BIODIESEL PRODUCTION FROM WASTE COOKING OIL VIA SINGLE STEPS TRANESTERIFICATION PROCESS WITH THE AID OF SODIUM METHOXIDE AS A CATALYST

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A report submitted in partial fulfillment of the requirement for the award of the degree of Bachelor Engineering in Chemical Engineering

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I declare that this thesis entitled “*Biodiesel Production from Waste Cooking Oil via Single Steps Transesterification Process with the Aid of Sodium Methoxide as a Catalyst*” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : ....
Name of Candidate: MOHD GHADAFI BIN ISMAIL
Date : 14 MAY 2008

Special dedication to my beloved father, mother,
brothers and sisters..

Al-fatihah;
my beloved father
Hj Ismail Bin Kassim, 1947-1997

for their love support and best wishes..

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ABSTRACT

Biodiesel popularly known as an alternative diesel fuel in developed countries mainly for transportation and agriculture industry. Now days, biodiesel became more important due to insufficient of petroleum fuel and the needs of environmental friendly energy sources. The high price of crude petroleum oil to has made biodiesel become more favorable in the market. Due to the high cost of raw material, waste cooking oil use as raw material instead of conventional method using vegetable oil. However, waste cooking oil contain high amount of free fatty acid and thus, single steps transesterification process with the aid of homogeneous catalyst were implemented in this experiment with sodium methoxide is use as homogeneous catalyst. Methanol was chosen as alcohol solvent because its price is more cheaper compare to others type of alcohol. In the transesterification process, the triglycerides will react with a methanol to form esters and a by product glycerol. In this experiment, Response surface methodology (RSM) was used to studies the effect of two variables which are reaction time (varied from 30 minutes to 90 minutes) and catalyst concentrations (0.5 wt.% to1.0 wt%). The oil to methanol ratio was fixed at 1:6 and temperature was fixed at 65^{o}C. The sample of each experiment was analyzed using thin layer chromatography (TLC) and the yield of biodiesel was recorded. The optimal reaction condition to achieve highest methyl ester content was at reaction time 70.15 minutes and catalyst concerntration was at 1.50wt.% while the optimal reaction condition to achieve highest biodiesel yield was at reaction time 64.66 minutes with the catalyst concerntration of 0.92wt.%.

ABSTRAK

Biodiesel yang juga dikenali sebagai sumber alternatif bagi bahan api di negara-negara moden sebagai pengganti bagi minyak petro-diesel terutamanya didalam sector pengangkutan dan pertanian. Pada masa kini, biodiesel semakin penting sebagai pengganti bahan api kerana kekurangan bahan api petroleum dan untuk mencari sumber yang lebih mesra alam. Harga bahan api di pasaran yang tinggi telah meningkatkan lagi permintaan terhadap biodiesel. Oleh kerana itu, sisa miyak masak digunakan sebagai bahan mentah menggantikan cara konventional yang menggunakan minyak sayuran sebagai bahan mentah. Walau bagaimanapun, sisa minyak masak mengandungi asid lemak bebas yang tinggi dan oleh itu, satu langkah proses transesterifikasi telah diaplikasikan didalam eksperimen ini dengan natriun metoksida digunakan sebagai mangkin homogenus. Methanol digunakan sebagai pelarut alkohol kerana ianya lebih murah berbanding pelarut alkohol yang lain. Didalam proses transesterifikasi, triglycerida akan bertindak balas dengan methanol untuk menghasilkan esters dan gycerol sabagai hasil sampingan tindak balas. Didalam eksperimen ini, dua pemboleh ubah yang akan mempengaruhi hasil biodiesel adalah masa tindak balas dan kepekatan mangkin dikaji. *Response surface methodology* (RSM) digunakan untuk mengkaji kesan dua ubah ini iaitu masa tindak balas (30minit-90 minit), dan kepekatan mangkin (0.5 wt.%-1.5 wt.%). Nisbah minyak kepada methanol adalah adalah malar pada 1:6 dan suhu tindak balas tetap pada 65^{o}C. Setiap sampel akan dianalisis menggunakan ‘Thin Layer Chromatography’ dan hasil (yield) untuk mengkaji hasil biodiesel dan pertukaran asid bebas lemak ketika eksperimen. Keadaan eksperimen yang paling optimum bagi kandunagn metil esters adalah pada masa tindak blasa pada 70.15 minit dan kepekatan mangkin pada 1.5wt.% manakala bagi hasil produk adalah pada masa tindak balas 64.66 minit dan kepekatan mangkin pada 0.92wt.%.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Introduction

In the recent years, the world was hit by energy crisis. Now days, the world major energy demand is fulfilled by conventional energy sources such as coal and fossil. The global are now concern about the source for petroleum based fuel are very limited reserves and only concentrated in certain regions of the world. The source in many countries is getting in the verge of extinct. Many experts suggest that current oil and gas reserves would only last for the next few decades. This in conjunction with political instability in Gulf country such as Iraq has made the price of crude petroleum oil to soar.

It is well known that most of transportation vehicles use fossil fuel such gasoline, liquid petroleum gas, and diesel fuel as fuel. Thus the use of alternatives energy such as hybrid technology and hydrogen cell requires extra modification to the vehicles engine. This makes it needs higher cost, higher time to develop, and not suitable in short term replacement to fossil fuel. In order to meet global rising of energy demand, more reliable energy sources that not depended on fossil fuel are needed. Thus exploring new energy sources, such as biodiesel has become more importance in recent years.

1.2 Background of Study

Biodiesel which is also popularly known as biofuel is an alternative diesel fuel made from conventional vegetable oil or fats. Biodiesel commonly defined as alkyl esters class of long chain fatty acids derived from vegetable oil. Vegetable oil will react with alcohol to form alkyl esters and glycerol in the presence of catalyst. Biodiesel are being considered as the most preferable oil as diesel fuel substitute ever known. The combustion resulted by using biodiesel shown no decreasing in performance, instead its produce more cleanly exhaust emission. Three main criteria that biodiesel has been recognized as major renewable energy resources around the world are its renewable resources that could be sustainable developed in the future, environmental friendly and give significant economic potential that can be developed in the near future. Its special characteristic, combine with its environmental friendly promises a bright future in the fuel industry.

