OPTIMIZATION OF BIODIESEL FUEL USING EDIBLE VEGETABLE OIL

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DECLARATION

I declare that this project report entitled "Optimization of Biodiesel Fuel Using Edible Vegetable Oil" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature :

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APPROVAL

I hereby declare that I have read this project report and in my opinion this report is sufficient in terms of scope and quality for the award of the degree of Bachelor of Mechanical Engineering (Thermal-Fluids).

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Date **:**

ABSTRACT

Biodiesel produced by transesterification of triglycerides with alcohol, is the newest form of energy that has attracted the attention of many researches due to various advantages associated with its usages. Response surface methodology, based on a three level, three independent variables central composite design is used to analyze the interaction effect of the transesterification reaction variables in the experiment which consists of temperature, molar ratio of methanol to oil and catalyst concentration on biodiesel yield. The linear terms of methanol molar ratio, and also the quadratic terms methanol to oil ratio and temperature, had significant effects on the biodiesel production ($p<0.05$). Through optimization plot done in response surface design method, maximum yield for the production of methyl esters from corn oil was predicted to be 90.15 % under the condition of temperature of 50.85^{o}C, the molar ratio of methanol to corn oil of 7:1, and catalyst concentration of 0.722 wt%, with a fixed constant variable of stirring speed 300 rpm and a reaction time of 1hr.

ABSTRAK

Hasilan biodiesel melalui proses transesterifikasi trigliserida dan alkohol, merupakan suatu teknologi baru yang telah menarik perhatian golongna pengkaji disebabkan oleh pelbagai kelebihan berkaitan kegunaan minyak itu sendiri. Kaedah gerak balas permukaan, yang digunakan berdasarkan atas tiga peringkat, tiga pemboleh ubah bebas, memebentuk satu reka bentuk komposit pusat, bertujuan untuk mengkaji kesan dan hubungan di antara pemboleh ubah bebas tersebut yang digunakan di dalam eksperimen iaitu suhu, nisbah molar alkohol kepada minyak dan kepekatan pemangkin terhadap biodiesel yang dihasilkan. Istilah linear nisbah alkohol kepada minyak dan juga syarat kuadratik nisbah alkohol kepada minyak dan suhu, mempunyai pengaruh yang jelas terhadap penghasilan biodiesel melalui nilai p yang tidak melebihi 0.05. Melalui plot pengoptimuman yang telah dihasilkan melalui kaedah gerak balas permukaan juga, hasil maksimum yang dihasilkan melalui minyak sayur jagung yang digunakan adalah dijangkakan pada peratusan 90.15% dengan set pemboleh ubah suhu pada 50.85℃, nisbah metanol kepada minyak jagung pada 7:1 dan kepekatan pemangkin pada 0.722 peratusan berat%, berserta pemboleh ubah tetap kelajuan kacau 300 pusingan per minit dan masa reaksi selama sejam.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

The energy policies in Malaysia are formulated by the Energy Section of the EPU under the Prime Minister's Department and these policies are renewed for every five years as part of the Five Year Malaysia Plan. An overall energy policy was established in 1979 (National Energy Policy 1979) with broad guidelines on long term energy objectives and strategies to ensure efficient, secure and environmentally sustainable supplies of energy (Jalal & Bodger, 2009). This is the main policy that governs the energy sector in Malaysia. Other energy policies were later formulated to support the objective and the implementations of this policy.

In 2000, the Four Fuel Policy was amended to become the Fifth Fuel Policy as formulated in the Eighth Malaysia Plan, where renewable energy was announced as the fifth fuel in the energy supply mix. When the Fifth Fuel Policy was introduced in 2001, renewable energy was targeted to be a significant contributor to the country's national grid with the generation mix of 5% of the total electricity demand by 2005 (Osman, 2006).

The target of 5% of renewable energy penetration was then later revised to be 350MW in the Ninth Malaysia Plan. Out of this 350 MW energy capacity, 245 MW was aimed to be achieved from the production of the biomass sector whereas the remaining 105 MW was from hydropower sources. Clearly from the statistics, biomass is expected to be one of the leading energy producers in the future.

