EXPLORING OF THE TRANSESTERIFICATION OF CASTOR OIL TO PRODUCE BIODIESEL USING QUICKLIME AS A BASIC CATALYST

by

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A thesis submitted in fulfillment
of the requirements for the degree of
Bachelor of Chemical Engineering (Gas Technology)

Faculty of Chemical & Natural Resources Engineering

UNIVERSITI MALAYSIA PAHANG

JANUARY 2013

UNIVERSITI MALAYSIA PAHANG

BORANG PENGESAHAN STATUS TESIS♦

JUDUL : EXPLORING OF THE TRANSESTERIFICATION OF CASTOR OIL TO PRODUCE BIODIESEL USING QUICKLIME AS A BASIC CATALYST

SESI PENGAJIAN : 2012/2013

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I hereby declare that this thesis entitled “Exploring of The Transesterification of Castor Oil to Produce Biodiesel Using Quicklime as a Basic Catalyst” is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of other degree.

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Special dedication to my family members

ACKNOWLEDGEMENTS

As a vicegerent who is being created, I put myself down to express my highest thankful to Allah S.W.T. for giving me strength and spirit to complete this final project with full of pride and dignity.

I would like to express my deepest gratitude to the following persons for their unlimited and kindness help as well as guidance enabled me to complete this research project in time as a partial fulfillment of the requirement of the degree of Bachelor Chemical Engineering (Gas Technology).

First and foremost, to Prof. Dr. Ghazi Faisal Najmuldeen, my lovely supervisor thanks a lot for helping me during the progress of the research project. Without his generosity in sparing his precious time to guide me and answer my doubts, the aim of project may not be fulfilled. My sincere thanks go to the staffs of the Chemical Engineering Department and Mr. Aimi Ilmar bin Ramli from Central Laboratory, who helped me in many ways and made my stay at UMP pleasant and unforgettable.

Special thanks should be given to my fellow course mates and friends for theirs assistances, advices and ideas in producing a resourceful, fruitful and practicable research. I would like to acknowledge their comments and suggestion, which was crucial for the successful completion of this study.

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LIST OF ABBREVIATIONS

CaO	Calcium oxide
FFA	Free fatty acids
EPA	Environmental Protection Agency
SFA	Saturated fatty acids
UFA	Unsaturated fatty acids
THF	Tetrahydrofuran
FAME	Fatty acid methyl ester
GC-MS	Gas Chromatography Mass Spectrometry
HC	Hydrocarbon
CO	Carbon monoxide
PM	Particulate matter
NO_X	Nitrogen oxides

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ABSTRAK

Pada dasarnya, kajian ini adalah untuk meneroka proses transesterifikasi terhadap minyak jarak untuk menghasilkan biodiesel dengan menggunakan kalsium oksida sebagai pemangkin. Objektif utama kajian adalah untuk menggunakan kalsium oksida sebagai pemangkin yang mungkin dapat menghasilkan kandungan biodiesel yang tinggi daripada minyak jarak. Dalam kajian ini, minyak jarak telah dipilih sebagai bahan mentah kerana ia telah dihasilkan di Malaysia dan merupakan minyak yang tidak boleh dimakan. Metanol telah dipilih sebagai pelarut kerana harganya yang lebih murah berbanding dengan alkohol yang lain. Melalui proses transesterifikasi, biodiesel dihasilkan apabila berlakunya tindak balas antara *triglycerides* (minyak jarak) dengan alkohol (metanol) dengan kehadiran pemangkin (kalsium oksida) untuk menghasilkan asid lemak metil ester (biodiesel) dan *glycerol*. Eksperimen ini dijalankan dengan menggunakan dua pembolehubah yang berbeza iaitu nisbah metanol kepada minyak (3:1 dan 4:1) dan masa (60 minit, 120 minit, dan 180 minit). Kepekatan pemangkin telah ditetapkan pada 1% dan suhu juga telah ditetapkan pada 60^{o}C. Sampel daripada setiap eksperimen telah dianalisis dengan menggunakan Gas Kromatografi Jisim Spektrometri. Berdasarkan keputusan eksperimen yang telah diperolehi, nilai kandungan biodiesel yang tertinggi adalah 82% pada keadaan 3:1 nisbah metanol kepada minyak, 180 minit, 1% kepekatan kalsium oksida dan suhu 60^{o}C.

ABSTRACT

This research is basically an experiment to exploring the transesterification of Castor oil to biodiesel using quicklime (CaO) as solid base catalyst. The objectives of this research are to use heterogeneous catalyst quicklime for possible high yield production biodiesel from castor oil. In this research, castor oil has been chosen as feedstock because it is readily available in Malaysia and non-edible oil. Methanol was chosen as alcohol solvent because its price is cheaper compare to other type of alcohol. Through a process called transesterification, biodiesel is made by reacting triglycerides (castor oil) with alcohol (methanol) in the presence of a catalyst (quicklime) to produce fatty acid methyl esters (biodiesel) and glycerol (co-product). This experiment was conducted with two different parameters which are methanol: oil ratio (3:1 and 4:1) and reaction time (60 minutes, 120 minutes and 180 minutes). The catalyst concentration was fixed at 1 wt% and the temperature was fixed at 60^{o}C. The sample of each experiment was analysed using Gas Chromatography Mass Spectrometry (GC-MS). The best yield biodiesel product was 82% at reaction conditions; 3:1 methanol/oil ratio, 180 minutes, 1 wt% of CaO and 60^{o}C.

CHAPTER 1

INTRODUCTION

1.1 General Background

With the rise in concern for pollution caused by fossil fuels such as petroleum, coal and natural gas, and the realization that energy supplies are not infinite, alternative fuels and renewable source of energy such as biodiesel are being considered worldwide.

In the United States and Europe, the requirement for transportation fuel has increased and this trend will continue. In developing countries, such as India, Malaysia, South Africa, Vietnam and China, energy use will continue to increase for economic growth and improved standards of living. With the increasing reliance on imported petroleum, these countries are extremely vulnerable to fuel price fluctuations and supply disruption.

Fossil fuels use in transportation is the leading contributor to urban air pollution and to global warming. The fossil fuels produced from petroleum, like gasoline and diesel, come in the category of non-renewable fuel and will last for limited period of time. In recent years, new sulfur and aromatic compound limits give the petroleum producers a new challenge to lower the sulfur and aromatic content of traditional fuel. The World Energy Forum predicted that fossil oil will be exhausted in less than 10 decades, if new oil wells not found (Sharma and Singh, 2009). Figure 1 presents the projection of energy demand for the new future, indicating that there is an urgent need to find more renewable energies sources to assure energy security world.

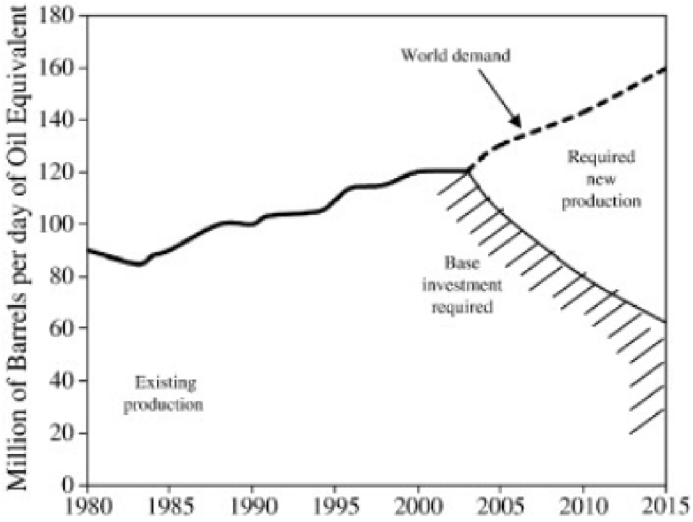


Figure 1.1: Projection of energy demands for the new future (Sources: Biotechnology Advances, 2010)

As a result, the cost associated with fuel-production and engine-modification will increase in order to meet the more stringent environmental legislation. People throughout the world are looking for effective, cost-competitive technologies to comply with current and pending regulations. Hence, vegetable oils are emerging as a great alternative fuel because of their renewable and environmental benefits (Sharma et al., 2009).

Biodiesel has been defined as a methyl-ester produced from vegetable or animal oil, of diesel quality, to be used as biofuel (Encinar, F. Gonzalez, Martinez, Sanchez and G. Gonzalez, 2010). Biodiesel obtained from different vegetable oils is being considered as a potential source of energy. This is mainly due to biodiesel being nontoxic and biodegradable which makes it an environmentally friendly fuel. In addition, the emissions of carbon dioxide, sulfur dioxide, unburned hydrocarbons, and particulate matter are reduced during the biodiesel combustion process. Generally speaking, biodiesel is obtained by the transesterification of triglycerides. These triglycerides are converted to the corresponding alkyl ester and glycerol by transesterification with short chain alcohols, typically methanol. The main purpose of transesterifying the vegetable oil is to lower its viscosity and raising the volatility. At the same time, improving its fuel quality applications in the compression-ignition (diesel) engine (Chakrabarti and Ahmad, 2008; Boey, Maniam and Abd. Hamid, 2011).

As a tropical country, Malaysia has a suitable climate and soil for cultivating the Castor trees. Castor oil is a very pale yellow liquid with mild or no odor. It is cultivated around the world because of the commercial importance of its oil is used in the manufacture of a number of industrial chemicals like surfactants, cosmetics and personal care products, pharmaceutical and other. The comparative advantage of castor is that its growing period is much shorter than that of Jatropha and Pongamia which can reach a height around 12 meters (Casa Kinabalu, 2012). In addition, there is considerably greater experience and awareness among farmers about its cultivation. Being an annual crop it gives the farmers the ability to rotate or shift away easily depending on market conditions.

1.2 Problem Statement

In the past few decades, fossil fuels mainly petroleum, natural gas and coal have been playing an important role as the major energy resources worldwide. However, these energy resources are non-renewable and are projected to be exhausted in the near future. This has caused the price of crude petroleum to hit a record high of USD (US dollar) 90 per barrel in October 2007 and still rising. Therefore, there is an urgent need to find a new energy resource that is renewable, clean, reliable and yet economically feasible as a substitution to the current fossil fuels. In this context, recently biodiesel derived from vegetable oil has been shown to be a potential alternative replacing petroleum-derived diesel oil for diesel engine. Although there is continuous increase in the production of vegetable oil, however the ending stocks of vegetable oils are continuously decreasing due to increasing production of biodiesel. Eventually, with the implementation of biodiesel as a substitute fuel for petroleum-derived diesel oil, this may lead to the depletion of edible-oil supply worldwide. So, castor oil is chosen as non-edible oil to produce biodiesel. The beans contains toxin that makes the oil and cake inedible. It was chosen for the study because it widely available, has no other commercial uses and unlike vegetable oils such as soya beans, would not compete for other uses such as consumption.

1.3 Research Objective

The objectives of this research are:

1. To use heterogeneous catalyst quicklime for possible high yield production biodiesel from castor oil.
2. To determine the effect of time reaction and methanol/oil ratio in transesterification process using calcium oxide as a basic catalyst.

1.4 Research Scope

This research is an experimental study in production of biodiesel using castor oil as the feedstock. In order to realize these research objectives, I used the time reaction of 1 hour, 2 hours and 3 hours. Besides that, I used the ratio of alcohol to oil of 3:1 and 4:1. While the catalyst concentrations and the temperatures are fixed at 1wt% and 60^{o}C.

1.5 Significance of Research

The significance of my research is to use non-edible vegetable oil as source of production biodiesel to maintain important of food oil. The use of non-edible vegetable oils as compared to edible oils is very significant in developing countries because of the tremendous demand for edible oils as food and they are far too expensive to be used as fuel at present.

In this context, recently biodiesel derived from vegetable oil has been shown to be a potential alternative replacing petroleum-derived diesel oil for diesel engine.

Although there is continuous increase in the production of vegetable oil, however the ending stocks of vegetable oils are continuously decreasing due to increasing production of biodiesel. Eventually, with the implementation of biodiesel as a substitute fuel for petroleum-derived diesel oil, this may lead to the depletion of edible-oil supply worldwide. So, castor oil is chosen as non-edible oil to produce biodiesel. The beans contains toxin that makes the oil and cake inedible. It was chosen for the study because it widely available has no other commercial uses and unlike vegetable oils such as soya beans, would not compete for other uses such as consumption. It grows very well on marginal land. Bello et., al (2011) state that it is draught and pest resistant and has yield of about 1413 liter per hectare when cultivated.

CHAPTER 2

LITERATURE REVIEW

2.1 The Current Status of Biodiesel

According to Kawashima, Matsubara and Honda (2009), biodiesel consist of methyl or ethyl esters derived from vegetable oil, animal fat, waste oil and microalgae oil through the process of transesterification.

In the early literature, there are several terminologies for these ester-forming reactions, namely alcoholysis, acidolysis and ester interchange but recently it is more common to use the term transesterification to describe the ester reaction, which when carried out with an alcohol in the presence of an acid or base catalyst is known as alcoholysis. Depending on the specific alcohol used, alcoholysis is referred to as methanolysis, ethanolysis, propanolysis, and butanolysis and other. In this project, methanolysis will be adhered to throughout this whole work.

Since the worldwide energy shortage and oil crisis in the late 1970's and early 1980's. Vegetable oils and waste oil have attracted attention as a potential renewable resource for the production of an alternative to petroleum-based diesel fuel. Various products from vegetable oils and waste cooking oils have been proposed as an alternative fuel for diesel engines. Researches also studied the biodiesel made from free fatty acids. This reaction is catalyzed by acid at elevated pressure.

Since biodiesel is made entirely from vegetable oil or animal fats, it is renewable and biodegradable. Biodiesel also contains very little sulphur, polycyclic aromatic hydrocarbons and metals (Vasudevan and Briggs, 2008). Petroleum-derived diesel fuels can contain up to 20% polycyclic aromatic hydrocarbons. For an equivalent number of carbon atoms, polycyclic aromatic hydrocarbons are up to three orders of magnitude more soluble in water than straight chain aliphatics. The fact that biodiesel does not contain polycyclic aromatic hydrocarbons makes it a safe alternative for storage and transportation. Biodiesel fuels can be used in regular diesel vehicles without making any changes to the engines, although older vehicles may require replacement of fuel lines and other rubber components (Vasudevan et al., 2008). Since biodiesel is oxygenated, it is a better lubricant than diesel fuel, increasing the life of engine and is combusted more completely. Indeed, many countries are introducing biodiesel blends to enhance the lubricity of low-sulphur diesel fuels. Researchers also found that the higher flash point of biodiesel makes it a safer fuel to use, handle and store. With its relatively low emission profile, it is an ideal fuel for use in sensitive environments such as heavily polluted cities.

There are some advantages of biodiesel as a substitute for diesel fuel. First and foremost, the transportation sector with its great demand for gasoline and diesel fuel relies almost exclusively on petroleum for energy. Biodiesel can be produced domestically from agricultural oils and from waste fats and oils. Because it can be used directly in diesel engines, biodiesel offers the immediate potential to reduce our demand for petroleum. The burning of fossil fuels during the past century has dramatically increased the levels of carbon dioxide and other greenhouse gases that trap heat in our atmosphere. Their implications are hotly debated, but the levels of these gases have unquestionably risen at unprecedented rates in the context of geological time. To the extent that biodiesel is truly renewable, it could help reduce greenhouse gas emissions from the transportation sector. Since regular diesel engines like those in tractor trailer trucks and heavy construction equipment can use biodiesel in their existing engines, it is one of the simplest alternative fuels to use.

2.2 Comparison of Diesel and Biodiesel

The most commonly used fuel that contains biodiesel is a mixture of 20% biodiesel and 80% regular petroleum diesel called B20. Fuel that is 100% biodiesel is called B100. Table 2.1 presents properties comparison for diesel, B20 and B100.

Table 2.1: Properties of diesel and biodiesel (Tyson, Bozell, