PRODUCTION OF BIODIESEL FROM JATROPHA CURCAS L USING NaOH AND AMANO LIPASE M CATALYST IN AN AIRLIFT REACTOR

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A thesis submitted in fulfillment
of the requirements for the award of the Degree of
Bachelor of Chemical Engineering (Biotechnology)

Faculty of Chemical & Natural Resources Engineering
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DECEMBER 2010

ABSTRACT

Currently there is an urgent need of develop alternative energy resources, such as biodiesel fuel due to the gradual reduction of world petroleum reserves and the impact of environmental pollution of increasing exhaust emissions. Based on the research before, the percentages of Biodiesel yield from J.Curcas L. is too low (30% yield). So, in this research the improvement of the production yield of biodiesel from J.Curcas L is done using Sodium hydroxide (NaOH) and Amano M. lipase in an airlift reactor. Biodiesel is a monoalkyl esters of long chain fatty acids derived from vegetable oils or animal fats by the transesterification with alcohols in the present of catalyst. The objective of this research is to investigate the best parameter of methanol to oil ratio, reaction time and temperature to produce high yield of biodiesel. Multiple step acid-base catalyzed transesterification and enzymatic transesterification process using airlift reactor are the methods used in this research. The concentration of sodium hydroxide (NaOH) and sulphuric acid (H_2SO_4) used are 1.5% (w/w), meanwhile the enzyme catalyst (Amano M lipase) used is 1 g. The methyl ester are analyze using GC/FID with the standard concentration of 0.004, 0.008,0.012, 0.016, 0.020 mg/mL. In this research, the optimal yield of biodiesel from jatropha oil at optimal sodium hydroxide catalyst concentration 1.5% (w/w), reaction temperature 50°C, reaction time one hour and molar ratio of methanol to oil 6:1. While the optimal yield of biodiesel from jatropha oil with Amano M. lipase enzyme is at temperature 35°C, reaction time 24 hour and molar ratio of methanol to oil 3:1. The enzymatic take long time of reaction but the quality of the biodiesel is more higher compare to the acid-base transesterification. Alcohol to oil ratio, reaction time, reaction temperature, and catalyst concentration are four primary factors affecting the yield of biodiesel.

ABSTRAK

Pada ketika ini, pembangunan sumber tenaga alternatif, seperti bahan bakar biodiesel amat di perlukan disebabkan penurunan secara berperingkat minyak dunia dan kesan pencemaran alam sekitar dari peningkatan emisi gas buang yang semakin memberangsangkan. Berdasarkan kajian sebelum ini, peratusan hasil Biodiesel dari J. Curcas L. adalah terlalu rendah (30 hasil%). Jadi, dalam kajian ini peningkatan hasil pengeluaran biodiesel dari J. curcas L dilakukan dengan menggunakan Natrium hidroksida (NaOH) dan Amano lipase M. dalam reaktor Airlift. Biodiesel adalah monoalkyl ester asid lemak rantai panjang berasal dari minyak tumbuhan atau lemak haiwan oleh pengtransesteran dengan alkohol dalam kehadiran katalis. Matlamat kajian ini adalah untuk megenalpasti parameter terbaik kuantiti metanol terhadap minyak, masa reaksi dan suhu untuk menghasilkan hasil yang tinggi dari biodiesel. Beberapa langkah pengtransesteran menggunakan katalis asid-alkali dan proses pengtransesteran enzim menggunakan reaktor Airlift adalah kaedah yang digunakan dalam kajian ini. Konsentrasi sodium hidroksida (NaOH) dan asid sulfat (H_2SO_4) yang digunakan adalah 1.5% (w / w), sedangkan mangkin enzim (Amano M lipase) yang digunakan adalah 1 g. Ester metil dianalisis dengan menggunakan GC / FID dengan kepekatan standard 0.004,, 0.008,0.012 0,016 mg, 0,020 / mL . Dalam kajian ini, hasil yang optimum biodiesel dari minyak jarak pada konsentrasi mangkin natrium hidroksida optimum 1.5% (w / w), suhu 50 ° C, masa reaksi satu jam dan nisbah molar metanol terhadap minyak 06:01. Sedangkan hasil yang optimum biodiesel dari minyak jarak dengan enzim lipase M. Amano adalah pada suhu 35 ° C, masa reaksi 24 jam dan nisbah molar metanol terhadap minyak adalah 3:1. Proses pengtransesteran menggunakan mangkin enzim memerlukan masa yang lama tetapi hasil biodiesel lebih tinggi berbanding dengan pengtransesteran Asid alkali. Kuantiti alkohol terhadap minyak, masa, suhu, dan konsentrasi mangkin alkali merupakan empat faktor utama yang mempengaruhi hasil biodiesel.