In Malaysia, biodiesel has been widely accepted in the country. The National Biofuel Policy which was launch by the prime minister in 2006 has boosted the industry to the next level. The demand for biofuel in Europe is projected to increase from 3 million tonne in 2005 to 10 million tonne in 2010 (The National Biofuel Policy, 2006). Other country such as India, Japan, Brazil and United States has started to invest heavily in the biofuel industry. Thus, Malaysia as the largest palm oil producer and exporter is now looking forward to be pioneer in palm oil based biofuel producer. The main and the only vegetable oil use in commercial scale to produce biodiesel in Malaysia is palm oil.

Palm oil is one of seventeen major oil traded in the global edible oil and fats market. Palm oil is consumed world wide in more than 100 countries in the world (MPOC, 2007). Among others vegetable oil, palm oil is the most efficient which produces the highest tonnage of oil per hectare per year. In 2006, palm oil contributes the highest percentage, 27.1% from 146.28 million tonnes total world consumption of vegetable oil and fats. Figure 1.1 shows the total of world oil and fats consumption. Malaysia exports most of its palm oil which resulted in billion of Ringgit earnings to the country. In 2006, palm oil being the largest contributor to the agricultural sector, recorded strong export earnings of RM21.6 billion or 51.4% of total agricultural exports value.

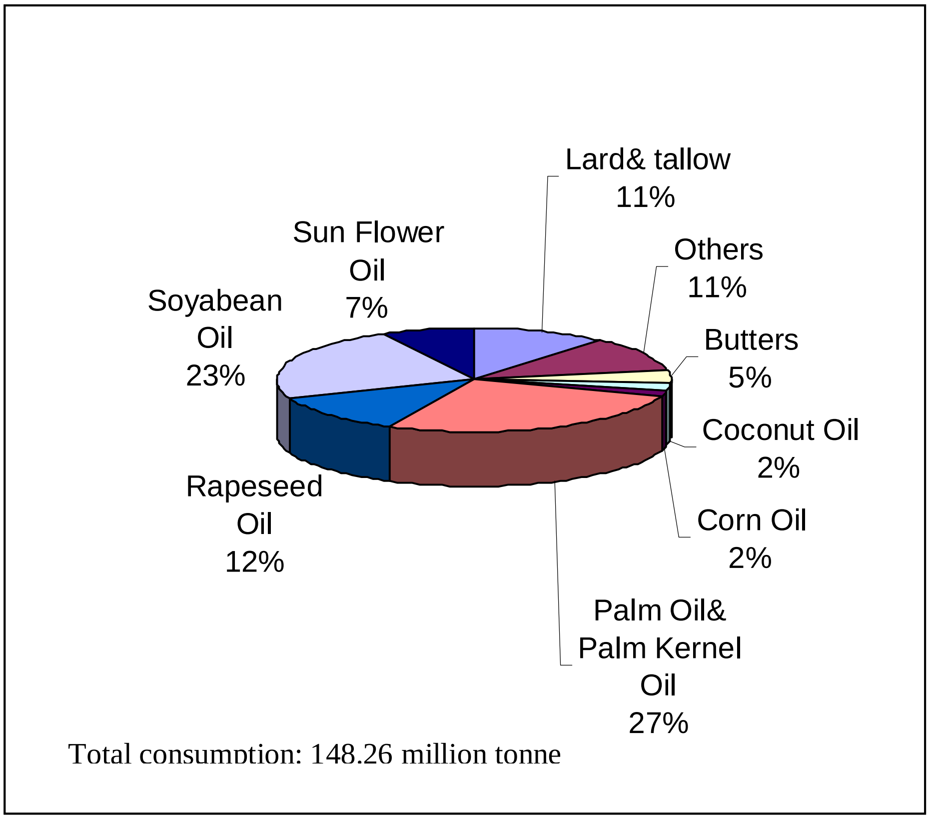


Figure 1.1 World consumption of oil & fats in 2006 (MPOC, 2007)

Palm oil offer wide range of product from cooking oil, biodiesel to oleochemical product. Because of this, the price of palm oil is very sensitive and volatile, but palm oil can still be considered as the cheapest vegetable oil compare to the other vegetable oil. The most consumption of palm oil is use in cooking oil. The cooking oil produced from palm oil can withstand excessive temperature without chemical change (APOC, 2007). Many modern countries such as Japan, South Korea and China has started to use cooking oil from palm oil instead of traditionally using animal fats as frying oil.

The Malaysian government is refocusing the use of palm oil to the production of biodiesel to cater the huge demand from European countries. Malaysia has started the research and development of biodiesel since 1982, and now has successfully produced commercially palm oil methyl esters B5 which is blend of processed palm oil (5%) with petroleum diesel (95%) as a suitable fuel for the transport and industrial sectors. The production of biodiesel or popularly known as Envodiesel shows that how the government has seriously focus on the industry. To meet the demand from European countries, the Malaysia government has now built up five plant biodiesel with five more plant to be built by the year end. The Malaysian biofuel project, when fully implemented in 2008, is expected to absorb up to 500,000 tonnes of palm oil per annum. Malaysia has also agreed to set aside up to 40% (about six million tonnes) of the country's total palm oil production for biodiesel (The National Biofuel Policy, 2006).

Malaysia is now moving forward towards the vision 2020. During this modernization era, Malaysia will face up several global issues which we need to overcome wisely. The world energy crisis has made us to find an alternatives energy sources. The depletion of fossil fuels will require Malaysia to use more sources of renewable energy for the sustainability of its development. Current fossil fuel sources only can last just another 20 to 30 years. Exported of crude petroleum oil also recorded the highest earning to the Malaysia economic (MPOB, 2007). Thus in the next 20 or 30 years, a replacement for crude petroleum oil are needed to maintain the economy stability. The production of biodiesel will be the key factor to overcome this problem.

Malaysia as a party of United Nations Framework Convention on Climate Change (UNFCCC) must continuously find initiatives to prevent global pollution (The National Biofuel Policy, 2006).The using of biodiesel will help to reduce air pollutant especially in urban area such as Klang Valley, Pulau Pinang, and Johor Bharu. The use of biodiesel in transportation sector will improve air quality and reduce greenhouse emission effect. This surplus with using waste cooking oil as raw material for biodiesel production and hence minimizes the oil pollution to the environment.

1.3 Problem Statement

Malaysia has the potential to lead the way in biofuel production capitalizing on its vast production of agricultural products and by-products. This will contribute in utilizing local resources for biofuel, exploiting local technology to generate energy for the transportation and industrial sectors, and paving the way for exports of biofuel. The price of biodiesel is much higher compare to conventional diesel makes it is less chosen by the customer. Thus the aim of this project is to produce biodiesel as diesel substitute with minimum cost with potential to be commercialized.