Biomass in Malaysia generally can be seen of the production or development of organic matter available on a renewable basis, including forest and mill residues, wood wastes, agricultural crops and wastes, animal wastes and municipal solid waste. Malaysia is the world's second largest palm oil producer with 38% of the global market, and is the largest palm oil exporter, consisting of about 88% of the market's palm oil in 2011. As one of the world's leading producers of palm oil, an average of 50 million tons of dry oil palm residues are produced each year and expected to reach 100 million tons by 2020.

Oil palm biomass emerges as a potential major contributor to renewable energy as the government has now shifted from conventional energy sources such as coal, oil and gas to promoting renewable energy sources in order to increase energy security (Umar, et.al, 2008). Table 1.1 depicts the expected renewable energy capacity in electricity generation in the future. In the table, biomass as highlighted to contribute one of the most energy capacities compared to other renewable resources in the country in the future.

Table 1.1 : Renewable energy capacity in electricity generation (source:Ministry of Plantation Industries and Commodities. 2006)

Year	Renewable energy installation capacity (MW)						Share in electricity generation capacity
	Biomass	Biogas	Small-hydro power	Solar PV	Solid waste	Total	
2015	330	100	290	55	200	975	6%
2020	800	240	490	175	360	2065	10%
2030	1340	410	490	854	390	3484	13%
2050	1340	410	490	8874	430	11,544	34%

Biodiesel was identified as one of the potential renewable energy sources for vehicle fuel, and based on the Fifth Fuel Policy, the government of Malaysia has launched the National Biofuel Policy in 2006 to encourage the use of environmentally friendly, sustainable and viable sources of biomass energy (Ministry of Plantation Industries and Commodities, 2006).

There is a renewed interest in considering crop species as a substitute in producing energy since fossil fuels are quickly being depleted over time (Ahmad, et.al, 2009). Regarding fuels, biodiesel is the most widely used biofuel nowadays. Biodiesel is a renewable alternative fuel for diesel engines with non-toxic and biodegradable characteristics consisting of Fatty Acid Methyl Esters (FAME) mainly of vegetable oils and animal fat origin. The reduction of the CO_2 emissions by its use is one of the main advantages while the poor oxidation stability and contamination problem is a field still under investigation. (Basha, et.al, 2009; Dodos, et.al, 2009).

It is also manufactured from plant oils (soybean oil, cotton seed oil, canola oil), recycled cooking greases or oils (e.g., yellow grease), or animal fats (beef tallow, pork lard). Using crop species or products such as vegetable oils, transformation of vegetable oils into biodiesel can be realized using three different methods, which are pyrolysis or catalytic cracking, micro-emulsification and transesterification using low molecular alcohols.

Transesterification is the most used method of conversion and refers to the reaction of a vegetable oil or animal fat with an alcohol in the presence of a catalyst to produce alkyl esters and glycerol. The alkyl esters are what are called biodiesel. The purpose of the transesterification process is to lower the viscosity of the oil. There are various parameters affecting the production of alkyl esters or the biodiesel yield from the transesterification reaction. Temperature, alcohol to oil molar ratio, catalyst concentration, reaction time and stirring rate are influential factors to be considered in biodiesel production using vegetable oils. Different vegetable or feedstock oils also may have different 'recipe' in terms of optimum yield of biodiesel as each of these vegetable oils has different composition of fatty acids which are to be reacted with alcohol and catalyst in transesterification process.

1.2 PROBLEM STATEMENT

Expectancy of the biodiesel through the biomass energy is high towards ensuring the energy sustainability in the future but there are few drawbacks that may needed to be considered. Biodiesel production is facing several issues and challenges like tough global competition, feedstock issue, food *versus* fuel war, sustainability, and limited land for use and deforestation (Chong, et.al, 2015).

Other viable alternatives should have been sought out immediately as abundance of palm oil may cause setbacks such as mentioned above. Different vegetable oils possess different characteristics and should be experimented and explored on their usage and ability to produce other forms of oil. Methods of producing biodiesel vary from micro-emulsifications, pyrolysis and transesterification. Using feedstock oil, transesterification process is best suited and most convenient method to perform production of biodiesel. Chemical process in transesterification reduces the fatty acid chain in reaction with alcohol with presence of catalyst to obtain biodiesel. However, various reaction parameters are monitored and controlled in ensuring that maximum yield (and/or conversion) and purity is achieved.