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LIST OF SYMBOLS/ABBREVIATIONS

NaOH	- Sodium Hydroxide
H_2SO_4	- Acid Sulphuric
GC	- Gas Chromatography
wt%	- Weight Percent
^{o}C	- Degree Celsius
FKKSA	- Fakulti Kejuruteraan Kimia Sumber Asli
M	- Molar
µm	- Micrometer
pH	- Potential For Hydrogen Ion Concentration
Ca	- Concentration
g	- Gram

CHAPTER 1

INTRODUCTION

1.1 Research Background

Currently there is an urgent need of develop alternative energy resources, such as biodiesel fuel due to the gradual reduction of world petroleum reserves and the impact of environmental pollution of increasing exhaust emissions. Vegetable oil is a promising alternative because it has several advantages, it is renewable, environ-friendly and produced easily in rural areas, where there is an acute need for modern forms of energy. Therefore, in recent years several researches have been studied to use vegetable oils such as Jatropha Curcas L as fuel in engines as biodiesel (Pramanik, 2003; Bozbas, 2005). Furthermore, vegetable oil-based products hold great potential for stimulating rural economic development because farmers would benefit from increased demand for vegetable oils. Various vegetable oils, including palm oil, soybean oil, sunflower oil, rapeseed oil, and canola oil have been used to produce biodiesel fuel and lubricants (Demirbas, 2003).

The exhaustion of world petroleum reserves and the increased environmental concerns have stimulated the search for alternative sources for petroleum-based fuel, including diesel fuels. Because of the closer properties, biodiesel fuel (fatty acid methyl ester) from vegetable oil is considered as the best candidate for diesel fuel substitute in diesel engines. With increasing demand on the use of fossil fuels, stronger threat to clean environment is being posed as burning of fossil fuels is associated with emissions like CO2, CO, SOx, NOx and particulate matter and are currently the dominant global source of emissions. The harmful exhaust emissions from the engines, rapid increase in the prices of petroleum products and uncertainties of their supply have jointly created renewed interest among the researchers to search for suitable alternative fuels. Compressed natural gas, propane, hydrogen, and alcohol-based substances (gasohol, ethanol, methanol, and other neat alcohol) all have their proponent.

The prices of fuel are going up day after day in the world. So, ways and means have been sought for many years to be able to produce oil-substitute fuel. Biodiesel extracted from vegetable oil is one such renewable alternative under consideration. The production of biodiesel would be cheap as it could be extracted from non-edible oil sources. Jatropha curcas (Linnaeus), a non-edible oil-bearing and drought-hardy shrub with ecological advantages, belonging to the Euphorbiaceae family, was found to be the most appropriate renewable alternative source of biodiesel. The extracted oil could not be used directly in diesel engines because of its high viscosity. High viscosity of pure vegetable oils would reduce the fuel atomization and increase fuel spray penetration, which would be responsible for high engine deposits and thickening of lubricating oil. The use of chemically altered or transesterified vegetable oil called biodiesel does not require modification in engine or injection system or fuel lines and is directly possible in any diesel engine.