The sensitivity of oil palm price resulted in instability of oil palm price. The higher prices of crude petroleum oil will shift the market trend favourable towards the palm oil. Thus, the high market demand of palm oil makes the prices more volatile. Even though the price of palm oil is much cheaper than crude petroleum oil, the Malaysia government gives subsidized to petroleum oil in transportation sector resulted in lower prices compare to biodiesel. The main reason of high prices in production of biodiesel is because of its raw material. Thus, using waste cooking oil as raw material will make the biodiesel price more comparable than subsidized petroleum diesel. The availability, cost and continuity are the main criteria for good raw material. The easy availability of waste cooking oil and continuity of supply make it as a good choice of raw material.

Single steps transesterification process will be used in synthesizing waste cooking oil to methyl ester. Single steps transesterification process provide less time in reaction, lower temperature and pressure, and hence will result in less cost of production. The high content of free fatty acid in waste cooking oil need to be synthesize using homogenous catalyst. Even though the use of homogenous catalyst resulted in higher formation of soap, homogenous catalyst provides shorter reaction time compare to heterogeneous. Powdered sodium methoxide is used as homogenous catalyst in this experiment. In the transesterification process, methanol will use as alcohol solvent because of its price is cheaper among other alcohol solvent.

1.4 Objective

The objective of this research is to produce biodiesel from waste cooking oil via single steps transesterification process with the aid of sodium methoxide as a catalyst.

1.5 Scope of Research

This research is an experimental study in production of biodiesel using waste cooking oil as the feedstock. In order to realize this research objective, two scopes have been identified to be studied in this experiment. The three scopes are:

i. To study the effect of time and catalyst concentration on methyl esters content in a single step alkaline base catalyzed transesterification process using degree of experiment.

ii. To study the effect of time and catalyst concentration on biodiesel yield in a single step alkaline base catalyzed transesterification process using degree of experiment.

CHAPTER 2

LITERITURE REVIEW

2.1 Biodiesel

Biodiesel is popularly known as an alternative diesel fuel especially as diesel substitute in developed countries mainly for transportation and agriculture industries. In recent decades, biodiesel are more important due to insufficient of petroleum fuel and the needs of environmental friendly energy resources. Biodiesel is a renewable energy sources that are made from natural vegetable oil, animal fats, or singles cell oil. The concept vegetable oil use as fuel substitute was first found by Dr Rudolf Diesel in 1895 by using peanut oil as a fuel to run his engine (Nistake and Wilson, 1965). Choo and Cheah (2000) stated that the use of biodiesel as an alternative fuel has been extensively evaluated in many countries especially in modern countries which are very sensitive about the environment and pollution. Figure 2-1 shows the world production of biodiesel. It is noted that because of nation environment sensitivity, modern technology and encouragement from the government, western European countries such as German and United Kingdom produce the highest amount of biodiesel.

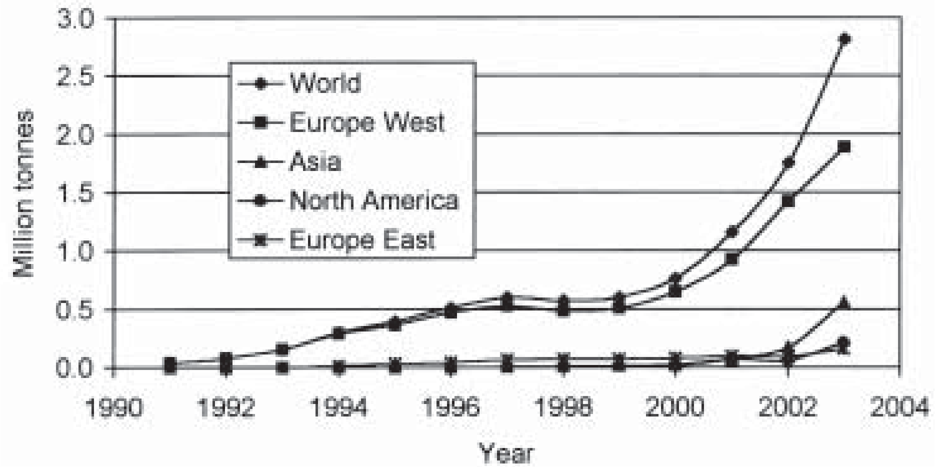


Figure 2.1 World production of Biodiesel (Kourbitz, 2002)

The American Society for Testing and Material (ASTM) defined biodiesel fuel as monoalkyl esters of long chain fatty acids derived from renewable lipid feedstock such as vegetable oils or animal fats. Biodiesel is the only alternative fuel that can be used directly in any diesel engine because it has similar properties to petroleum diesel. It can be used in a neat form or blend with petroleum based diesel. B100 or neat biodiesel is referring as 100% biodiesel fuel while biodiesel blend is pure biodiesel blended with petroleum diesel. Biodiesel blend is referring as Bxx which is the xx indicates the amount of biodiesel blend ((i.e., a B70 blend is 70% biodiesel and 30% petroleum diesel). Table 2.1 shows the ASTM standard specification for neat biodiesel, B100 to be used in diesel engine.

Table 2.1: ASTM standard of biodiesel and diesel fuel.

Test Method	**ASTM D975 (petroleum diesel)**	**ASTM D6751 (biodiesel, B100)**
D93	325K min	403 K
D 2709	0.05 max vol%	0.05 ,ax vol%
D445	1.3 to 4.1 mm2/s	1.9 to 6.0 mm2/s
D874	~	0.02 max wt%
D482	0.01 max wt%	~
D5453	0.05 max wt%	~
D2622/129	~	0.05 max wt%
D 130	No 3 max	No 3 max
D 613	40 min	47 min
D1319	35 max vol%	~
D4530	~	0.05 max mass%
D 524	0.35 max mass%	~
D1160	555K min to 611K max	~

The advantages of using biodiesel include non-toxic to human skin, liquid nature portability, renewable, environmental friendly, higher combustion efficiency, environmental friendly and availability (Mudge and Pereira, 1999; Speidel *et al.*, 2000; Zhang *et al.*, 2003). Biodiesel has higher flash point around 130^{o}C compare to petroleum diesel around 52^{o}C which make it liquid nature portability. In many experiment, testing on the exhaust emission of diesel engine operating on B100 shows reduction in carbon monoxide (CO), total hydrocarbon (THC), and particular matter (PM) emission and smoke together with the increment of nitrogen oxide (NOx) (Kalligeros *et al.*, 2003 ; Lin *et al.*, 2006). Carbon Dioxide (CO_2) produce by combustion of biodiesel can be recycled by photosynthesis and hence reduce the greenhouse gas emission effect. Labeckas and Slavinkas (2006) found that maximum NOx emission increased with increased mass percent of oxygen in the biodiesel and increased engine speed. Thus it shows that biodiesel has higher combustion efficiency than petroleum diesel. Other advantages of using biodiesel include surplus to agricultural sector which will improve rural economy and hence minimize poverty in certain countries. Von Wedel (1999) stated that lubricating properties of biodiesel can reduce engine wear and extend engine life. Biodiesel has higher cetane number which makes it easier to starting and quieter to operate. Cetane number is a measure of the ignition quality of fuel based on ignition delay in an engine. The higher the cetane number, the shorter the ignition delay and the better the ignition quality.

In 1983, JAOCS Symposium on Vegetable Oil and Diesel Fuels concealed that the vegetable oil has a very good potential as an alternative fuel if the main problem and the long term effect could be overcome (Adams *et al.*, 1983; Styer *et al.*, 1983; Klopfenstein and Walker, 1983; Pryde, 1983). The main problem is high viscosity, low volatility, reactivity (polymerization) and the long term effect to engine. Lower volatilities result in formation of deposit in engine due to incomplete combustion and incorrect vaporization characteristic (Meher *et al.*, 2006). Generally, overtime biodiesel will soften and degrade certain type of elastomer and natural rubbers compound. This will affect engine systems which use elastomer or natural rubber for its material. For example, biodiesel can affect fuel system component which consist of fuel hoses and fuel pump seals that contain elastomer compound incompatible with biodiesel and hence required more regularly engine servicing. Others disadvantages of using biodiesel are not weather resistant. Generally, neat biodiesel will begin to freeze at -4^{o}C. Thus during cold weather in some countries, engine will start filter plugging due to high levels of monoglycerides. Monoglycerides are only partially soluble in biodiesel and occur because of incomplete reaction in the production of biodiesel. Thus as biodiesel get cold, monoglycerides will drop out of solution resulting in a gummy substance that may cause filter plunging problem. Table 2.2 summarizes the fuel performance problems on the compression –ignition engine.

Table 2.2: Effect of performance of fuel on compression-ignition engine (Anjana Srivasta and Ram Prasad, 1999).

Performance problem	**Probable fuel-related causes**
1. Poor combustion, smoking	a) low cetane number b) water contamination c) improper cloudpoint d) light/ heavier fuel contamination
2. Excess cylinder wear	a) fuel dilution b) high sulphur content c) dirt(silicon) contamination
3. Injector nozzle plugging/wear	a) soluble metal contaminants b) heavy end impurities c) preformed gum impurities
4. Injector pump fouling sticking	a) high sulphur/ hetero atom content b) heavy end contamination c) gasoline contamination d) low fuel viscosity
5. Filter plugging	a) water contamination b) fuel impurities c) improper cloudpoint
6. Excess engine deposit	a) heavy end contamination b) low cetane number c) high supphur/ hetero atom content

Generally, there are four methods to produce biodiesel from vegetable oil and animal fats (Fangrui and Miltord, 1999). There are direct use and blending, microemulsion, thermal cracking (pyrolysis) and transesterification. The most commonly used method is transesterification. Transesterification is a reaction of lipid with an alcohol to form esters and a by product glycerol. Nowdays, the production using transesterification process has been scaled up to commercialization stage. However, the main obstacle for commercialization of biodiesel is the high cost of production biodiesel compare to petroleum diesel. In several countries such as

Malaysia, the government give subsidized to petroleum diesel makes people tend to used petroleum based diesel. The high cost of production is mainly due to high cost of raw material virgin oil (Krawczgk, 1996; Connemann and Fischer, 1998). Those more research needs to be done to explore new sources of raw material such as to reduce the biodiesel production cost.

2.2 Renewable Sources for Raw Material in Biodiesel Production

There are several sources that can be use as raw material for biodiesel production that is non-edible oil, animal fats and vegetable oil. The raw material must contain triacyglycerols (triglycerides) which consist of three long chains fatty acid esterifies to a glycerol back bone. Figure 3 shows the structure of typical triglycerides molecules.

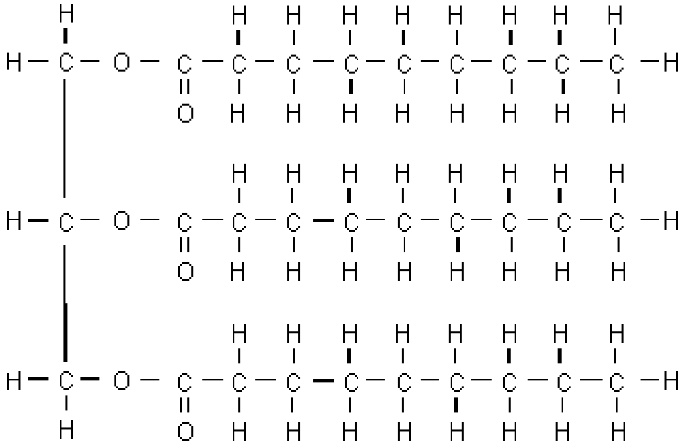


Figure 2.2 Structure of typical triglycerides molecules (Anjana Srivasta and Ram Prasad 1999).

2.2.1 Animal fats

The studied of animal fats for production of biodiesel has not extensively studied as researcher studied in vegetable oil. It is because some method of vegetable oil for biodiesel production is not applicable in animal fats. Generally animal fats and oil are triacylglycerol but with different chemical properties. Animal fats are solid but oil is liquid at room temperature. Thus animal fats cannot be use as fuel in its original form. Fangrui Ma and Milford A. Hanna (1999) has studied that animal fats contains more saturated fatty acid than vegetable oil and thus several problem will occurs such as carbon deposits in the engine, engine durability and lubricating oil contamination because of incompatible with the engine. Most common example of animal fats use is beef tallow, lard and yellow grease.

2.2.2 Vegetable oil

Vegetable oil is divided to two main categories, edible oil and non-edible oil. Edible oil is oil which is use in food industry while non-edible oil is oil which is not use in food industry. Normally, non-edible oil is from vegetable oil which is growth wildly and can survive in bad weather condition.