It is equally important that the process be optimized and cost reduced to the minimum so as to make biodiesel competitive in the market. The use of statistical method such as RSM, is sought after in determining the optimum parameters for yield production of biodiesel. However, the proper choice of factorial design and obtained regression model is very important in any response surface investigation. This is true because the quality of prediction, as measured by the size of the prediction variance, depends on the design matrix. Determination of an optimal value over the specified region of interest, for which in the case, the biodiesel yield, depends on the best fitted response model (Khuri & Mukhopadhyay, 2010).

1.3 OBJECTIVES

The objectives and the aim of the study are to study :

- The use of transesterification process for the conversion of the edible vegetable oils to biodiesel, and

- The process optimization of process parameters for maximum biodiesel yield

1.4 SCOPE OF PROJECT

In this experimental study, the scope that will be covered throughout the research are the factors that is considered in conducting transesterificiation which are methanol to oil molar ratio, reaction temperature and the concentration of catalyst. The limitations of the study goes as far as finding the optimum operating conditions of concerning factors mentioned above for the maximum yield of biodiesel production.

The concerns of other criterias such as other characteristics such as mixing intensity, and method production of biodiesel methods , are not discussed in details. In this case, corn oil was chosen for edible vegetable oil to be converted to the biodiesel after weighing on its cost, availability, and chemical properties of the oil itself. This study covers only the conversion of corn oil into biodiesel and other vegetable oil were only discussed in passing.

CHAPTER 2

LITERATURE REVIEW

2.1 VEGETABLE OIL

The use of vegetable oils as fuels dates back almost as far as the diesel engine itself. In the 1920s, soybean oil was used to fuel the early diesel engines (Kubičková & Kubička, 2010). The inexpensive, petroleum-derived, hydrocarbon-based fuels then dominated the market for decades. Research interest in vegetable oil- derived fuels decreased drastically, transitioning to petroleum derivatives. The use of vegetable oils as an alternative renewable fuel to compete with petroleum was re-introduced in the beginning of the 1980s (Bartholomew, 1981).

Vegetable oils are a renewable and potentially inexhaustible source of energy with an energetic content close to diesel fuel and historically, it is believed that Rudolf Diesel himself started research with respect to the use of vegetable oils as fuel for diesel engines (Zaher, 1990). In the following decades, the studies became more systematic and, nowadays, much is known about its use as fuel. There are several advantages in the use of vegetable oils as diesel, which are: portability; ready availability; renewability; higher heat content, lower sulphur content and lower aromatic content than that of mineral diesel; and biodegradability (Demirbas, 2008).

But direct usage of the vegetable oils will be impractical for a long term run to be applied in the available diesel engines due to high viscosity, acid contamination, free fatty acid formation. Hence vegetables oils are processed through several means so as to achieve and acquire properties as similar to that of fossil fuels and the processed fuel can be directly used in the diesel engines available without damaging the mechanism.

2.1.1 Palm oil in Malaysia

Malaysia is the second palm oil producer in the world after Indonesia. Palm planted area is expected to expand to 6.0 million hectares in 2016/17 with expansion mainly in

East Malaysia, area harvested increased to 4.9 million hectares while fully matured hectare equivalent (MHE) area, plantation with palm trees that producing fruits at least 4 times a year, is estimated at 2.75 million hectares.

Yields are expected to drop in 2015/16 due to adverse weather condition and will rebound in 2016/17 as the weather improves in line with increases in mature hectare equivalent (MHE). Consequently, output is forecast to grow to 21.0 million tons. (Malaysia oil seeds and product annual, 2016).

As Malaysia is one of the biggest producing palm oil country in the world, palm oil itself is a known conflict in whether to be applied into a grand scale of producing biofuel or biodiesel. An issue of food versus energy can arise from the involvement of palm oil. Thus in the study, although palm oil is abundant and can be easily available for the use of the transesterication process, a different oil was chosen as the subject instead.

2.1.2 Corn oil

Biodiesel, is produced through a reaction known as transesterification. In a transesterification reaction, one mole of triglyceride in vegetable oils in this case will react with three moles of alcohol (molar ratio of methanol to vegetable oil of 3:1) to form one mole of glycerol and three moles of the respective fatty acid alkyl esters. The process is a sequence of three reversible reactions, in which the triglyceride molecule is broken down from diglyceride until it becomes monoglyceride and glycerol (Mittelbach and Remschmidt, 2004).