Pure biodiesel (B100) can be used in any petroleum diesel engine, though it is more commonly used in lower concentrations. Since biodiesel is more often used in a blend with petroleum diesel, there are fewer formal studies about the effects on pure biodiesel in unmodified engines and vehicles in day-to-day use. Fuel which meets the standards and engine parts that can withstand the greater solvent properties of biodiesel are expected to and in reported cases does run without any additional problems than the use of compared to petroleum diesel.

Advantages of biodiesel

1. Produced from sustainable / renewable biological sources.
2. Eco-friendly and oxygenated fuel.
3. Sulphur free, less Carbon (CO) and HC, particulate matter and aromatic compound emissions.
4. Income to rural community.
5. Biodiesel provides better engine lubrication than Low Sulphur Petro diesel.
6. Fuel properties similar to the conventional fuel.
7. Used in existing unmodified diesel engines.
8. Reduce expenditure on oil imports.
9. Non toxic, biodegradable and safety to handle.
10. Less Global Warming: Biofuel contain carbon that was taken out of the atmosphere by plants and trees as they grew. The Fossil fuels are adding huge amounts of stored carbon dioxide (CO_2) to the atmosphere, where it traps the Earth's heat like a heavy blanket and causes the world to warm. Studies show that biodiesel reduces CO_2 emissions to a considerable extent and in some cases all most nearly to zero.

Jatropha Curcas Linnaeus

Jatropha is a genus of approximately 175 succulent plants, shrubs and trees (Jatropha Curcas L) from the family Euphorbiaceae. The oil yielding plant *Jatropha Curcas* L. is a multipurpose and drought resistant large shrub, which is widely cultivated in the tropics as a live fence. The Jatropha plant can reach a height up to 5 m and its seed yield ranges from 7.5 to 12 tons per hectare per year, after five years of growth. The oil content of whole Jatropha seed is 30-35 % by weight basis.

Jatropha Curcas plants have the following unique qualities:

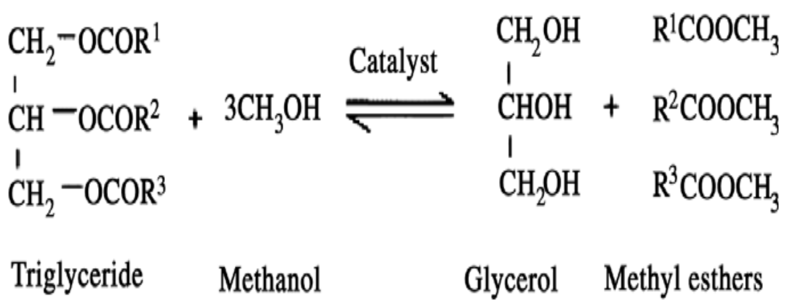
1. Oil yield, approximately 33%.
2. Thrives well in tropical climates such as Malaysia.
3. Fast growth; produces fruits after 6 months of cultivation.
4. Low maintenance - the use of pesticides and other polluting substances are not necessary, due to the pesticidal and fungicidal properties of the plant.
5. Life expectancy of more than 45 years.
6. One Jatropha fruit contains 2-4 seeds that are processed into oil, which will then be used to produce biodiesel.
7. Small-sized and shady shrubs which makes it easy to harvest.
8. An acre of land is capable of accommodating cultivation of 800 plants. A 10-inch seedling is sold at the prices of RM 2.50 at the nurseries.
9. Per acre yield of 3.6 metric tons of fruits in the first three years and multiply after the third year.

Table 1.1 : Fatty acid composition of Jatropha Curcas oil (ASTM standard)

Fatty acid composition of *Jatropha curcas* oil.