2.2.3 Non-edible oil

The example of non-edible oil use for biodiesel production includes Jatropha Curcas, Pongamia Pinnata, Algae and Madhuca Indica plants (Rakesh Sarin *et al.,* 2007). The most commonly use was Jatropha Curcas which widely use in India and Indonesia because of its easy availability growth wildly in arid, semiarid and wasteland. Jatropha requires little of water and fertilizers and even can survive on infertile soils. Because of it's wildly growth, pest-resistant, high-seed yield and 30–40 years lifetime the cost of raw material using Jatropa plant is lower than other vegetable oil. The advantages of using Jatropa are cheap and can growth in wasteland and hence providing green cover to the waste land (Malhotra and Sarin, 2004). Nagel and Lamke have examined that alga as potential sources of methyl ester diesel fuel.

Algae can grow practically in every place where there is enough sunshine and can even growth in saline water. The advantages of using algae are biodiesel yield, wildly growth and faster, hence lower the biodiesel production of cost. Sheehan *et al.,* (1998) estimated that the yield (per acre) of oil from algae is over 200 times the yield from the best-performing vegetable oils. Microalgae are the fastest growing photosynthesizing organisms which are can complete their entire life cycle for just a few days. The production of algae to harvest oil for biodiesel has not been undertaken on a commercial scale but more studies are going to made in this matter.

2.2.3.1 Virgin oil

Vegetable oil can be divided into two main categories that are virgin oil and waste cooking oil. Virgin oil is oil a pure vegetable oil such as sunflower oil, palm oil, soy bean oil and rapeseed oil while waste cooking oil is vegetable oil from used frying oil collected from restaurants, catering, and hotel. The major vegetable oil use as feedstock in European countries is rapeseed oil because of it widespread availability while in United States, mainly use soybean oil. In tropical countries such as Malaysia and Indonesia, palm oil is widely use as biodiesel feedstock. The use of methyl esters as fuel necessitates a low proportion of unsaturated fatty acids in order for the fuel to be useable even at low temperatures. Therefore, in cold regions rapeseed oil and olive oil would have been the best feedstock. Among 350 types of vegetable oil identified, only soybean, palm, sunflower, safflower, cottonseed, rapeseed and peanut oils are considered as potential alternative fuels for diesel engines (Goering *et al.,* 1982; Pryor *et al.,* 1982). Table 2.3 shows the world consumption of vegetable oil from several types of plant from year 1998 to 2003. Several sources of vegetable oil such as soybean, rapeseed and palm oil are used to produce biodiesel.

Table 2.3: World vegetable oil consumption (Demirbas, 2005).

Oil	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**
Soybean	23.5	24.5	26	26.6	27.2	27.9
Palm	18.5	21.2	23.5	24.8	26.3	27.8
Rapeseed	12.5	13.3	13.1	12.8	12.5	12.1
Sunflower seed	9.2	9.5	8.6	8.4	8.2	8
Peanut	4.5	4.3	4.2	4.7	5.3	5.8
Cottonseed	3.7	3.7	3.6	4	4.4	4.9
Coconut	3.2	3.2	3.3	3.5	3.7	3.9
Palm kernel	2.3	2.6	2.7	3.1	3.5	3.7
Olive	2.2	2.4	2.5	2.6	2.7	2.8
TOTAL	79.6	84.7	87.5	90.5	93.8	96.9

(million metric tonnes)

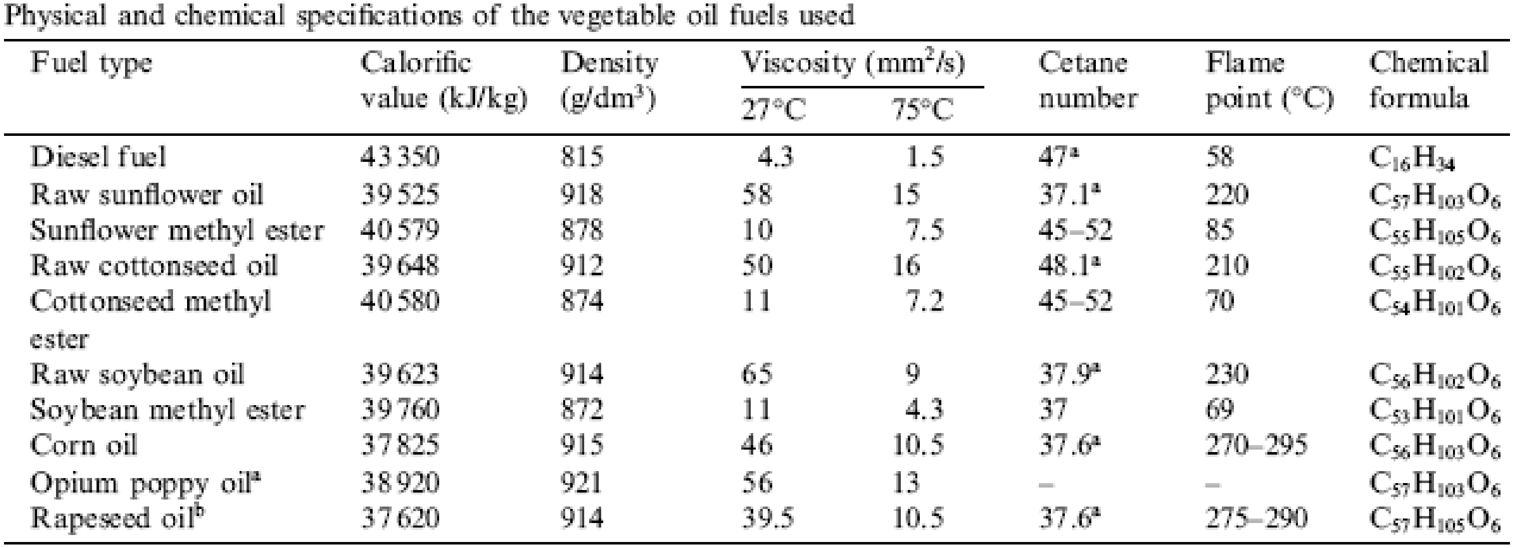
Sunflower oil is one of potential raw material for biodiesel production. Bruwer *et al.,* (1980) studied the use of sunflower seed oil as a renewable energy source and found that by using sunflower oil run in engine tractor, it reported that a power loss occurred after 1000 hour of operation. The cottonseed oil is abundantly produced in Pakistan. The properties cottonseed oil of methyl ester is also very much similar to petroleum diesel. It is reported that cottonseed oil and diesel fuel blends behaved like petroleum-based fuels in short-term performance and emissions tests. The flash point of rapeseed oil is 220^{o}C, which is much higher than diesel fuel. It makes the ignition relatively difficult, but the transportation and handling is much safer.