Several types of vegetable oils available, have different and various composition in fatty acids. They are all can be used in the production of a biodiesel. Four oil crops clearly dominate the feedstock sources used for world-wide biodiesel production such as soybean (Sensöz and Kaynar, 2006; Xie et al., 2006), rapeseed (Cvengros and Povazanec, 1996; Peterson et al., 1996), palm (Kalam and Masjuki, 2002) and sunflower (Antolín et al., 2002; Vicente et al., 2005). However, there are no obligations to use only these types of oil crops and no restrictions towards the use of other vegetable oils.

As we all know, maize or commonly known as corn is an abundant food and feed crop. Diverse use of any feed crop would add higher value to its cultivation and production. Corn for example is one such crop which yields several useful products. Hence it remains one of the favourite crops in industrial sector. Although relatively a new emergence, corn oil is becoming popular among edible oils owing to its unique health related benefits (Rajendran et.al, 2012). Table 2.1 shows the kinematic viscosity of different oils and biodiesel, obtained from different sources. It can be appreciated that the oil from which is obtained will affect in different ways the kinematic viscosity of the product.

Table 2.1 : Kinematic viscosity of different oils

Species	Kinematic viscosity of oil (centistokes, at 40°C)	Kinematic viscosity of biodiesel (centistokes, at 40°C)
Rapeseed	35.1	4,3-5,83
Soybean	32.9	4.08
Sunflower	32.6	4.9
Palm	39.6	4.42
Peanut	22.72	4.42
Corn	34.9	3.39
Canola	38.2	3.53
Cotton	18.2	4.07
Pumpkin	35.6	4.41

(source:Dennis et.al, 2010)

Apart from that, there are some other important factors in choosing the oil to be used in the transesterification process. For instance, the possibility of obtaining a kind of vegetable oil depending on the geographical location and, indeed, the suitability of the biodiesel obtained from that oil depending on the climate conditions. Based on Malaysia own weather and climates, corn oil is considered relatively a foreign concept of edible oil used into production of biodiesel.

The properties of the triglyceride and the biodiesel fuel are determined by the amounts of each fatty acid that are present in the molecules. Different type of vegetable would possess different amount of fatty acids, and thus affect the transesterification process in which the molar ratio needed to convert a mole of the triglyceride in the vegetable oils with three mole of alcohol would be of different quantity. Thus, it is important to specifically know the contents of the fatty acid of the experimented vegetable oil in a transesterification process in obtaining the most accurate result. Table 2.2 lists the fatty acids contained in a number of vegetable oils and corn oil is highlighted as a subject of the study.

Table 2.2 : Fatty acid composition (wt%) of vegetable oils

Fatty acid	Palm	Olive	Peanut	Rape	Soybean	Sunflower	Grape	H.O. Sunflower	Almond	Corn
Lauric (C12:0)	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Myristic (C14:0)	0.7	0.0	0.1	0.0	0.0	0.0	0.1	0.0	0.0	0.0
Palmitic (C16:0)	36.7	11.6	8.0	4.9	11.3	6.2	6.9	4.6	10.4	6.5
Palmitoleic (C16:1)	0.1	1.0	0.0	0.0	0.1	0.1	0.1	0.1	0.5	0.6
Stearic (C18:0)	6.6	3.1	1.8	1.6	3.6	3.7	4.0	3.4	2.9	1.4
Oleic (C18:1)	46.1	75.0	53.3	33.0	24.9	25.2	19.0	62.8	77.1	65.6
Linoleic (C18:2)	8.6	7.8	28.4	20.4	53.0	63.1	69.1	27.5	7.6	25.2
Linolenic (C18:3)	0.3	0.6	0.3	7.9	6.1	0.2	0.3	0.1	0.8	0.1
Arachidic (C20:0)	0.4	0.3	0.9	0.0	0.3	0.3	0.3	0.3	0.3	0.1
Gadoleic (C20:1)	0.2	0.0	2.4	9.3	0.3	0.2	0.0	0.0	0.3	0.1
Behenic (C22:0)	0.1	0.1	3.0	0.0	0.0	0.7	0.0	0.7	0.0	0.0
Erucic (C22:1)	0.0	0.0	0.0	23.0	0.3	0.1	0.0	0.0	0.1	0.1
Lignoceric (C24:0)	0.1	0.5	1.8	0.0	0.1	0.2	0.0	0.3	0.0	0.1
Nervonic (C24:1)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.0