Fatty Acid	Formula	% Composition
Palmitic acid (P)	$C_{16}H_{32}O_2$ $CH_3(CH_2)_{14}COOH$	14.1
Palmitolileic acid	$C_{16}H_{30}O_2$ $CH_3(CH_2)_5CH=CH-(CH_2)_7-COOH$	0.5
Stearic acid (S)	$C_{18}H_{38}O_2$ $CH_3(CH_2)_{16}COOH$	6.8
Oleic acid (O)	$C_{18}H_{34}O_2$ $CH_3(CH_2)_7-CH=CH-(CH_2)_7COOH$	38.6
Linoleic acid (L)	$C_{18}H_{32}O_2$ $CH_3(CH_2)_4\,CH=CH-CH_2-CH=CH-(CH_2)_7$ COOH	36.0
Linolenic acid (LL)	$C_{18}H_{30}O_2$ $CH_3(CH_2)_4CH=CH-CH_2-CH=CH-CH_2-$ $CH=CH-(CH_2)_4\,COOH$	0.2
Arachidice acid	$C_{20}H_{40}O_2$ $CH_3-(CH_2)_{18}\,COOH$	0.2
Gadolic Acid	$C_{20}H_{36}O_2$	3.6

In the production of biodiesel process, Jatropha Curcas L seed will be extracting to form crude oil and the crude oil (triglyceride) then will mix together with methanol to produced biodiesel (glycerol) and methyl esters. The reaction is simplified as this : (anonymous, 2003)



Transesterification reaction will take part in this process to produce the high quality biofuel. Finally, the product of jatropha oil can be use as a biodiesel in transportations and vehicles.

In the pilot biodiesel plant, jatropha oil is blended with alcohol and catalyst mixture in transesterification reactor. The reactor is kept at reaction temperature for specific duration with vigorous agitation. After reaction, the biodiesel and glycerol mixture is sent to the glycerol settling tank. The crude biodiesel is collected and washed to get pure biodiesel. Depending upon the need, the size of the unit can be scaled up to get higher production capacity. The fuel properties of jatropha biodiesel produced in the pilot plant are given in the Table 1.2 and Table 1.3 shows the feedstock for biodiesel production and their physicochemical properties.
(Gubitz et al., (1999).

Table 1.2 Fuel properties of jatropha oil and its biodiesel Properties

	Jatropha Oil	**Jatropha biodiesel**	**Diesel**
Density, g/ml	0.920	0.865	0.841
Viscosity @ 40 ^{o}C, Cst	3.5	5.2	4.5
Calorific value, MJ/kg	39.7	39.2	42.0
Flash point, ^{o}C	240	175	50
Cloud point, ^{o}C	16	13	9

Table 1.3 The feedstock for biodiesel production and the properties (Patil PD et.al, 2009)

Feedstocks for biodiesel production and their physicochemical properties.

Type of oil	Species	Main chemical composition (fatty acid composition wt.%)	Density (g/cm³)	Flash point (°C)	Kinematic viscosity (cst, at 40 °C)	Acid value (mg KOH/g)	Heating value (MJ/kg)
Vegetable oil							
Edible oil	Soybean	C16:0, C18:1, C18:2	0.91	254	32.9	0.2	39.6
	Rapessed	C16:0, C18:0, C18:1, C18:2	0.91	246	35.1	2.92	39.7
	Sunflower	C16:0, C18:0, C18:1, C18:2	0.92	274	32.6	-	39.6
	Palm	C16:0, C18:0, C18:1, C18:2	0.92	267	39.6[a]	0.1	-
	Peanut	C16:0, C18:0, C18:1, C18:2, C20:0, C22:0	0.90	271	22.72	3	39.8
	Corn	C16:0, C18:0, C18:1, C18:2, C18:3	0.91	277	34.9[a]	-	39.5
	Camelina	C16:0, C18:0, C18:1, C18:2 C18:3, C20:0, C20:1, C20:3	0.91	-	-	0.76	42.2
	Canola	C16:0, C18:0, C18:1, C18:2, C18:3			38.2	0.4	
	Cotton	C16:0, C18:0, C18:1, C18:2	0.91	234	18.2		39.5
	Pumpkin	C16:0, C18:0, C18:1, C18:2	0.92	>230	35.6	0.55	39
Non-edible oil	Jatropha curcas	C16:0, C16:1, C18:0, C18:1, C18:2	0.92	225	29.4	28	38.5
	Pongamina pinnata	C16:0, C18:0, C18:1, C18:2, C18:3	0.91	205	27.8	5.06	34
	Sea mango	C16:0, C18:0, C18:1, C18:2	0.92	-	29.6	0.24	40.86
	Palanga	C16:0, C18:0, C18:1, C18:2	0.90	221	72.0	44	39.25
	Tallow	C14:0, C16:0, C16:1, C17:0, C18:0, C18:1, C18:2	0.92	-	-	-	40.05
	Nile tilapia	C16:0, C18:1, C20:5, C22:6, other acids	0.91	-	32.1[b]	2.81	-
	Poultry	C16:0, C16:1, C18:0, C18:1, C18:2, C18:3	0.90	-	-	-	39.4
Others	Used cooking oil	Depends on fresh cooking oil	0.90	-	44.7	2.5	-

