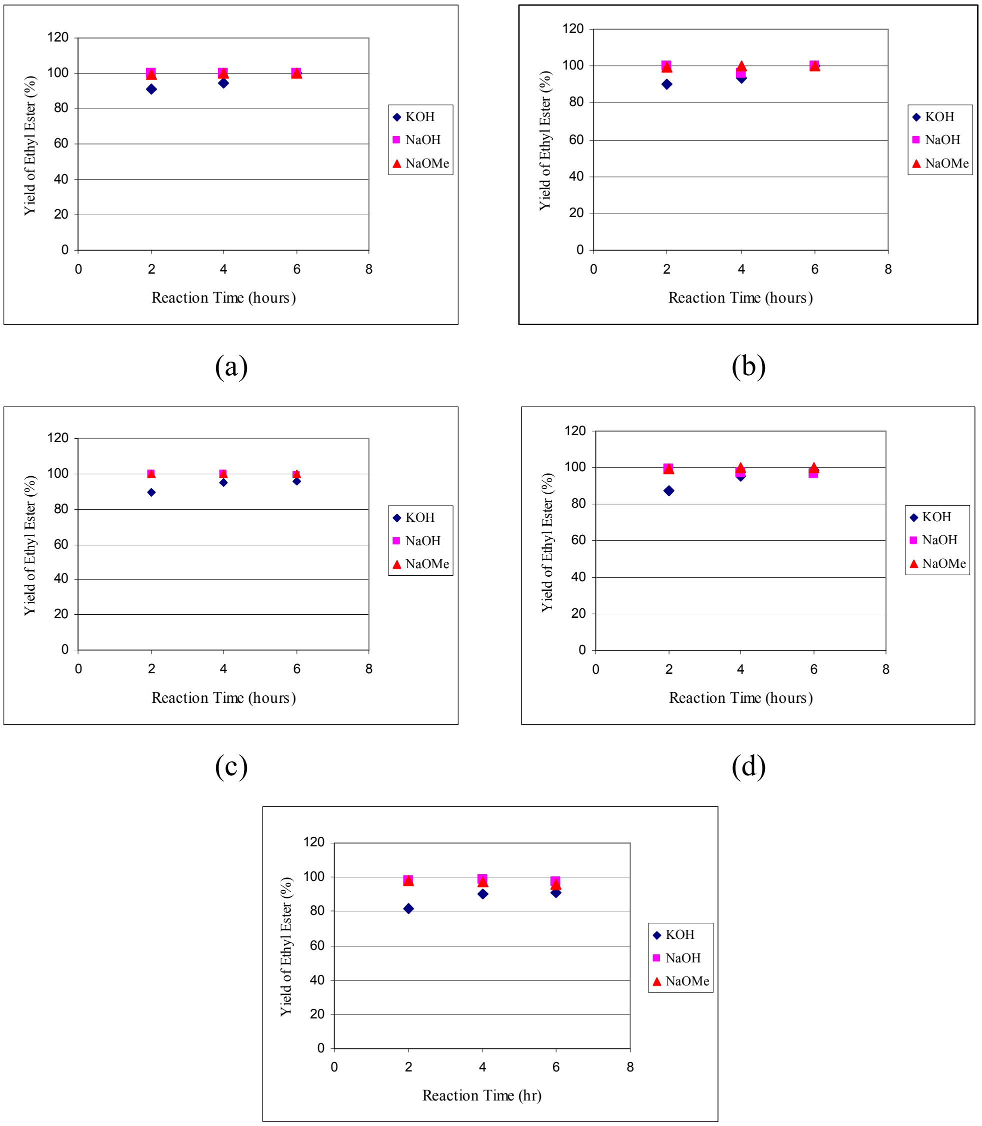
There were many variables that were investigated related to the in situ ethanolysis of *Jatropha* seed, for instances: reaction time of 2, 4 and 6 hours, type of catalysts (KOH, NaOH and NaOMe) and their concentration of 0.5, 1.0, 1.5, 2.0 and 2.5 wt.%, stirrer speed of 200, 400 and 600 rpm and reaction temperature of 30, 40, 50, 60 and 70^{o}C. All the above manipulated variables were investigated to observe their effect on the yield of the biodiesel produced. The effect of these manipulated variables on the yield of biodiesel will be discussed in the following sections.

4.3.1 Effect of Reaction Time

There are several references discussing the effect of reaction time on the transesterification of vegetable oil, animal fat or waste cooking oil [46, 84]. To investigate the effect of the reaction time on the synthesis of biodiesel, the reaction was conducted at three different reaction time of 2, 4 and 6 hours with reaction temperatures of 30, 40, 50, 60 and 70°C in the presence of 2.5 wt.% of alkali catalyst of KOH, NaOH and NaOMe.

The effect of reaction time on the yield of ethyl ester will be discussed based on the Figure 4.3. As illustrated in the Figure 4.3, it can be observed that the profile of the yield of ethyl ester is similar to each other. It showed that the yield of ethyl ester nearly reached 100% in two hours. Increasing the reaction time to 6 hours slightly decreased the yield of ethyl ester especially when sodium hydroxide and sodium methoxyde were used. This might be caused by the reversible transesterification reaction which was involved in this process.

The experiments were conducted in a constant-volume batch reactor. Consequently, the longer the reaction time, more products were produced. When the product was continuously produced for 6 hours, the reaction tends to shift to the left since the reaction was completed in 2 hours. This phenomenon can be explained through Le Chatelier’s principle. Therefore, to produce a maximum product, the reaction should be stopped when the reaction had reached an equilibrium condition wherein the maximum conversion obtained.



(a)

(b)

(c)

(d)

(e)

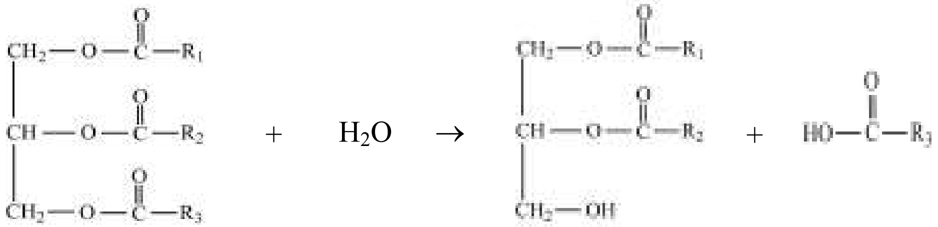
Figure 4.3 Effect of reaction time on the synthesis of biodiesel using catalyst concentration of 2.5 wt.% at various reaction temperature of (a) 30°C, (b) 40°C, (c) 50°C, (d) 60°C and (e) 70°C

From Figure 4.3, when KOH was used to enhance the reaction, it can be concluded that the longer the reaction time the higher the yield of ethyl ester was obtained. It showed that the amount of KOH used was insufficient to accelerate the reaction for completion in a short time. At the same concentration, KOH requires longer time than that of NaOH and NaOMe to achieve the same yield of ethyl ester. It might be caused either by the formation of water during the preparation of KOH or higher molecular weight of KOH compared to NaOH. The formation of water is illustrated by the following reaction :

$$CH_3{-}OH \quad + \quad OH^- \quad \rightarrow \quad CH_3{-}\ddot{\underset{\cdot\cdot}{O}}{:}^- \quad + \quad H_2O$$

Methanol Hydroxide ion Methoxide ion Water

The presence of water can inhibit the reaction since it causes soap formation and also hydrolyze the triglyceride to form diglyceride and free fatty acid. It is illustrated as follows :



Triglyceride Water Diglyceride Fatty Acid

Kildiran G *et al.,* (1996) reported that as the reaction time increased, the more amount of oil dissolved in ethanol [47]. They conducted the in situ transesterification of 50 g soybean with 150 ml of 98.8% ethanol in the presence of 6 ml of concentrated sulphuric acid for 3 hours at 78°C [47]. After 3 hours, the oil dissolved in the ethanol was 97%. However, only 80.7% of the oil was converted to ethyl ester [47]. It showed that either catalyst concentration or reaction time was not enough to achieve the reaction to be completed.

In this work, the amount of oil dissolved in ethanol was similar to the result that reported by Kildiran G *et al.,* (1996) [47]. It was found that the oil dissolved in ethanol was 97.59 % in 2h while Kildiran G *et al.,* (1996) found that the oil dissolved in the ethanol reached 97% in 3h. On the other hand, the amount of the fatty acid ethyl ester produced in this work was higher than that reported by Kildiran G *et al.,* (1996) [47]. Kildiran G *et al.,* (1996) concluded that the content of the ethyl ester in the biodiesel sample was found to be 80.7%. Meanwhile, in this work the amount of the ethyl ester reached up to 98.12%.

The different amount of the biodiesel yield was due to the different types of catalyst used. Kildiran G *et al.,* (1996) applied sulphuric acid as catalyst whereas in this work sodium methoxide was employed as catalyst. As mentioned in Chapter 2, an acid catalyst requires longer reaction time to complete the reaction than that of a base catalyst. This might be caused by the difference of the activity formation of a more electrophilic species (acid catalysis) and a stronger nucleophile (base catalysis) [30]. This discrepancy might be also due to the different of the stirrer speed used. Sufficient stirrer speed is required to promote the homogeneity between reactants. Thus, this increases the reaction rate. However, the information about the stirrer speed that they used is not stated in their paper.

4.3.2 Effect of type of catalysts and their concentration

Base catalyst is the most common used to accelerate the transesterification reaction on the synthesis of biodiesel. There are several base catalysts that usually employed in the biodiesel production which include sodium hydroxide, potassium hydroxide and sodium methoxide. Therefore, to investigate the effect of type of the base catalyst and its concentration, all the three catalysts were used in this research. The synthesis of biodiesel from *Jatropha curcas* using in situ method was carried out in a batch reactor equipped with a reflux condenser for 2, 4 and 6 hours.