(source:Ramos et.al, 2008)

Palm oil which is much more commonly used in the country is a rather conservative choice of producing biodiesel from vegetable oil available in Malaysia. Given the cultivation plan planned by the government, corn plantation would be a viable alternative towards a brand new biodiesel based fuel to be used by Malaysia.

2.1.3 Malaysia's corn market

With the weakening Malaysian ringgit, and the gloomy outlook of the national economy, it may as well retarded the potential growth of corn imports to 3.45 million tons in 2015/16 from 3.22 million tons in 2014/15. The trend was visible for marketing year 2014/15, when imports of corn dropped by 7.6 percent to 3.2 million tons from 3.4 million tons in 2013/14. For 2014/15 total value of import was US$779 million (Grain & Feed Annual Kuala Lumpur. 2016) as shown in Table 2.3.

Larger drawbacks towards the Malaysia's corn imports after the USA have been set after the presidency has been handed over to Donald Trump. Trump's policy of reducing US exports may have significant effect towards the import of corn in Malaysia. 45 percent tariff has been imposed on China from Boeing order to agricultural imports (Daniels.J, 2016). There is no predicting the future and assurance that Malaysia may or may not be included in the tariff as well.

Table 2.3 : Malaysia's corn imports (source:Grain & Feed Annual Kuala Lumpur. 2016)

Import Trade Matrix			
Country	Malaysia		
Commodity	Corn		
Time Period	Market Begin Oct	Units :	1000MT
Imports for:	2013/2014		**2014/2015**
United States	10	U.S	30
Others		**Others**	
Argentina	1,168		1,538
Brazil	1,345		1,437
India	792		129
Paraguay	40		75
Australia	0		2
Thailand	47		0
Ukraine	71		0
Total for others	3,473		3,211
Others not listed	3		10
Grand Total	3,476		3,221

(source:Grain & Feed Annual Kuala Lumpur. 2016)

The data above clearly depicts Malaysia as an importer for the corn crop market and Malaysia do not produce corn mostly on yearly basis. However, Malaysia is expanding its maize cultivation with the first commercial planting to start in Kemaman, Terengganu by month's end.

Malaysia has been importing up to four million metric tons of maize grains every year, costing RM33.33 billion. High cost of investment causes the rising maize prices, and to overcome this, efforts to plant maize in the country will be expanded (Datuk Seri Ahmad Shabery Cheek, June 2016). Federation of Livestock farmers' Association of Malaysia expressing their indignation against rising prices of maize grain imports also has been the catalyst in driving maize plantation to cultivate in Malaysia and the need to stop depending on imports from other countries such as Argentina.

2.2 TRANSESTERIFICATION AND ITS PARAMETERS

2.2.1 Transesterification or Alcoholysis

In the USA and Europe, the surplus edible oils like soybean oil, sunflower oil, and rapeseed oil are being used as feedstock for the production of biodiesel (Ramadhas et.al, 2004). However, vegetable oil is about ten times more viscous than diesel. As a result, vegetable oils can cause poor fuel atomization, incomplete combustion, and carbon deposition on the injector and valve seats (Sarin & Sharma, 2007).All of these implicaations can contribute to damaging the engine system. Common methods have been used by means of reducing the viscosity of vegetable oils include by blending with diesel, emulsification, pyrolysis, cracking, and also transesterification.

Among these, the transesterification of vegetable oils to alkyl esters is deemed to be the best method (Fangrui et.al, 1999). Transesterification is the most used method of conversion and refers to the reaction of a vegetable oil or animal fat with an alcohol in the presence of a catalyst to produce alkyl esters and glycerol. The alkyl esters are what are called biodiesel. The purpose of the transesterification process is to lower the viscosity of the oil. Generalized steps in transesterification process are displayed and visualized through Figure 2.1.

The transesterification reaction proceeds well in the presence of some homogeneous catalysts such as potassium hydroxide (KOH)/ sodium hydroxide (NaOH) and sulfuric acid, or heterogeneous catalysts such as metal oxides or carbonates.

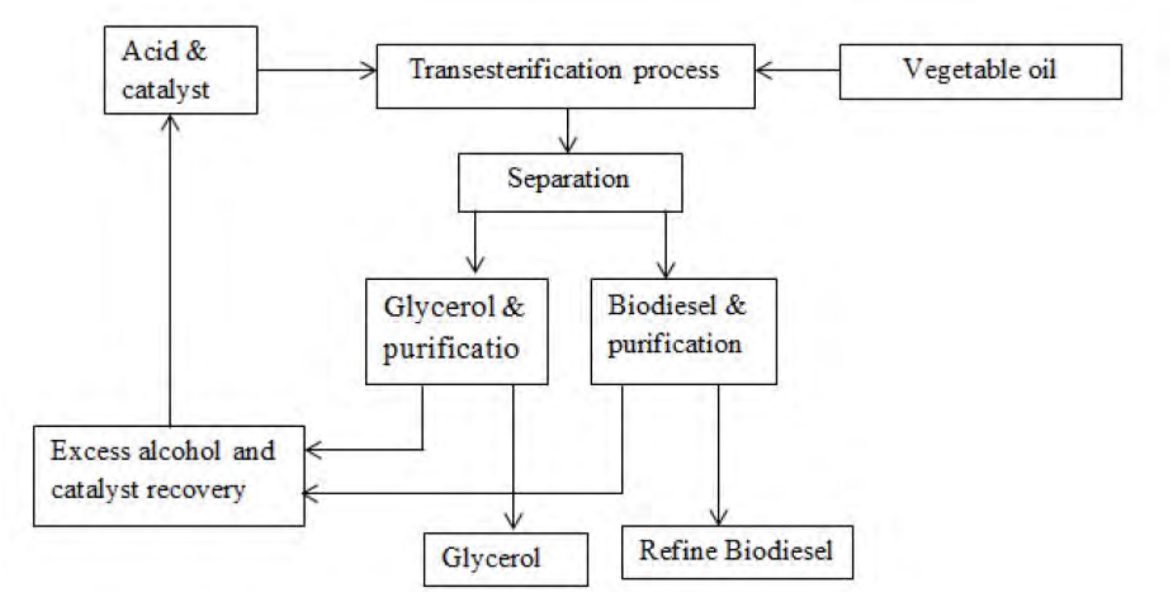

Figure 2.1 : Transesterification process

(source: Rajalingam et.al, 2016)

Transesterification also called alcoholysis which is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis except that an alcohol is used instead of water (Murugesan et.al., 2009). The transesterification process can be represented in the form of a chemical reaction represented in Figure 2.2.

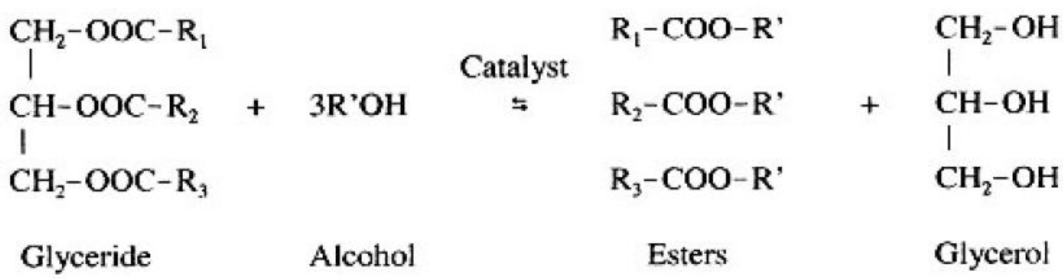

Figure 2.2 : Chemical reaction in transesterification

(source: Ma & Hanna, 1999)

The biodiesel manufacturing process converts oils and fats into long-chain mono alkyl esters, or biodiesel. (Paintsil, 2013). In the transesterification reaction, triglyceride is reacted with an alcohol (methanol, ethanol), in the presence of a catalyst to produce glycerol and fatty acid alkyl esters. The whole biodiesel production is summarized by this