[a] Kinematic viscosity at 38 °C, mm²/s.
[b] Kinematic viscosity at 37 °C, mm²/s.

1.2 Problem Statement

Based on the previous research, the percentages of Biodiesel yield from J.Curcas L. is still low (30% yield). The low yields of the biodiesel production lead to the economical problem. For this research, the optimal parameters (methanol oil ratio, temperature, reaction time and concentration of NaOH) has been searching due to optimization of biodiesel production. The abundant of Jatropha tree in the world are wasted if there are no use toward industry because it is not suitable for human consumption due to the presence of some toxic components in the oils. Other than that, the prices of fuel are going up day after day in the world. So, ways and means have been sought for many years to be able to produce oil-substitute fuel and in this research, Jatropha Curcas L is used to reduce the cost of biodiesel production. Moreover, the improvement of the production yield of biodiesel from J.Curcas L has been testing using airlift reactor in order to achieve the suitable process equipment for the maximum biodiesel production.

1.3 Research Objectives

The main objectives of this research are:

1. To produce Biodiesel from Jatropha Curcas Linnaeus oil using NaOH and Amano lipase M catalyst in airlift reactor.
2. To improve the parameters effect (molar ratio oil : metanol, temperature, and reaction time) to produce high yield of Biodiesel from Jatropha Curcas L using NaOH and Amano Lipase M catalyst in an airlift reactor.

1.4 Scope of Research

The main scope of this research is:

- Biodiesel production from J.Curcas L using NaOH and Amano lipase M in an airlift reactor.
- Analyzed of biodiesel using Gas Chromatography (GCMs)
- Evaluate the parameters used in this research for both catalyst used.

NaOH catalyst	Amano Lipase M catalyst
Methanol/oil ratio (3:1,4:1,5:1,6:1,7:1)	Methanol/oil ratio (3:1,4:1,5:1,6:1,7:1)
Temperature (50 ˚C & 65 ˚C)	Temperature (35 ˚C)
Reaction time (1,1.5,2) h	Reaction time (5,24,48) hours

1.5 Research Advantages

1. The Jatropha Curcas L oil will be substitutes petroleum as a raw material of for biodiesel production.
2. Biodiesel from Jatropha Curcas L oil can kept the environment safe from sulphur produce by petroleum.
3. Economic of Malaysia will be stable and will growth fast.

1.6 Rationale & Significance of Research

This research is proposed to improve the capability of Jatropha Curcas L as a biodiesel feedstock in the present worldwide due to the increasing demand of biodiesel, the environmental concern and limited resources of petroleum oil. Many researches before use J.Curcas L to produced biodiesel but the yield of biodiesel is still low. Hence, this research is a further research on finding the suitable parameters that can produce higher yield of biodiesel. Novozyme 435 is a lipase that will be use as a catalyst in this process. Using air-lift bioreactor can help to reduce power consumption in producing biodiesel.