Various catalyst concentrations in this work were also used to investigate their effect on the biodiesel yield produced. Their concentration include 0.5, 1.0, 1.5, 2.0 and 2.5 wt.% (based on the oil). The experiments were conducted at four different reaction temperatures of 30, 40, 50 and 60°C. The profiles influence of catalyst concentration and biodiesel yield is shown in Figure 4.5.

The following presented chromatogram, Figure 4.4, illustrates the effect of type of base catalyst on the synthesis of biodiesel from *Jatropha curcas* using in situ transesterification process. The existence of glycerol, mono-, di- and triglyceride in the biodiesel samples represents the quality of the biodiesel. It is stated in ASTM D 6751 – 07a that the maximum allowable value of free and total glycerine in the biodiesel is 0.02 and 0.24 wt.%, respectively [52]. The amount of the free glycerine was determined by Gas Chromatography.

The total glycerine content of the biodiesel was calculated based on the following equation :

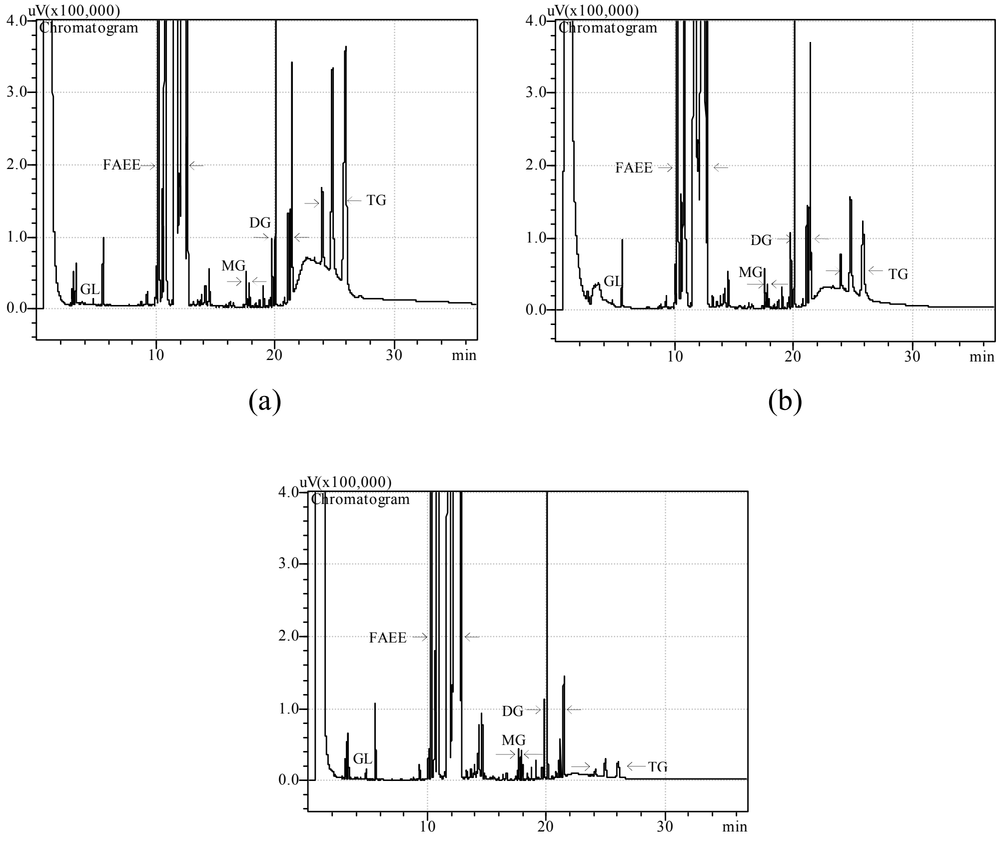
$$Total\ Glycerin = Free\ Glycerin + Bound\ Glycerin \tag{4.1}$$

Where bound glycerine was determined follow the equation (4.2) :

$$Bound\ Glycerin = \sum \left(Gl_M, Gl_D, Gl_T \right) \tag{4.2}$$

Where Gl_M, Gl_D and Gl_T was calculated based on equation 3.2.

According to Figure 4.4, either the reaction was catalyzed by 1.0 wt.% KOH, NaOH or NaOMe, the free glycerine content in the biodiesel was meet the requirement of the ASTM D 6751 – 07a since its value was 0.02 wt.%. The free glycerine was successfully removed during the water washing process. The free glycerine was diluted in the water and separated by settling gravity. The excessive free glycerine in biodiesel will have a problem since it creates a viscous mixture during settling out in storage tank. As a consequence, it plugs fuel filters and cause combustion problem in the engine [72].



(a)

(b)

(c)

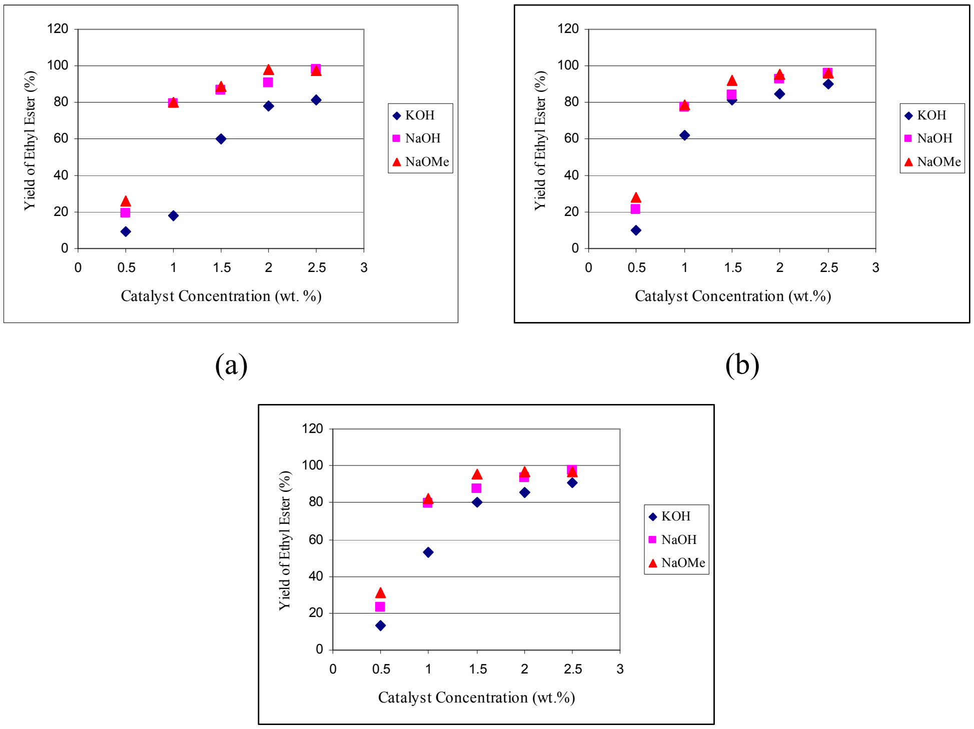
Figure 4.4 GC Chromatogram of biodiesel from *Jatropha curcas* at various of alkali catalyst (a) 2.0 wt.% KOH, (b) 2.0 wt.% NaOH, (c) 2.0 wt.% NaOMe

As shown in Figure 4.4, the area under the peak of mono-, di- and triglyceride indicates the amount of the mono-, di- and triglyceride, respectively that is unconverted to alkyl ester. If all these compounds are added to the free glycerine, it is known as total glycerine. The ASTM D 6751 – 07a specification requires the amount of the total glycerine must be less than 0.24 wt.% of the final biodiesel product. The amount of total glycerine in the biodiesel samples as presented in the chromatogram in Figure 4.4 (a), (b) and (c) are 2.41 wt.%, 1.08 wt.% and 0.23 wt.%, respectively. It shows that the only sample which meets the requirement of the ASTM is sample (c).

The sample (c) was catalyzed by 2.0 wt.% NaOMe whereas samples (a) and (b) were catalyzed by 2.0 wt.% KOH and 2.0 wt.% NaOH, respectively. The reaction was conducted at 70^{o}C for 2h with stirrer speed of 600 rpm. The yield of ethyl ester in sample (a), (b) and (c) was 77.71, 90.41 and 98.16 %, respectively. It showed that the performance of NaOMe was better that that of KOH and NaOH to initiate the reaction to reach the completion. It might be caused by the methoxide ion produced is more stable when NaOMe was applied as catalyst than that of NaOH and KOH. It was also caused by water formation during catalyst preparation when NaOH and KOH used. It affects the yield of biodiesel since water can stop the reaction [72].

One of the most important variables which affect the yield of biodiesel is concentration of the catalyst [20]. The following profiles of catalyst concentration as shown in Figure 4.5 and 4.6 are used to describe the effect of catalyst concentration on the biodiesel yield. As presented in Figure 4.5, all of the catalysts have a similar trend on the yield of ethyl ester. The higher the concentration of the catalyst, the more ethyl ester was produced. At lower catalyst concentration (0.5 wt.%), the performance of NaOMe in enhancing the reaction was better than that of NaOH and KOH.

However, if the quantity of the catalyst was less than 1.5 wt.%, the amount was insufficient to catalyze the reaction to completion. At higher concentration (2.0 wt.% and 2.5 wt.%), the yield of ethyl ester produced was similar for both NaOMe and NaOH. On the other hand, the yield of biodiesel was slightly lower than that of NaOH and NaOMe when KOH was used to initiate the reaction. It showed that higher amount of KOH was required to produce similar biodiesel yield. This higher KOH concentration was used to account for the difference in molar mass between KOH and NaOH. This was in accordance with the result reported by Kucek K T *et al.,* (2007) [20].



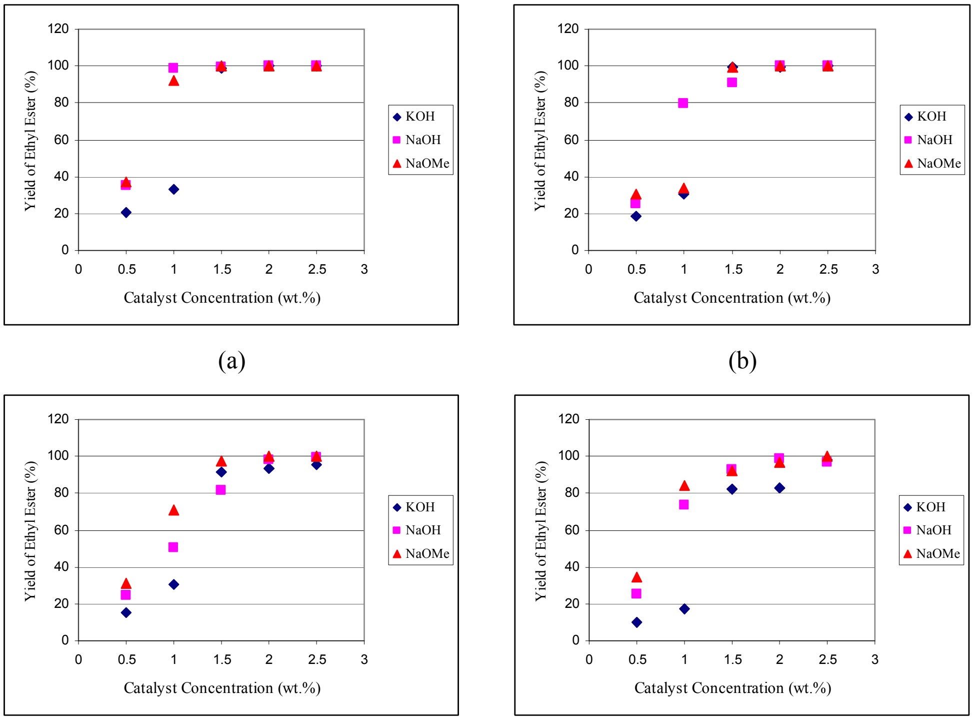
(a) (b)

(c)

Figure 4.5 Influence of catalyst concentration on biodiesel yield synthesis from *Jatropha curcas* at 70°C for different reaction time: (a) 2h, (b) 4h, (c) 6h

Kucek K T *et al.,* (2007) reported that the yield of the ethyl ester decreased from 97.2% to 90.4% when the NaOH concentration was increased from 0.3 wt.% to 1 wt.% [20]. On the other hand, in this work as the NaOH concentration was increased from 0.5 wt.% to 2.5 wt.% the yield of the ethyl ester increased from 19.59% to 98.03%. This discrepancy was due to the different acid value of the raw material used. Kucek K T *et al.,* (2007) used refined soybean oil with acid value of 0.12 mg KOH/g whereas the *Jatropha* oil's acid value was 1.391 ± 0.1 mg KOH/g. It showed that the acid value of the *Jatropha* oil was 12 times higher than that of soybean oil. Therefore, the concentration of the NaOH used in this work was higher to compensate for the catalyst lost to soap formation due to the presence of higher free fatty acid.

Akgun and Iscan (2007) reported that catalyst concentration was the main factor affecting the reaction [50]. They used sunflower oil with free fatty acid content of 0.398 % and conducted the experiment at 65°C and agitation speed of 1000 rpm. The experiment using conventional method was designed using response surface methodology. A quadratic polynomial equation was obtained by multiple regression analysis. They concluded that the optimum catalyst concentration and reaction time to produce biodiesel was 1.3 wt.% and 2h, respectively. As compared to result obtained in this work, the concentration of the NaOH needed to complete the reaction is lower because of lower level of free fatty acid.



(a) (b)

(c) (d)

Figure 4.6 Influence of catalyst concentration on biodiesel yield synthesis from *Jatropha curcas* for 6 hours at different temperatures: (a) 30°C, (b) 40°C, (c) 50°C, (d) 60°C

Figure 4.6 illustrated the effect of catalyst concentration and reaction temperature on the yield of ethyl ester (biodiesel). As shown in Figure 4.6, the optimum catalyst concentration to produce a high yield of ethyl ester was 1.5 wt.% NaOMe, NaOH and KOH. It obtained when the reaction was conducted at 30, 40 and 50°C. At higher reaction temperature, 60°C, higher catalyst concentration was required to complete the reaction. This additional amount of catalyst used to compensate for the catalyst lost to soap formation [75]. Triglyceride saponification occurred at higher reaction temperature. Thus, the yield of biodiesel decreased [83].

According to Figure 4.6, it can also be concluded that once the reaction was completed, increasing the catalyst concentration will decrease the yield of the biodiesel due to soap formation. According to the experimental observations, the higher the amount of the sodium methoxide used the more viscous the solution would be. Consequently, the yield of biodiesel produced was lesser. This observation is in accordance with the results reported by Dorado *et al.,* (2004) [100].

Dorado *et al.* (2004) investigated the effect of catalyst concentration on the biodiesel production through conventional process [100]. The catalyst concentration was varied from 0 to 1.9 wt.% KOH with a 4 : 1 molar ratio of methanol to oil. Used olive oil with free fatty acid of 1.02% was used as a raw material and the reaction was conducted at 25°C and stirrer speed of 1100 rpm. They concluded that the optimum KOH concentration was achieved at 1.26 wt.% to obtain the biodiesel yield higher than 90%, whereas the KOH concentration required to complete the reaction in this work was 1.5 wt.%.

This discrepancy was due to the difference of the process and stirrer speed used. Dorado *et al.* (2004) used conventional method and higher stirrer speed, therefore the oil was dispersed faster into alcohol and reaction took place simultaneously. As a consequence, even at lower catalyst concentration, the reaction reached completion due to the homogeneity between oil and base-alcohol solution. However, both process obtained the highest yield of the biodiesel at room temperature. This was also in accordance with the result reported by Vicente *et al.* (2007).

Table 4.6 Total glycerine

Catalyst Con. (wt.%)	Total Glycerine (wt.%)
0.5 wt.%	7.82 ± 0.13
1.0 wt.%	0.45 ± 0.10
1.5 wt.%	0.22 ± 0.12
2.0 wt.%	0.22 ± 0.31
2.5 wt.%	0.21 ± 0.23

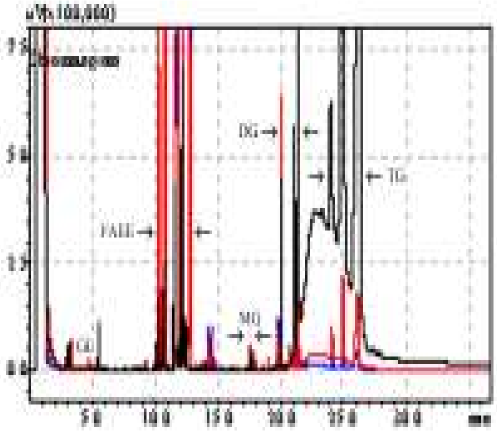


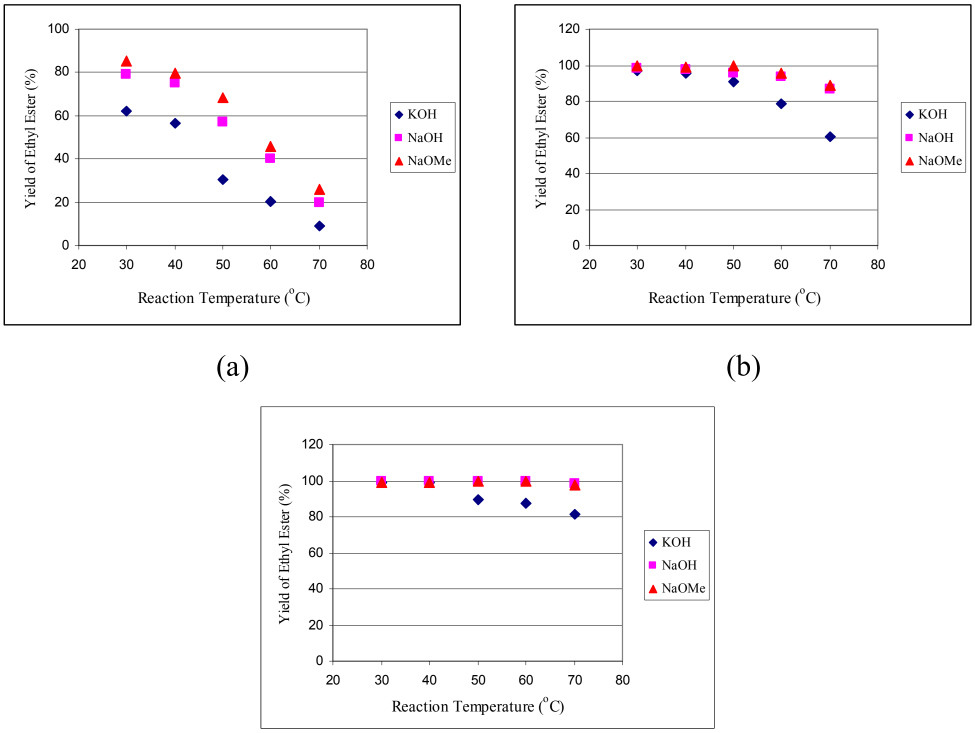
Figure 4.7 GC Chromatogram at various NaOMe concentration of 0.5 wt.% (Black), 1.5 wt.% (Red) and 2.5 wt.% (Blue) at 70°C

Figure 4.7 displays the peak of the glycerol, fatty acid ethyl ester, monoglyceride, diglyceride and triglyceride which represent the quantity and quality of the biodiesel samples produced at 70°C for 2h of reaction time. As mentioned earlier, the area under the peak of mono-, di- and triglyceride represented the amount of glyceride that was unconverted to biodiesel. As the catalyst concentration was decreased, the content of total glycerine in the biodiesel increased. It is shown in the Table 4.6. 0.5 wt.% catalyst concentration was insufficient to promote the reaction to completion. The reaction was completed at higher catalyst concentration of 1.5 and 2.5 wt.%.