Schoedder (1981) used rapeseed oil as a diesel fuel with mixed results. The engine tests indicated rapeseed oil had comparable energy outputs to diesel fuel. The properties of soybean oil are also very close to diesel. The flash point of the ester is higher than that of diesel, which requires higher compression ratio and modifications in fuel injector to ignite the fuel in a smooth pattern. Table 2.4 shows the comparison of physical and chemical properties of vegetable oil with diesel fuel. It was noted that most of vegetable oil has similar properties among each other. However, petroleum diesel differs from vegetable oils in several properties such as density, viscosity, calorific value, and flame point.

Palm oil used as vegetable oil to produce biodiesel was first experiment in 1920 in Africa.(Van Den Abeelee, 1992).Palm oil widely produces in Malaysia and Malaysian Palm Oil Board (MPOB) has conducted systematic studies on the production and evaluation of alternative fuel from palm oil and palm oil derivatives (Ong *et al.*, 1992; Choo Ym *et al.,* 1995). The studied found that methyl esters from crude palm oil has comparable characteristic to Malaysian petroleum diesel. Like many other vegetable oils, its flash point is also higher than diesel (1101^{o}C). Table 2.5 shows the fuel characteristic of alkyl esters of crude palm oil (CPO) and crude palm sterin (CPS).

From the table, it is noted alkyl esters from palm oil are slightly higher than petroleum diesel. The sulphur content of these esters is very low compared with the Malaysian petroleum diesel. The exhaust emissions will therefore contain very little SO_2. The viscosities of alkyl esters of CPO are higher but they are still in acceptable value and able to flow under warm condition. Pour point is defined as the lowest temperature that the product still can be poured by gravity. Even though the pour points of alkyl esters of crude palm oil are high, it is still can be considered. Sapaun *et al.,* (1996) reported that studies in Malaysia, with palm oil as diesel fuel substitute, exhibited encouraging results. Performance tests indicated that power outputs were nearly the same for palm oil, blends of palm oil and diesel fuel, and 100% diesel fuel. Short-term tests using palm oil fuels showed no signs of adverse combustion chamber wear, increase in carbon deposits, or lubricating oil contamination. Ejaz Shahid and Younis Jamal (2007) stated that rapeseed oil and palm oil are the most suitable vegetable oil as feedstock in biodiesel production.

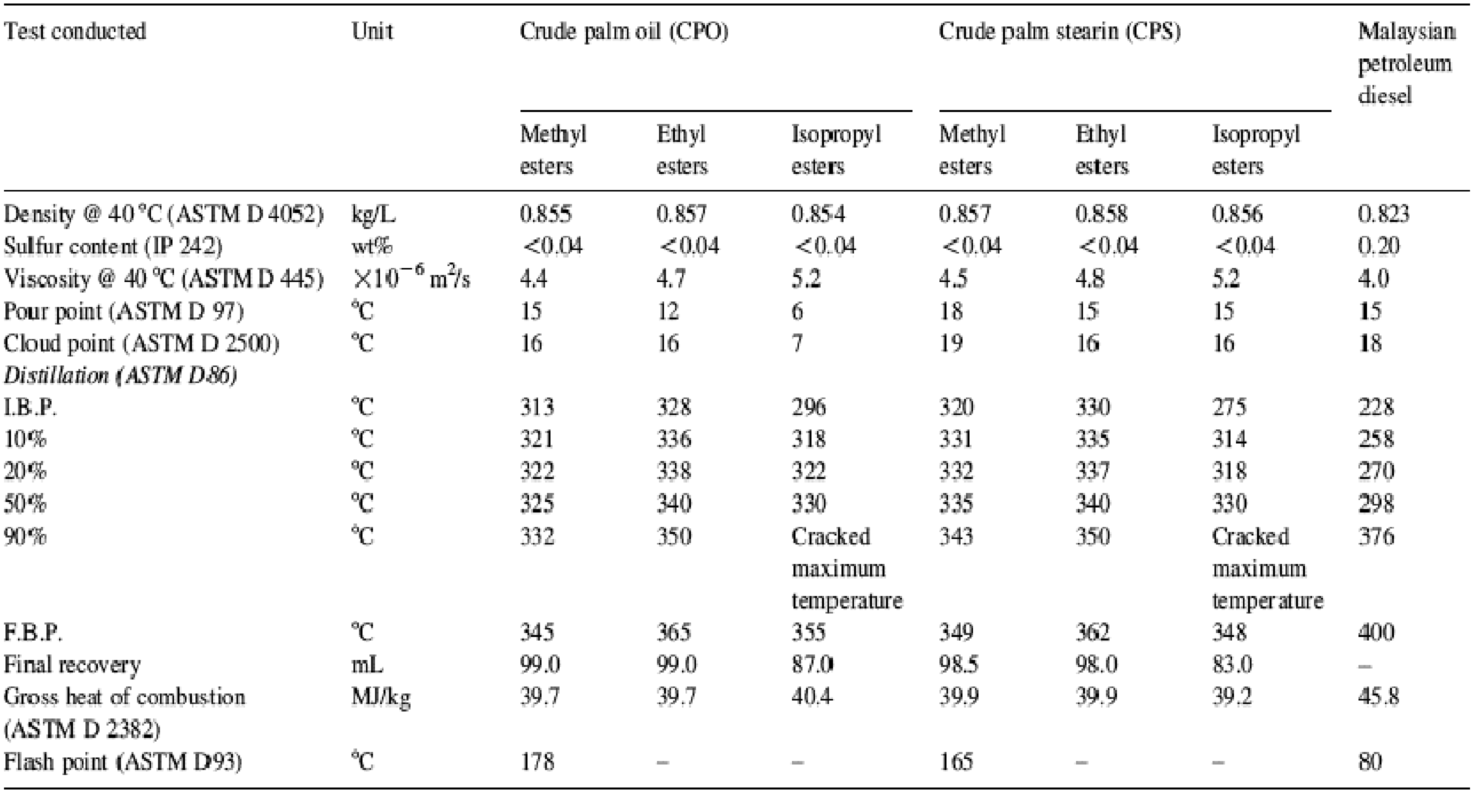
Table 2.4: Physical and chemical specification of the vegetable biodiesel fuel (Doysan, 1999; Paksoy, 1999; Recep Altim *et al.*, 2000).



Physical and chemical specifications of the vegetable oil fuels used

Fuel type	Calorific value (kJ/kg)	Density (g/dm^3)	Viscosity (mm^2/s)		Cetane number	Flame point (°C)	Chemical formula
			27°C	75°C			
Diesel fuel	43 350	815	4.3	1.5	47[a]	58	$C_{16}H_{34}$
Raw sunflower oil	39 525	918	58	15	37.1[a]	220	$C_{57}H_{103}O_6$
Sunflower methyl ester	40 579	878	10	7.5	45–52	85	$C_{55}H_{105}O_6$
Raw cottonseed oil	39 648	912	50	16	48.1[a]	210	$C_{55}H_{102}O_6$
Cottonseed methyl ester	40 580	874	11	7.2	45–52	70	$C_{54}H_{101}O_6$
Raw soybean oil	39 623	914	65	9	37.9[a]	230	$C_{56}H_{102}O_6$
Soybean methyl ester	39 760	872	11	4.3	37	69	$C_{53}H_{101}O_6$
Corn oil	37 825	915	46	10.5	37.6[a]	270–295	$C_{56}H_{103}O_6$
Opium poppy oil[a]	38 920	921	56	13	–	–	$C_{57}H_{103}O_6$
Rapeseed oil[b]	37 620	914	39.5	10.5	37.6[a]	275–290	$C_{57}H_{105}O_6$

Table 2.5: Fuel characteristic of alkyl esters of crude palm oil (CPO) and crude palm stearin (CPS) (Choo Yuen May *et al.*, 2004).



Test conducted	Unit	Crude palm oil (CPO)			Crude palm stearin (CPS)			Malaysian petroleum diesel
		Methyl esters	Ethyl esters	Isopropyl esters	Methyl esters	Ethyl esters	Isopropyl esters	
Density @ 40 °C (ASTM D 4052)	kg/L	0.855	0.857	0.854	0.857	0.858	0.856	0.823
Sulfur content (IP 242)	wt%	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	0.20
Viscosity @ 40 °C (ASTM D 445)	$\times 10^{-6}\ m^2/s$	4.4	4.7	5.2	4.5	4.8	5.2	4.0
Pour point (ASTM D 97)	°C	15	12	6	18	15	15	15
Cloud point (ASTM D 2500)	°C	16	16	7	19	16	16	18
Distillation (ASTM D86)								
I.B.P.	°C	313	328	296	320	330	275	228
10%	°C	321	336	318	331	335	314	258
20%	°C	322	338	322	332	337	318	270
50%	°C	325	340	330	335	340	330	298
90%	°C	332	350	Cracked maximum temperature	343	350	Cracked maximum temperature	376
F.B.P.	°C	345	365	355	349	362	348	400
Final recovery	mL	99.0	99.0	87.0	98.5	98.0	83.0	–
Gross heat of combustion (ASTM D 2382)	MJ/kg	39.7	39.7	40.4	39.9	39.9	39.2	45.8
Flash point (ASTM D93)	°C	178	–	–	165	–	–	80

2.2.3.2 Waste cooking oil

Waste cooking oil can be the possible low cost feedstock for biodiesel production. As mention earlier, waste coking oil are collected from hotel, catering, camp and restaurant. This collected wasted cooking oil has variety of qualities and posses properties different from neat vegetable oil (Leung and Guo, 2006). Thus, neat vegetable oil is the best starting material compare to waste cooking oil because of the conversion of triackylglycerides to fatty acid methyl ester is high and the reaction time is relatively short. Waste cooking oil contains higher free fatty acid than neat vegetable oil. Encinar (2007) stated that the high temperature of typical cooking processes and water from the foods accelerate the hydrolysis of triglycerides and increase the free fatty acid content in the oil. Physical and chemical properties of waste cooking oil and palm oil are shown in Table 2.6. As can be seen in the table, the waste cooking oil has properties much different from those from the neat oil. Waste cooking oil posses much higher acid value which indicates the high presence of free fatty acid and hence could not be converted to biodiesel using an alkaline catalyst.

The advantages of using waste cooking oil to produce biodiesel are the low cost and prevention of environment pollution. Waste cooking oil need to be treat before dispose to the environment to prevent pollution. Due to the high cost of disposal, many individuals dispose waste cooking oil directly to the environment especially in rural area. Thus by recycling waste cooking oil will help to prevent pollution in the environment. Encinar (2007) concludes that use of waste cooking oil is an effective way to reduce the cost of biodiesel production. Mittlebach (1996) stated that production of biodiesel by using waste cooking oil has been done in a small plant in Austria and gives satisfactory result.

Table 2.6: Physical and chemical properties of used frying oil and neat canola oil (Leung *et al.*, 2006).

Property	**UFO***	**Neat Palm Oil**
Acid value (mg KOH/g)	2.1	< 0.5
Kinematic viscosity at 40 °C (cSt)	35.3	30.2
Fatty acid composition (wt.%)		
Myristic (C14:0)	0.9	1
Palmitic (C16:0)	20.4	42.8
Stearic (C18:0)	4.8	4.5
Oleic (C18:1)	52.9	40.5
Linoleic (C18:2)	13.5	10.1
Linolenic (C18:3)	0.8	0.2
Others	6.7	0.9

* Sample has been pre-treated by filtering and dehydration before analysis.

2.3 Process

Vegetable oil was extensively discovered as diesel substitute in early 1980's. Generally there are four methods to produce biodiesel from vegetable oil that is direct use and blending, micro-emulsion, pyrolysis (thermal) cracking and the most widely used method used is transesterification. In recent years, this four method are extensively studied to optimize it condition and yield.