Biodiesel have so many advantages such as, is a renewable energy sources, safe for use in all conventional diesel engines, offers the same performance and engine durability as petroleum diesel fuel, non-flammable and nontoxic, reduces tailpipe emissions, visible smoke and noxious fumes and odors. So, Jatropha Curcas L is used as a raw material to substitutes the petroleum because it is easy to grow especially in our tropics country.

CHAPTER 2

LITERATURE REVIEW

2.1 Jatropha Curcas Linnaeus (J.Curcas L)

Jatropha curcas L., a multipurpose, drought resistant, perennial plant belonging to Euphorbiaceae family has gained lot of importance for the production of biodiesel. The properties of the crop and its oil have persuaded investors, policy makers and clean development mechanism (CDM) project developers to consider Jatropha as a substitute for fossil fuels to reduce greenhouse gas emissions. However, basic agronomic properties of Jatropha are not thoroughly understood and the environmental effects have not been investigated yet.

Jatropha is easy to establish, grows relatively quickly and is hardy, being drought tolerant. It is not browsed, for its leaves and stems are toxic to animals, but after treatment, the seeds or seed cake could be used as an animal feed (Becker K et.al 1998). Various parts of the plant are of medicinal value, its bark contains tannin, the flowers attract bees and thus the plant has a honey production potential; its wood and fruit can be used for numerous purposes including fuel. Jatropha has important implications formatting the demand for rural energy services and also exploring practical substitutes for fossil fuels to counter greenhouse gas accumulation in the atmosphere. These characteristics along with its versatility make it of vital importance to developing countries (Foidl and Kashyap, 1999).

The raw materials being exploited commercially by the biodiesel countries constitute the edible fatty oils derived from rapeseed, soybean, sunflower, etc. (Li et al., 2006; Xie and Huang, 2006; Antolin et al., 2002). Use of such edible oil to produce biodiesel in China is not feasible in view of a big gap in demand and supply

of such oils as food and they are far too expensive to be used at present. Obviously, the use of non-edible vegetable oils compared to edible oils is very significant.
Jatropha curcas L. oil, due to the presence of toxic phorbol esters is considered a non-edible oil. Jatropha curcas is a drought resistant shrub or tree belonging to the family Euphorbiaceae, which is cultivated in South America, Southeast Asia, India, Africa and China (Schmook et al., 1997; Gubitz et al., 1999; Martinez-Herrera et al., 2006). The role of Jatropha curcas as a substitute for diesel is very remarkable. If Jatropha curcas is grown in large-scale plantations, it has the potential to create a new agricultural industry to provide low-cost biodiesel feedstock. The oil yielding plant Jatropha curcas L. is a multipurpose and drought resistant large shrub, which is widely cultivated in the tropics as a live fence. The Jatropha plant can reach a height up to 5 m and its seed yield ranges from 7.5 to 12 tones per hectare per year, after five years of growth. The oil content of whole Jatropha seed is 30-35 % by weight basis.

Yaakob, et. al.(2009) investigated that one way of reducing the biodiesel production costs is to use the less expensive feedstock containing fatty acids such as inedible oils, animal fats, waste food oil and by products of the refining vegetables oils The fact that Jatropha oil cannot be used for nutritional purposes without detoxification makes its use as energy/fuel source very attractive. The lipid fraction of Jatropha oil seed were extracted and analyzed for their chemical and physical properties such as acid value, percentage free fatty acids (% FFA), iodine value, peroxide value and saponification value as well as viscosity, and density. The fatty acid and triacylglycerol (TAGs) composition of the extracted lipid was revealed using the gas chromatography (GC) and high pressure liquid chromatography (HPLC) method. Both oleic acid (44.7%) and linoleic acid (32.8%) were detected as the dominant fatty acids while palmitic acid and stearic acid were the saturated fatty acids found in the Jatropha oil.