At lower concentration (0.5wt.%), the biodiesel can not be used as a fuel to replace the petrodiesel since its total glycerine value is higher than the requirement of ASTM D 6751 – 07a (0.24 wt.%). The more unconverted glyceride presented in biodiesel, the more viscous it would be. Therefore, it can cause problem in diesel engine such as coking, trumpet formation on the injector and carbon deposit [1, 8]. Meanwhile, the produced biodiesel when the reaction was catalyzed by 1.5 and 2.5 wt.% fulfilled the requirement of the ASTM D 6751–07a in terms of total glycerine.

4.3.3 Effect of Reaction Temperature

To study the effect of the reaction temperature on the production of biodiesel, the experiments were carried out at five different reaction temperatures of 30, 40, 50, 60 and 70°C. The reaction was conducted with catalyst concentration of 0.5, 1.5 and 2.5 wt.% for 2 hours. Figure 4.8 shows the effect of reaction temperature on the yield of ethyl ester produced. It shows that NaOMe and NaOH are superior to KOH to speed up the reaction especially at reaction temperature of 50, 60 and 70°C.



(a) (b)

(c)

Figure 4.8 Influence of reaction temperature on biodiesel yield synthesis from *Jatropha curcas* for 2 hours at different catalyst concentration : (a) 0.5 wt.%, (b) 1.5 wt.%, (c) 2.5wt.%

According to Figure 4.8, all type of catalysts used produced similar trend of the biodiesel yield versus reaction temperature. The yield of ethyl ester decreases with an increase in the reaction temperature from 30 to 70°C as presented in Figure 4.8.

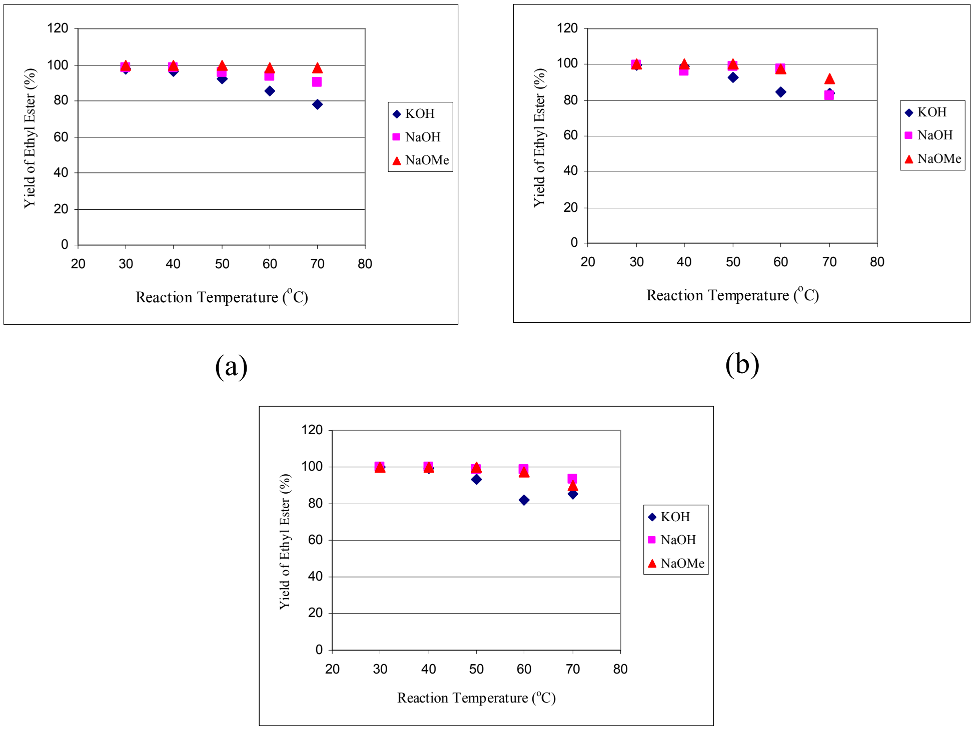
It is caused by triglyceride saponification at higher reaction temperature and followed by dissolution of ethyl ester into glycerol which means increasing solubility of ethyl ester in glycerol [83, 87]. Consequently, it reduces the yield of ethyl ester since at higher temperature promotes the ethyl ester to dissolve into glycerol. This observation is in accordance with the results reported by Dorado *et al.*, (2004) [102], Leung *et al.,* (2006) [84] and Vicente *et al.,* (2007) [87].

To support previous explanation, saponification values of the sample which were produced at those temperatures of 30, 40, 50, 60 and 70^{o}C with catalyst concentration of 1.5 wt.% were calculated based on AOCS method [103]. Table 4.7 shows the result obtained. As shown in Table 4.7, the higher the temperature, the higher the saponification value of the sample. It means that at higher temperature, more triglyceride is converted to form soap. Due to their polarity, the soap dissolves into the glycerol phase during separation. Therefore, it increases the alkyl ester solubility into glycerol. Consequently, it will reduce the biodiesel yield.

Table 4.7 Saponification value of the biodiesel sample at various temperatures

Temperatures (^{o}C)	Saponification value (mg KOH/gr)
30	116.88 ± 0.21
40	121.65 ± 0.23
50	135.58 ± 0.13
60	140.67 ± 0.26
70	147.09 ± 0.48

Free fatty acid (FFA) neutralization also produces soap. Therefore, this side-reaction is also considered as a factor that can reduce the biodiesel yield. However, this variable can be ignored in this work since the acid value of the *Jatropha* oil is 1.391 ± 0.1 mg of KOH/g. In another word, the free fatty acid content in the *Jatropha* oil is 0.69%. This value is lower than the value suggested by Gerpen (2005) if the raw material is catalyzed by alkali catalyst [75]. He recommended that up to 5% FFA, the base catalyzed still can be used to enhance the reaction.



(a) (b)

(c)

Figure 4.9 Influence of reaction temperature on biodiesel yield synthesis from *Jatropha curcas* using catalyst concentration of 2 wt.% at different reaction time : (a) 2h, (b) 4h, (c) 6h

As Illustrated in Figure 4.9, it can be seen the effect of reaction temperature on the yield of biodiesel at different reaction time. Increasing the reaction time from 2 to 6 hours did not affect the profile of the graph. The yield of the biodiesel decreased as the temperature was increased from 30 to 70°C at every reaction time. Thus, the effect of reaction time can be ignored. As mentioned earlier, the biodiesel yield decreased due to saponification of triglyceride.

Dorado *et al.,* (2004) reported that the maximum yield of ester was obtained when the reaction was conducted at temperature of 10 to 50°C [102]. They investigated the effect of reaction temperature on the yield of biodiesel by varying the temperature from 10 to 70°C. The experiment was carried out with stirrer speed of 1100 rpm and KOH concentration of 1.26 wt.%. Used olive oil with free fatty acid content of 1.02% was used as a raw material. They concluded that if the conventional method was conducted at 60°C or higher, the reactions tend to accelerate the saponification of the triglyceride by the alkaline catalyst before completion of the transesterification [102]. This was in accordance with the results obtained in this work.

4.4 Comparison of Methanol, Ethanol and Their Mixture (50% : 50%)(v/v) in the In Situ Transesterification of *Jatropha curcas*

As described previously in Chapter 2, monohydroxy alcohol such as methanol or ethanol is the most common alcohol used to produce biodiesel. In this work, both of these alcohols were used as solvent and reactant to synthesize the biodiesel from *Jatropha curcas*. During the experiments of in situ methanolysis of *Jatropha curcas*, it was observed that after in situ methanolysis for 24 hours the amount of oil produced was very low, which can be considered to be unsuccessful. However, the yield of the biodiesel achieved up to 99.97% when ethanol was applied as a solvent and reactant. Due to properties of methyl ester is better than that of ethyl ester therefore the alcohol was mixed to investigate the properties of the biodiesel.

4.4.1 Effect of Reaction Time

To study the effect of these alcohols on synthesis of biodiesel, all the parameters, for instances: the reaction time, the reaction temperature, the amount of the seed, the volume of the alcohol and the stirrer speed were kept constant.

Figure 4.10 shows the amount of biodiesel yield obtained at various alcohols used. The yield of the biodiesel (methyl ester) increased when the reaction time was increased from 4 to 24 hours. On the other hand, as the reaction time was increased, the yield of the biodiesel was constant for both when ethanol and mixture of methanol-ethanol (50% : 50%) (v/v) were used as reactant. Based on experimental observations, it was also found that increasing the reaction time from 2 to 6 hours would make the amount of oil dissolved in the ethanol constant. Therefore, the yield of ethyl ester obtained was constant because the strength of the catalyst was similar.

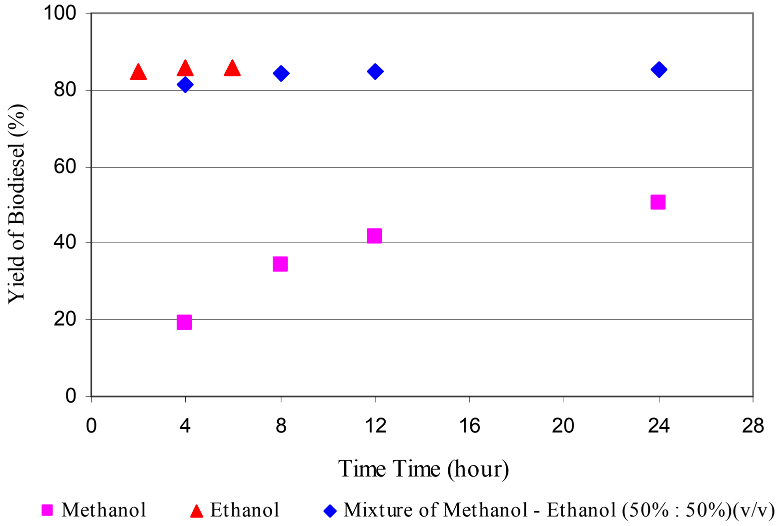


Figure 4.10 The effect of reaction time on biodiesel yield in the in situ alcoholysis of *Jatropha* seed using 1.0 wt.% NaOH with stirrer speed of 600 rpm at 60°C

The following GC chromatogram in Figure 4.11 shows the difference of the peak of glycerol, biodiesel, mono-, di- and triglyceride when ethanol and mixture of methanol-ethanol (50% : 50%) (v/v) were used to extract and convert the oil into biodiesel directly. The remaining unreacted glyceride in the biodiesel was less when ethanol was used compared to that when mixture of methanol-ethanol was employed. It is presented by the higher peak of glyceride (mono-, di- and triglyceride) observed in the mixture of the methanol-ethanol than that of ethanol. The glyceride peaks were used to determine the amount of total glycerine content in the biodiesel sample. Based on the Figure 4.11, it was found that the total glycerine was 1.66% and 2.22%, respectively when ethanol and mixture of methanol-ethanol were used as an alcohol. This value is higher than 0.24 wt.% that limited by ASTM D 6751 – 07a. Therefore, higher amount of catalyst concentration is required to convert all the triglyceride to biodiesel. Thus, the total glycerine will meet the requirement of the ASTM.

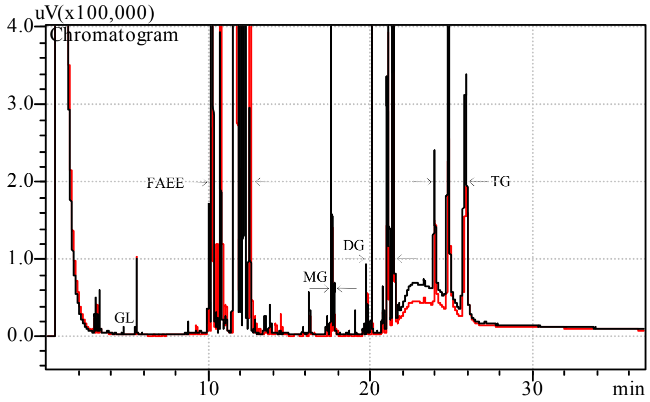


Figure 4.11 GC Chromatogram at various alcohols in which Black = Mixture Methanol-Ethanol and Red = Ethanol

4.4.2 Effect of Reaction Temperature

Reaction temperature has a negative effect on the yield of biodiesel. As temperature was increased from 30 to 70°C, the yield of biodiesel was found to decrease. This can be observed in Figure 4.12. When ethanol was used as alcohol, the yield decreased inversely with temperature due to side reaction of triglyceride saponification. This is in accordance with the results reported by Dorado *et al.,* (2004) and Vicente *et al.*, (2007).

Meanwhile, the usage of mixture of methanol-ethanol causes the yield of biodiesel increased as the temperature was increased from 30 to 60°C and decrease when the temperature was increased to 70°C. Decreasing the yield was due to the boiling point of the methanol. Since its boiling point is 64.7°C, if the reaction is conducted at 70°C, the methanol will evaporate. Consequently, the lower the amount of the alcohol, the lower the reaction rate will be. As a consequence, the yield of biodiesel diesel will decrease as shown in Figure 4.12.

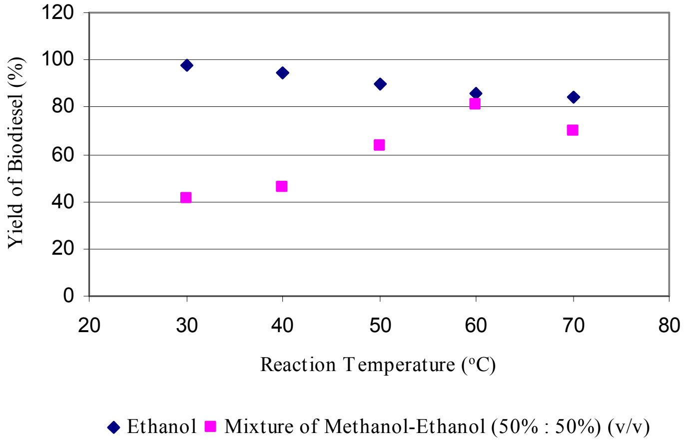


Figure 4.12 Influence of reaction temperature on the synthesis of biodiesel from *Jatropha curcas* using in situ technique

4.5 Reaction Kinetics of In Situ Transesterification of *Jatropha curcas*

There are a few references discussing about the kinetics of transesterification of vegetable oil. These include study on the kinetics of transesterification of palm oil [54], soybean oil [51, 65], *Pongamia* oil [66] and rapeseed oil [67]. The reaction kinetic is used to determine the reaction order and also reaction rate constant of the transesterification reaction. To determine the reaction order and reaction rate constant, the rate law must follow the design equation of a type particular of the reactor.

In this work, the rate law was derived based on the design equation of constant-volume batch reactor. In order to simplify the calculation, the analysis data was done by following the integral method. The integral method was used to determine the reaction order and reaction rate constant. It is assumed that the reverse reaction is very small which is 100 times slower than the forward reaction [65]. Therefore, the kinetics of the in situ transesterification of *Jatropha curcas* was only measured based on the forward reaction instead of backward reaction. The overall transesterification reaction is described as follows:

$$\text{Triglyceride} + 3C_2H_5OH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 3\text{FAEE} + \text{Glycerol} \qquad (4.3)$$

The profile of the reactants and the desired product (biodiesel) is presented in the Figure 4.13. As shown in the Figure 4.13, as reaction time was increased from 10 to 120 min, the weight concentration of the fatty acid ethyl ester (FAEE) increased. On the other hand, at longer reaction time, the weight of the mono-, di and triglyceride decreased. It showed that as reaction time increased, more reactant was converted to fatty acid ethyl ester. However, as can be seen in the Figure 4.13, the reaction was completed in 100 min.

Increasing the reaction time higher than 120 min will affect the yield of the product (biodiesel). The yield will slightly decrease since the reaction is reversible. Thus, once the reaction reached the completion, the reaction should be stopped in order to prevent the reaction shift to left side. The reaction can be stopped by adding an acid to neutralize the base catalyst or by adding a base to neutralize the acid catalyst.

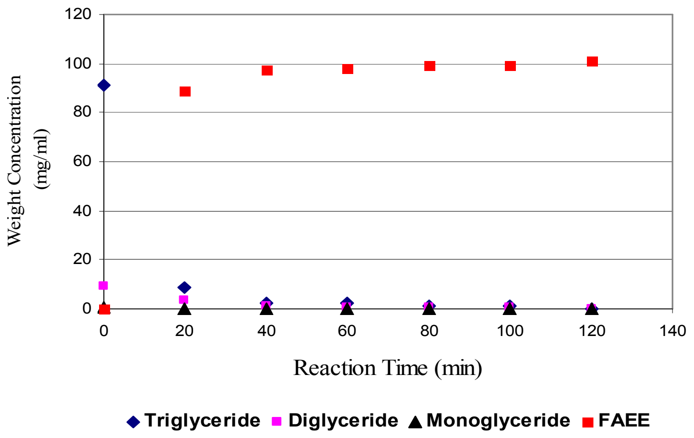


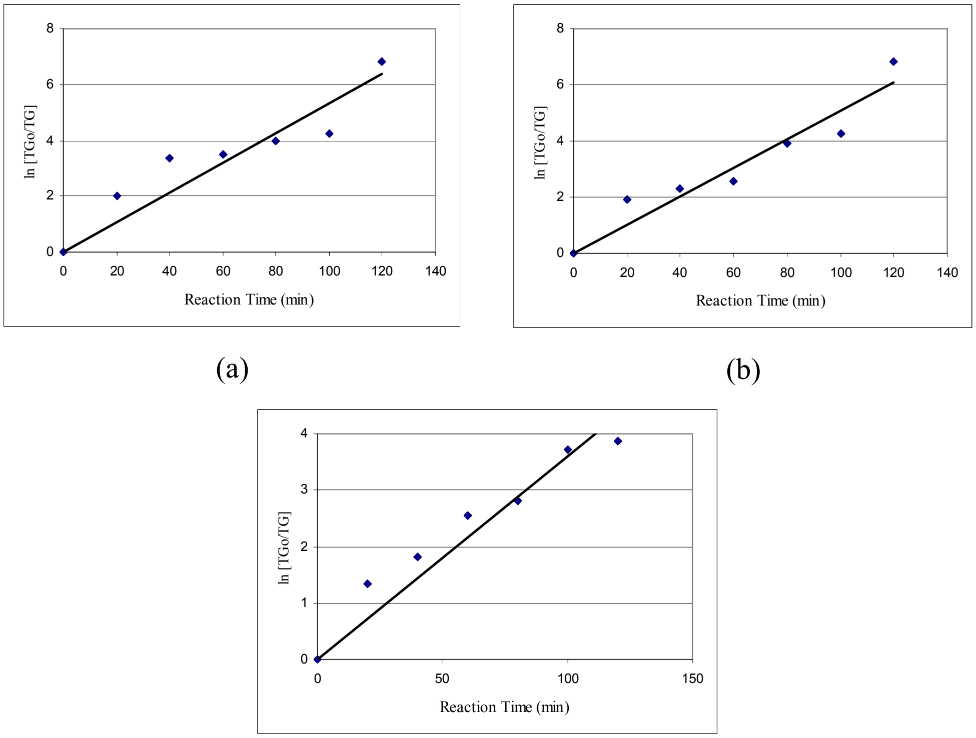
Figure 4.13 The product composition obtained in the in situ transesterification of *Jatropha curcas* using 2.0 wt.% NaOMe at 30°C

4.5.1 First-Order Kinetics

According to Eq. 4.3, if the reaction is assumed as a first-order and the reverse reaction is neglected, the rate law becomes:

$$d[TG]/dt = - k_1[TG] \tag{4.4}$$

If the assumption is true, it will give a straight line by plotting ln [TGo/TG] vs t. Unfortunately, the plotting line does not give a straight line therefore first-order kinetics can not be considered to represent the data. The graphs are shown in Figure 4.14.



(a) (b)

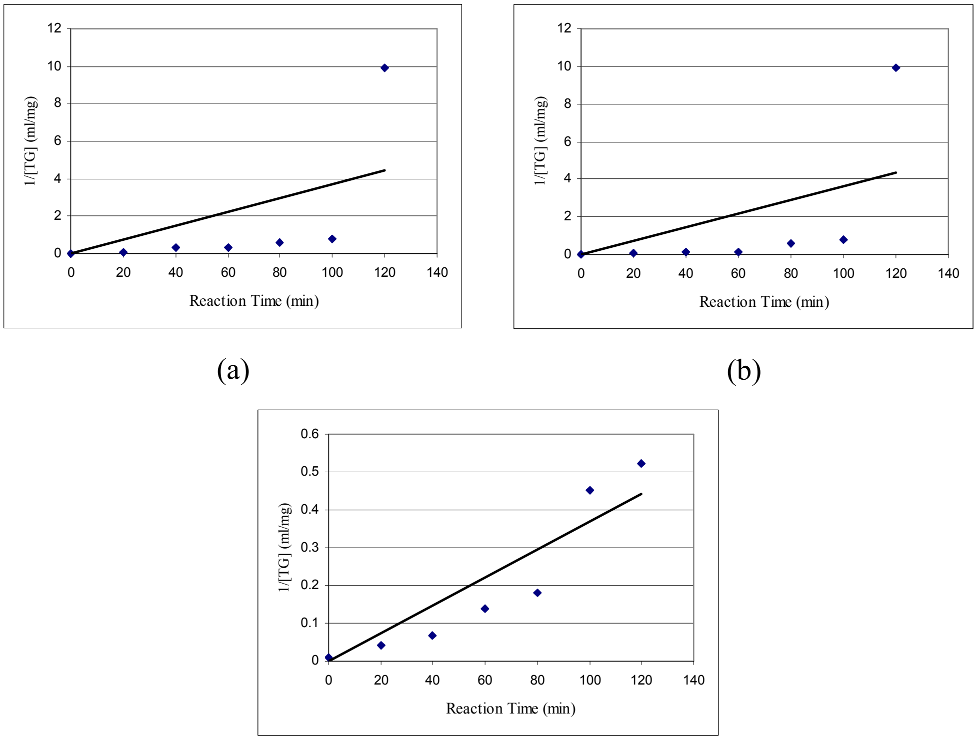
(c)

Figure 4.14 First-order reaction kinetics of in situ transesterification at various reaction temperatures of (a) 30°C (b) 50°C and (c) 70°C

4.5.2 Second-Order Kinetics

According to Equation 4.3, if the reaction order is assumed as a second-order and the backward reaction is neglected, the rate law becomes (Darnoko and Cheryan, 2000) [54] :

$$d[TG]/dt = - k_1[TG]^2 \tag{4.5}$$



(a) (b)

(c)

Figure 4.15 Second-order reaction kinetics of in situ transesterification at various reaction temperatures of (a) 30°C (b) 50°C and (c) 70°C

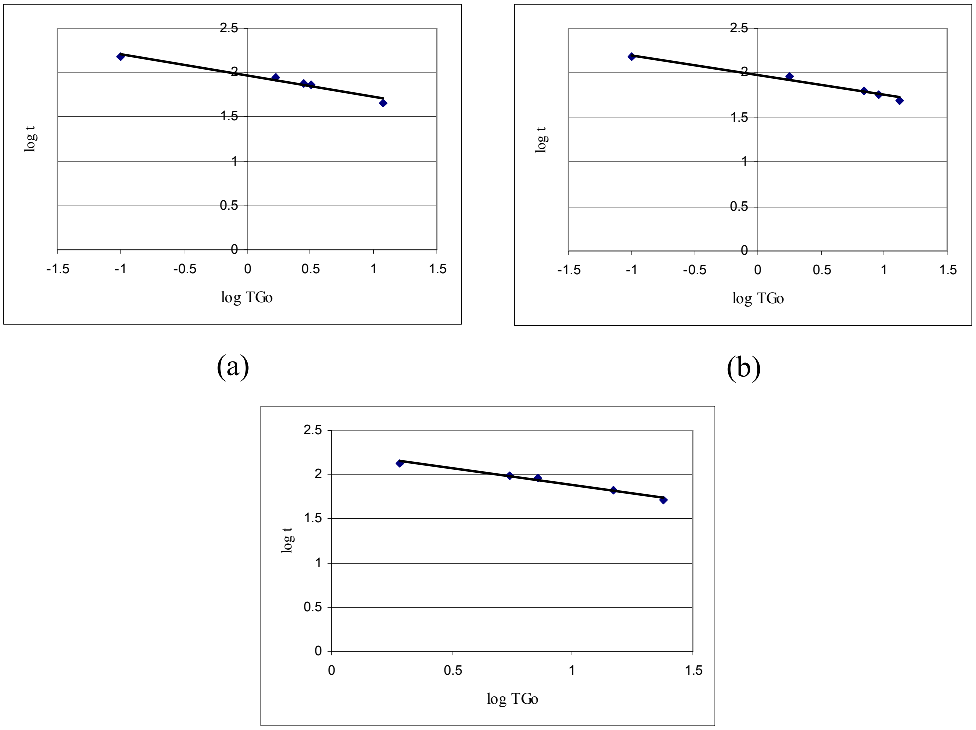
Integrating and rearranging Eq. 4.5 will give

$$\frac{1}{TG} - \frac{1}{TG_o} = kt \tag{4.6}$$

Plotting a graph of 1/TG as a function of time should be linear with slope k. However, the plots of concentration of glyceride versus time did not give a straight line. Thus, this could be concluded that the proposed reaction order did not fit the data. Therefore, the reaction is not a second order. Figure 4.15 shows the concentration of the glyceride as a function of time at various reaction temperatures.

4.5.3 nth-Order Kinetics

Nth-order is used to determine the reaction order of the reaction since the first and second-order reaction do not fit the data. By plotting a log t versus log TGo will give a slope which represents 1-n in which n is a reaction order. Figure 4.16 displays the plot line of log t versus log TGo which yield a straight line.



(a)

(b)

(c)

Figure 4.16 nth-order reaction kinetics of in situ transesterification at various reaction temperatures of (a) 30°C (b) 50°C and (c) 70°C

The reaction order (n), reaction rate constant (k) and coefficient of determination (R^2) obtained from Fig. 4.16 are tabulated as shown in Table 4.8.

Table 4.8 The value of reaction order, reaction rate and R^2 at various reaction temperatures

Parameters	Reaction Temperature (°C)		
	30	50	70
n	1.2394	1.2233	1.3731
k	0.0093	0.0085	0.0047
R^2	0.9553	0.9793	0.9777

According to the results in Table 4.8, the rate equation that represents the reaction is as follow :

1. At 30°C

$$-r_{TG} = \left(0.0093\frac{liter^{0.24}}{mol^{0.4}.\,s}\right)TG^{1.24} \qquad \frac{mol}{liter.\,s}$$

2. At 50°C

$$-r_{TG} = \left(0.0085\frac{liter^{0.22}}{mol^{0.22}.\,s}\right)TG^{1.22} \qquad \frac{mol}{liter.\,s}$$

3. At 70°C

$$-r_{TG} = \left(0.0047\frac{liter^{0.37}}{mol^{0.37}.\,s}\right)TG^{1.37} \qquad \frac{mol}{liter.\,s}$$

Darnoko and Cheryan, (2000) investigated the kinetic reaction of palm oil in a batch reactor. They conducted the reaction through conventional method. Their data was tested based on the equation 4.5. Since their data plotting of a reaction time (t) versus 1/[TG] was a straight line, they concluded that the model that they assumed was true. Therefore, they deduced that their data follow second-order with reaction rate constant equals to 0.018 $(\text{wt\%.min})^{-1}$[54].

4.6 Mechanism of Biodiesel Production through In Situ Transesterification of *Jatropha curcas*

In situ transesterification of *Jatropha curcas* is a process that combines the extraction and reaction into a single step. Thus, the *Jatropha* seed was extracted by base-alcoholic solution and converted continuously to biodiesel. The completeness conversion of the reactant into biodiesel not only depends on the mass transfer but also affected by ash diffusion and chemical reaction resistances. To study the kinetic of the biodiesel production through in situ process, the phenomenon can be approached by shrinking-core model.

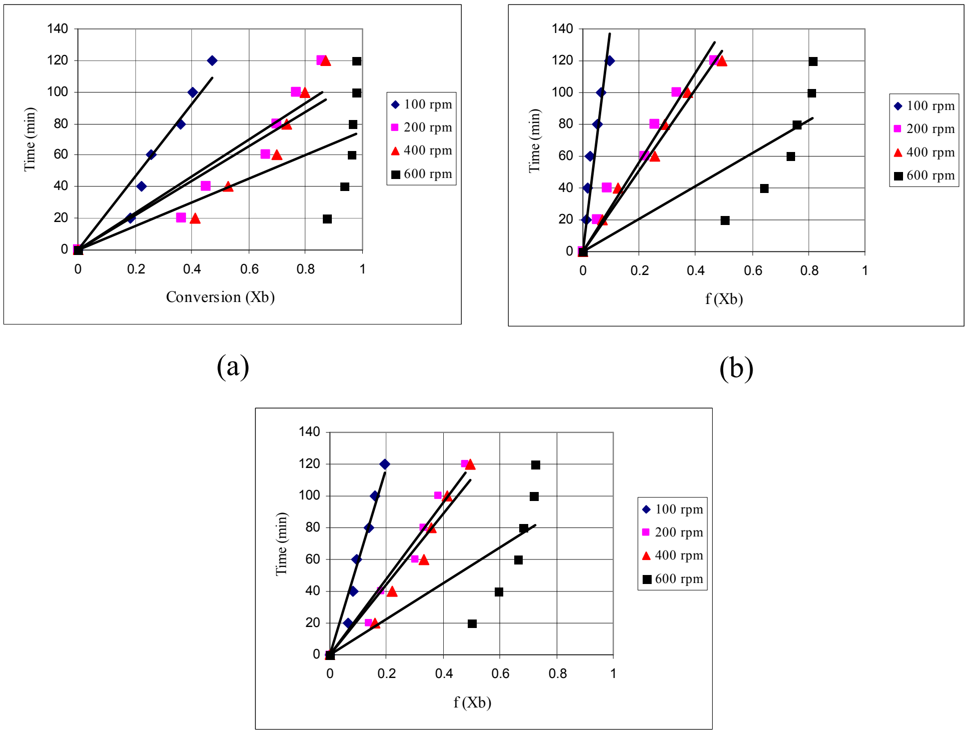
4.6.1 Effect of Stirrer Speed

To investigate the effect of the stirrer speed on the reaction rate, the agitation speed was varied from 100 to 600 rpm. The reaction was carried out at 70^{o}C in the presence of the 2.0 wt.% NaOMe for 20 to 120 min of reaction time. Either mass transfer, ash diffusion or chemical reaction can control the reaction rate. Therefore, to determine which parameters control the reaction, the following graph, Figure 4.17 is made. As shown in the Figure 4.17, the linear regression is used to calculate time for complete conversion (τ) and coefficient of determination (R^2). The value of the (τ) and R^2 are tabulated in the Table 4.9. Taking the value of the (τ) and R^2 into consideration, the rate of reaction is most probably ash diffusion controlled for all stirrer speed.

From Table 4.9, it can also be stated that at lower stirrer speed of 100 and 200 rpm, the reaction is also controlled by chemical reaction. On mass transfer controls, as agitation speed was increased from 100 to 600 rpm, the R^2 value decreased. The R^2 value under mass transfer control at 100 rpm was still lower than that obtained under chemical reaction control. Thus, the reaction was tending to chemical reaction controlled instead of mass transfer controlled.

Table 4.9 The value of τ (min) and R^2 on various stirrer speed and resistances

Stirrer speed (rpm)	Mass Transfer		Ash Diffusion		Chemical Reaction	
	τ (min)	R^2	τ (min)	R^2	τ (min)	R^2
100	231.13	0.9266	1414	0.8989	596.7	0.9538
200	116.18	0.8699	281.39	0.9529	238.68	0.9610
400	109.59	0.8243	256.68	0.9833	221.82	0.9398
600	74.842	0.4579	103.06	0.6855	112.51	0.6321



(a) (b)

(c)

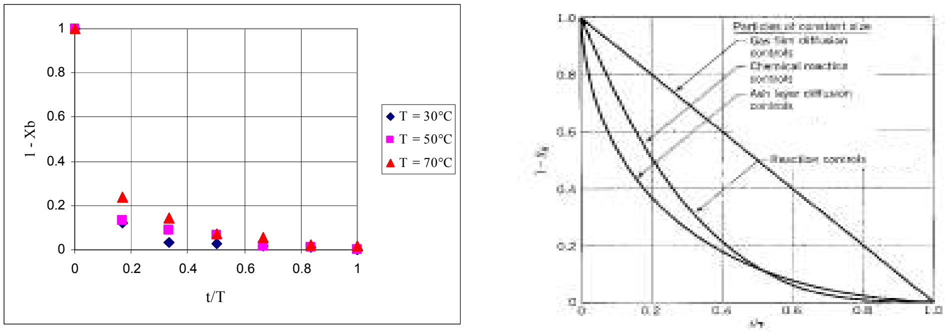
Figure 4.17 Various resistances that control the reaction rate (a) Mass transfer controls (b) Ash diffusion controls (c) Chemical reaction controls

Xb is conversion of B, f(Xb) for ash diffusion control equals to $1 - 3(1 - Xb)^{2/3} + 2(1 - Xb)$ and f(Xb) for reaction control equals to $1 - (1 - Xb)^{1/3}$

4.6.2 Effect of Reaction Temperature

To study the effect of the reaction temperature on the reaction rate, the reaction was conducted at three different reaction temperatures of 30, 50 and 70°C for 20 to 120 min. The reaction was catalyzed by 2.0 wt.% NaOMe at constant stirrer speed of 600 rpm.

According to experimental observations, the time required for complete conversion of the particle into biodiesel is 80 - 120 min except at 70°C. At 70°C, the reaction reached completion in 120 min. It is illustrated in the following Figure 4.18.

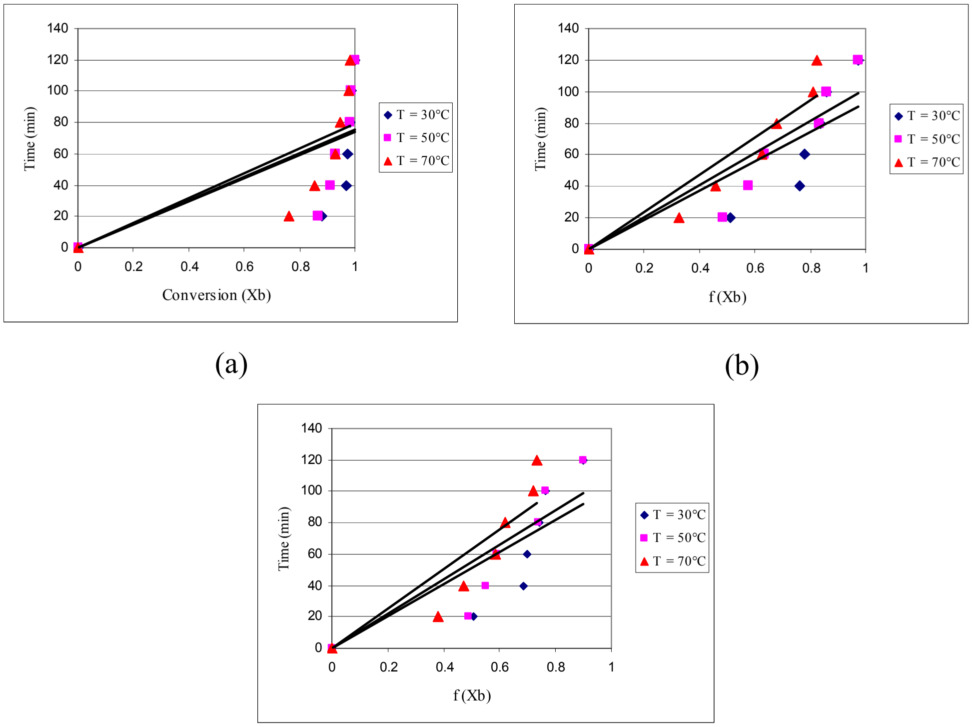


(a) (b)

Figure 4.18 Progress of reaction to reach the complete conversion (a) raw data (b) reference [68]

By comparing the graph in Figure 4.18 (a) to (b), it can be seen that the rate of the reaction is controlled by ash diffusion. In addition, at longer reaction time from 80 to 120 min, the chemical reaction also controlled the reaction. To obtain more accurate conclusion, analysis of the τ (min) and R^2 should be applied. The value of τ (min) and R^2 is used to investigate the resistances that control the reaction rate. Therefore, the τ value obtained from the linear regression of the following curve is compared to the reference (80-120 min) to decide the parameters that control the reaction.

The linear regression of the curve is presented in the Figure 4.19. The slope of the curve represents the time for complete conversion (τ). The value of τ and R^2 is tabulated in the Table 4.10.



(a)

(b)

(c)

Figure 4.19 Various resistance at different temperature that control the reaction rate (a) Mass transfer controls (b) Ash diffusion controls (c) Chemical reaction controls

Taking τ and R^2 value into consideration, the rate of reaction is most probably ash diffusion controlled.

Table 4.10 The value of τ (min) and R^2 on various stirrer speed and resistances

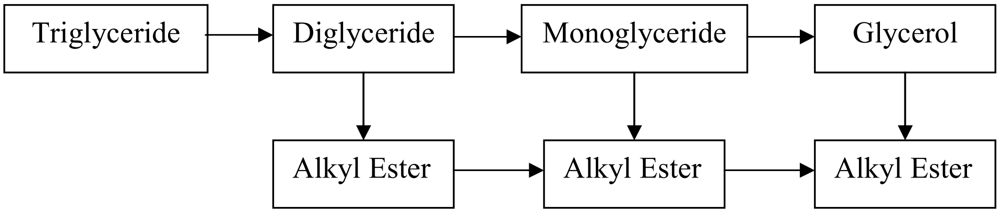
Temp. (°C)	Mass Transfer		Ash Diffusion		Chemical Reaction	
	τ (min)	R^2	τ (min)	R^2	τ (min)	R^2
30	73.585	0.4563	93.07	0.7176	102.34	0.7039
50	75.548	0.4939	101.61	0.8344	109.7	0.795
70	79.487	0.5623	118.52	0.8866	126.05	0.8027

4.7 Characteristics of Biodiesel

The produced biodiesel can be used as an alternative energy if it is fulfil the requirement of the ASTM D 6751 – 07a [98]. This standard specifies the parameter required for a biodiesel fuel to be used in the diesel engine without having problems. The quality of the product is related to the process involved and process on the post-treatment. In this work, the parameter that was measured to determine the quality of the biodiesel is explained in details as follow.

4.7.1 Completion of reaction

The most important issue on the production of biodiesel is the completeness of the reaction. As described previously in Chapter 2, the transesterification reaction is a consecutive reaction in which an alkyl ester is produced at every step. It can be illustrated as follow :



If the reaction is incomplete, the raw material for instance: mono-, di- and triglyceride will be detected in the biodiesel. The accumulation of the amount of mono-, di- and tiglyceride left in the biodiesel is limited by ASTM [52]. The parameters called as bound glycerine. Almost all the data (Appendix A) obtained through ethanolysis insitu transesterification meet the requirement of ASTM D 6751 – 07a except at low catalyst concentration of 0.5 and 1.0 wt.% KOH, NaOH and NaOMe.

4.7.2 Free glycerine

Free glycerol refers to its amount present in the biodiesel after separation and purification process. This amount is also limited by ASTM D 6751 – 07a, 0.02 wt.%. According to data obtained from GC chromatogram, the range of the free glycerine content in the biodiesel sample is 0 – 0.244 wt.%. The average amount of free glycerine in the biodiesel sample is 0.016 ± 0.6 wt.%. The low amount of the free glycerine is due to washing process. The sample was washed using distillate water repeatedly to remove the glycerol, alcohol and catalyst. These impurities were diluted in the water through washing. As a result, this step increased the purity of the biodiesel.

4.7.3 Water and sediment

The present of water in the biodiesel can cause problem especially in fuel injection equipment since it contributes to the corrosion of the closely fitting part [72]. The ASTM limits the water content in the biodiesel. The maximum allowable value of the water content in the biodiesel is 0.05 vol.%. During the process production of the biodiesel, the water was removed from the biodiesel by adding the drying agent for instance, magnesium sulphate or sodium sulphate. The average water content of the samples was found to be 0.04 vol.%. This value is slightly less than that suggested by ASTM which is 0.05 vol.%.

The characteristics of the biodiesel produced under the optimum conditions of 2 wt.% NaOMe, stirrer speed of 600 rpm, reaction temperature of 30°C and reaction time of 2 hours are tabulated as shown in Table 4.11 below:

Table 4.11 Characteristics of the biodiesel sample under optimum condition

Parameters	Value	ASTM D 6751–07a [52]
Acid Value	0.04 mg KOH/g	0.5 max
Free Glycerine	0	0.02 % mass
Total Glycerine	0.003	0.24 % mass
Flash Point	178°C	93 °C (min)
Vicosity	5.5 mm^2/s	1.9 – 6.0 mm^2/s

CHAPTER 5
CONCLUSSIONS AND RECOMMENDATIONS

5.1 Conclusions

Synthesis of biodiesel from *Jatropha curcas* using in situ transesterification process was investigated in this work. The yield of the biodiesel was studied by manipulating the reaction time, type of catalysts and their concentration, ratio of alcohol to *Jatropha* seed, stirrer speed, type of alcohol and reaction temperature. The biodiesel was analyzed using gas chromatography (GC) Shimadzu 2010A based on the ASTM D 6854 – 00 [98]. The biodiesel was also analyzed using thin layer chromatography (TLC) based on the method developed by Haas and Foglia (2003) [42].

The quality of the biodiesel was also analyzed. These include viscosity (40^{o}C), acid number, free fatty acid, free glycerine, total glycerine and flash point measurements. All the testing was done in duplicate to obtain an accurate data. According to the experimental observations and data analysis, it can be deduced that :

1. The maximum yield of the biodiesel obtained in the in situ methanolysis of *Jatropha curcas* seed was 39.79%.
2. The maximum yield of the biodiesel obtained in the in situ ethanolysis of *Jatropha curcas* seed was 99.97%.
3. To obtain the biodiesel yield around 97.78%, the concentration of sodium methoxide, sodium hydroxide and potassium hydroxide required was 1.0 wt.%, 1.5 wt.%, and 2.5.wt%.

4. The maximum yield of ethyl ester was obtained under the following conditions : reaction time of 2h, catalyst concentration of 2.0 wt.% NaOMe, reaction temperature of 30°C and stirrer speed of 600 rpm.
5. At optimum conditions, the biodiesel meets the requirement of ASTM D 6751 – 07a in term of viscosity (40°C), acid number, free fatty acid, free glycerine, total glycerine and flash point.
6. The kinetics reaction of the data follow reaction order of 1.24 with reaction rate constant equals to 0.009 liter$^{0.24}$/mol$^{0.24}$.s
7. The rate of reaction is most probably ash diffusion controlled.

5.2 Recommendations

There are many aspects that can be further investigated related to in situ transesterification of *Jatropha curcas*such as:

1. The in situ transesterification of non edible raw material in the presence of solid base catalyst by manipulating the size of the raw material and type of impeller/stirrer.
2. The production cost is the most critical issue that needs to be addressed. This alternative fuel must be cheaper than the existing petrodiesel fuel in market. Therefore, study related to the production cost of this in situ transesterification process of non edible oil through simulation tools such as chem cad or hysys is recommended.

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APPENDIX A
SAMPLE OF CALCULATION

A.1 Molecular Weight of Triglyceride

Fatty Acid	Wt.%	Structure[1]	Formula	Molecular Weight (g/mol)
Myristic	0.12	14 : 0	$C_{14}H_{28}O_2$	228.376
Palmitic	19.5	16 : 0	$C_{16}H_{32}O_2$	256.428
Stearic	6.8	18 : 0	$C_{18}H_{36}O_2$	284.481
Oleic	41.3	18 : 1	$C_{18}H_{34}O_2$	282.465
Linoleic	31.4	18 : 2	$C_{18}H_{32}O_2$	280.450
Linolenic	0.2	18 : 3	$C_{18}H_{30}O_2$	278.434
Average Molecular Weight of the Fatty Acid (MW_{FA})				276.781

[1] xx : y indicates that xx is carbon in the fatty acid chain with y represents double bonds

The average molecular weight of the triglyceride is :

$$MW_{TG} = (3 \times MW_{FA}) + MW_{Glycerol} - 3$$

$$MW_{TG} = (3 \times 276.781) + 92.10 - 3$$

$$MW_{TG} = 919.443 \text{ g/mol}$$

A.2 Yield of Ethyl Ester

Overall transesterification reaction,

$$Triglyceride + 3C_2H_5OH \rightarrow 3Ethyl\ Ester + Glycerol$$

Based on the soxhlet extraction using 20g of *Jatropha* seed and hexane as a solvent, it was found that the average oil recovered from the *Jatropha* seed was

53.92 ± 0.19 %. According to GC analysis, it was found that the percentage of the triglyceride in the *Jatropha* oil was 91.11%. Therefore, moles of triglyceride present in the feedstock are :

$$\frac{0.911 \times 0.539 \times 20}{919.443} = 0.01067\ mol$$

Assuming complete transesterification reaction,
Gram of ethyl ester produced is :

$$\begin{aligned} 3 \times 0.01067 &= 0.03201\ mol\ of\ \ ethyl\ ester \\ &= 0.032\ mol \times 321.843\ g/mol \\ &= 10.313g \end{aligned}$$

From GC chromatogram, it was found that the ethyl ester content was 99.97%. Thus, the yield of ethyl ester is :

$$\left(\frac{0.9997 \times 0.911 \times 0.539 \times 20}{10.313} \times \frac{965.529}{919.443} \right) \times 100\% = 99.967\%$$

Parameters	In Situ Ethanolysis - 2.0 wt.% NaOMe, 2 hours and 600 rpm				
	30^oC	40^oC	50^oC	60^oC	70^oC
Monoglyceride	0.03	0.03	0.03	0.09	0.13
Diglyceride	0	0.07	0	0.30	0.48
Triglyceride	0	0.22	0	1.11	1.23
Free Glycerine	0.016	0.019	0.02	0.012	0
Total Glycerine	0.024	0.060	0.028	0.196	0.207
Ethyl Ester	99.970	99.680	99.77	98.3	97.91
Ester Yield (%)	99.967	99.678	99.768	98.298	97.908

Note : Monoglyceride, diglyceride, triglyceride and ethyl ester have the same unit of wt.%.

An example of calculation :

$$\text{Total Glycerin} = \text{Free Glycerin} + \text{Bound Glycerin}$$

$$= 0.016 + (0.2591 \times 0.03) + (0.1488 \times 0) + (0.1044 \times 0)$$
$$= 0.024 \text{ wt.\%}$$

Parameters	In Situ Ethanolysis - 1.0 wt.% NaOMe, 2 hours and 600 rpm				
	30°C	40°C	50°C	60°C	70°C
Total Glycerine	0.34	0.72	0.83	1.72	2.41
	In Situ Ethanolysis - 1.0 wt.% NaOH, 4 hours and 600 rpm				
Total Glycerine	0.34	0.69	1.18	1.66	1.91
	In Situ Ethanolysis - 1.0 wt.% KOH, 6 hours and 600 rpm				
Total Glycerine	7.64	7.53	9.57	6.16	5.44