2.3.1 Direct use and blending

Vegetable oil can directly used or blending with petroleum diesel in engine. Fangrui Ma and Milford A. Hane (1998) stated that in 1980, Catterpillar Brazil were reported to use precombustion chamber engines with a mixture of 10% vegetable oil to maintain total power without any alterations or adjustments to the engine. Anon (1992) reported that a diesel fleet was powered by using two different types of oil that is filtered used frying oil and a blend of 95% used cooking oil and 5% diesel fuel. Blending for preheating was used as needed to compensate for cooler ambient temperatures. It is reported that no coking and carbon build-up problems occurred. The key was suggested to be the filtering and the only problem reported was lubricating oil contamination (viscosity increase due to polymerization of polyunsaturated vegetable oils). Thus, the lubricating oil had to be changed every 4,000 to 4,500 miles. After several experiment and testing having made, Fangrui Ma and Milford A. Hane (1998) concluded that direct use of vegetable oil or used of blend vegetable diesel oil can be considered as unsatisfactory and impractical for both direct and indirect diesel engine. The high viscosity, acid composition, free fatty acid content, as well as gum formation due to oxidation and polymerization during storage and combustion, carbon deposits and lubricating oil thickening are obvious problems. Table 2.7 shows the problem and the potential solutions for direct use of vegetable oil in diesel engine.

2.3.2 Micro-emulsions

Schwab *et al.,* (1987) defined micro-emulsion as colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1±150 nm range formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles. Micro-emulsion with solvents such as methanol, ethanol and 1-butanol has been studied to solve the problem of the high viscosity of vegetable oils. They can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles (Pryde, 1984). Goering *et al.*, (1982) stated that short term performances of both ionic and non-ionic micro-emulsions of aqueous ethanol in soybean oil were nearly meet the specification for biodiesel (ASTM D6751 biodiesel specification) except for the lower cetane number and energy content. All microemulsions with butanol, hexanol and octanol meet the maximum viscosity requirement for biodiesel specification (ASTM D6751).

Table 2.7: Known problems, probable cause and potential solutions for using straight vegetable oil in diesel engine (Harwood, 1984)

Problem	**Problem cause**	**Potential solution**
1. Cold weather starting	High viscosity, low cetane, and low flash point of vegetable oils	Preheat fuel prior to fuel injection. Chemically alter fuel to an ester
2. Plugging and gumming of filters lines and injectors	Natural gums (phosphatides) in vegetable oil. Other ash	Partially refine the oil to remove gums. Filter to 4-microns
3. Engine knocking	Very low cetane of some oils. Improper injection timing.	Adjust injection timing. Use higher compression engines. Preheat fuel prior to injection. Chemically alter fuel to an ester
Long-term		
4. Coking of injectors on piston and head of engine	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part load. Chemically alter the vegetable oil to an ester
5. Carbon deposits on piston piston and head of engine	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part load. Chemically alter the vegetable oil to an ester
6. Excessive engine wear	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils. Possibly free fatty acids in vegetable oil. Dilution of engine lubricating oil due to blow-by of vegetable oil	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part load. Chemically alter the vegetable oil to an ester. Increase motor oil changes. Motor oil additives to inhibit oxidation
7. Failure of engine lubricating oil due to polymerization	Collection of polyunsaturated vegetable oil blow-by in crankcase to the point where polymerization occurs	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part load. Chemically alter the vegetable oil to an ester. Increase motor oil changes. Motor oil additives to inhibit oxidation.

2.3.3 Pyrolysis (thermal cracking)

Sonntag (1979) defined pyrolysis as the conversion of one substance into another by means of heat or by heat with the aid of a catalyst. Pyrolysis involves heating in the absence of air or oxygen and cleavage of chemical bonds to yield small molecules (Weisz *et al.*, 1979). Pyrolytic chemistry is difficult to characterize because of the variety of reaction paths and the variety of reaction products that may be obtained from the reactions that occur. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. Sonntag (1979) stated that the pyrolysis of fats has been investigated for more than 100 years, especially in those nations which lack of petroleum fuel.

The first pyrolysis of vegetable oil was conducted in an attempt to synthesize petroleum from vegetable oil. Many studied have been made by researcher in pyrolysis of vegetable oils to obtain products suitable for fuel. Billaud *et al.*, (1995) studied the pyrolysis of rapeseed oil to produce a mixture of methyl esters in a tubular reactor between 500^{o}C to 850°C and in nitrogen. He found that the conversion of methyl colzate increased with an increase of the temperature of pyrolysis because high temperatures gave high yields of light hydrocarbons. The disadvantages of using pyrolysis are the equipment for thermal cracking is very expensive although the products are chemically similar to petroleum-derived gasoline and diesel fuel. Pyrolysis also produced some low value materials and such as sometimes produces more gasoline than diesel fuel (Fangrui Ma and Milford A. Hanna, 1999).

2.3.4 Transesterification

Transesterification also known as alcoholysis is a reaction of a lipid (triglycerides from fat or oil) with an alcohol to form esters and a byproduct glycerol. Generally, this reaction is produce in the presence of catalyst to improve the reaction rate and yield.

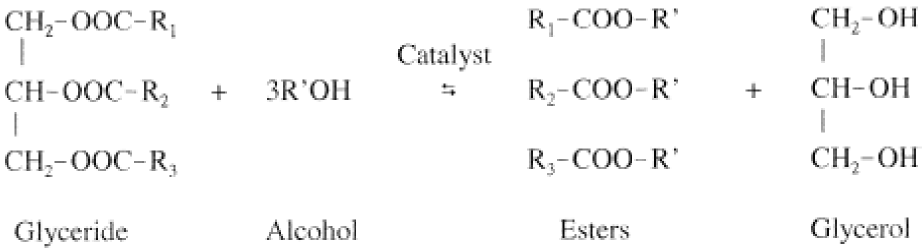


Figure 2.3 Tranesterification of tryglycerides with alcohol (Fangrui Ma and Milford A. Hanna, 1999).

From Figure 2.3 it is noted that that transesterification is a reversible reaction and thus excess alcohol is needed to shift the equilibrium to the product side. Basically, there are three types of catalysts which is acid catalyst, alkali catalysts and lipase catalyst. The product of transesterification process consist mixture of esters, glycerol, alcohol, catalyst and tri-glycerides, di-glycerides and mono-glycerides. Ma (1998) stated that we need to purify the product of transesterification process because the impurities could make the cloud point and pour point became higher. Thus, we need to remove the impurities such as mono-glycerides and di-glycerides. The by product, glycerol also need to be recover because of its value in chemical industry. Fangrui Ma and Milford A. Hanna, (1999) stated that glycerol can later be recover by gravitational settling or centrifuging process.

2.3.4.1 Reaction and mechanism of transesterification process.

In the transesterification process, triglycerides are firstly converted to diglycerides, then monoglycerides and lastly glycerol.