2.2 Biodiesel as a feedstock

Biodiesel is defined as the mono alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, for use in compression-ignition (diesel) engines. This specification is for pure (100%) biodiesel prior to use or blending with diesel fuel, US National Biodiesel Board (2008). Its energy content and the physical and chemical properties are similar to conventional diesel fuel, allowing its use either on its own or mixed with conventional diesel in any diesel engine without requiring any modifications either to the ignition system or the fuel injector. Indeed, to date biodiesel is the only alternative fuel that can be used directly in existing engines. In addition, biodiesel possesses better lubricant properties which enhance engine yield and extend engine life, Vasudevan and Briggs (2008). Biodiesel can be pumped, stored and handled using the same infrastructure, devices and procedure usually employed for conventional diesel fuel. In fact, as biodiesel does not produce explosive vapours and has a relatively high flash point (close to 150ºC), transportation, handling and storage are safer than with conventional diesel, (Al–Zuhair, 2007).

Biodiesel is a variety of ester-based oxygenated fuels derived from natural, renewable biological sources such as vegetable oils. It is name indicates, use of this fuel in diesel engine alternate to diesel fuel. Biodiesel operates in compression ignition engines like petroleum diesel thereby requiring no essential engine modifications. Moreover it can maintain the payload capacity and range of conventional diesel. Biodiesel fuel can be made from new or used vegetable oils and animal fats. Unlike fossil diesel, pure biodiesel is biodegradable, nontoxic and essentially free of sulphur and aromatics. Below are the method that are used for biodiesel production (Dennis et al., 2009).

Table 2.1 Different method for Biodiesel production
(Dennis et al., 2009)

Advantages and disadvantages at different types of catalysts used in the biodiesel production.

Type	Example	Advantages	Disadvantages
Alkali			
Homogeneous	NaOH, KOH	High catalytic activity, low cost, favorable kinetics, modest operation conditions	Low FFA requirement, anhydrous conditions, saponification, emulsion formation, more wastewater from purification, disposable
Heterogeneous	CaO, $CaTiO_3$, $CaZrO_3$, CaO–CeO_2, $CaMnO_3$, $Ca_2Fe_2O_5$, KOH/Al_2O_3, KOH/NaY, Al_2O_3/KI, ETS-10 zeolite, alumina/silica supported K_2CO_3	Noncorrosive, environmentally benign, recyclable, fewer disposal problems, easily separation, higher selectivity, longer catalyst lifetimes	Low FFA requirement, anhydrous conditions, more wastewater from purification, high molar ratio of alcohol to oil requirement, high reaction temperature and pressure, diffusion limitations, high cost
Acid			
Homogeneous	Concentrated sulphuric acid	Catalyze esterification and transesterification simultaneously, avoid soap formation	Equipment corrosion, more waste from neutralization, difficult to recycle, higher reaction temperature, long reaction times, weak catalytic activity
Heterogeneous	ZnO/I_2, ZrO_2/SO_4^{2-}, TiO_2/SO_4^{2-}, carbon-based solid acid catalyst, carbohydrate-derived catalyst, Vanadyl phosphate, niobic acid, sulphated zirconia, Amberlyst-15, Nafion-NR50	Catalyze esterification and transesterification simultaneously, recyclable, eco-friendly	Low acid site concentrations, low microporosity, diffusion limitations, high cost
Enzymes	Candida antarctica fraction B lipase, Rhizomucor mieher lipase	Avoid soap formation, nonpolluting, easier purification	Expensive, denaturation

2.3 Airlift reactor

Airlift systems offer well-known advantages, making them widely used for bioreactor applications (Chisti, 1989): simplicity of design and construction, lower power inputs, low shear-stress field. In this research, air pump is used to due the application of airlift system. Air is purge into the reactor so that the complete reaction will be achieve. This application is same with the other equipment that are using airlift system such as in batch reactor for biodiesel production.

Recently, there is an increased interest in new technologies related to mass transfer enhancement. Maeda et al. and Thanh et al. produced biodiesel from vegetable oils assisted by ultrasound which is a useful tool for strengthening the mass transfer of immiscible liquids. Ultrasonic irradiation causes cavitations of bubbles near the phase boundary between immiscible liquid phases. The asymmetric collapse of the cavitations bubbles disrupts the phase boundary and starts emulsification instantly. Micro jets, formed by impinging one liquid to another, lead to intensive mixing of the system near the phase boundary. With the use of ultrasound biodiesel can be produced without heating because the cavitations may lead to a localized increase in temperature at the phase boundary and enhance the reaction . Moreover, Wen et al. fabricated a new reaction vessel – Zigzag micro-channel reactor in recent years and found that less energy consumption for biodiesel synthesis can be achieved by using this reactor.

2.4 Reaction mechanism of transesterification

Triacylglycerols (vegetable oils and fats) are esters of long-chain carboxylic acids combined with glycerol. Carboxylic acids (R-C(=O)-O-CH3) by the action of the transesterification agent. The parameters affecting the methyl esters formation are reaction temperature, pressure, molar ratio, water content, and free fatty acid content. It has been observed that increasing the reaction temperature, has a favorable influence on the yield of ester conversion. The yield of alkyl ester increases with increasing the molar ratio of oil to alcohol (Demirbas, 2002).

Fatty acid (R_1COOH) + Alcohol (ROH) → R_1COOR + Water (4.19)
Triglyceride + ROH → Diglyceride + $RCOOR_1$ (4.20)
Diglyceride + ROH → Monoglyceride + $RCOOR_2$ (4.21)
Monoglyceride + ROH → Glycerol + $RCOOR_3$ (4.22)

Transesterification consists of a number of consecutive, reversible reaction. The triglyceride is converted stepwise to diglyceride, monoglyceride and finally glycerol, in which 1 mole of alkyl esters is removed in each step. The reaction mechanism or alkali catalyzed transesterification was formulated as 3 steps. The formation of alkyl esters from monoglyceride is believed to be a step that determines the reaction rate, since monoglyceride are the most stable intermediate compound (Ma and Hanna,1999). Several aspect including the type of catalyst (alkaline, acid and enzyme), alcohol or vegetable oil molar ratio, temperature, purity of the reactant (mainly water content) and free fatty acid content have an influence on the course of the transesterification. In the conventional transesterification of fats and vegetable oil for biodiesel production, FFA and water always produce negative effects, since the present of FFA and water causes soap formation, consumes the catalyst, and reduce catalyst effectiveness, all of which result in a low conversion (Kusdiana and Saka, 2004).

2.5 Gas Chromatography/FID

The method proposed by Plank and Lorbeer using capillary gas chromatography, can provide qualitative and quantitative information about the concentrations of contaminants in biodiesel. The method is appropriate for measuring minor and major component in a sample, give a high reliability of results, has simple instrumentation, requires a small amount of sample preparation and has a short analysis time (Plank, 1995). The Chromatography is a very important analytical tool because it allows the chemist to separate components in a mixture for subsequent use or quantification. Most samples that chemists want to analyze are mixtures. If the method of quantification is selective for a given component in the mixture, separation is not required. However, it is often the case that the detector is not specific enough, and a separation must first be performed. There are several types of chromatography depending on the type of sample involved. In this experiment, we'll use gas chromatography. The gas chromatograph makes it possible to separate the volatile components of a very small sample and to determine the amount of each component present. The essentials required for the method are an injection port through which samples are loaded, a "column" on which the components are separated, a regulated flow of a carrier gas (often helium) which carries the sample through the instrument, a detector, and a data processor. In gas chromatography, the temperature of the injection port, column, and detector are controlled by thermostat heaters.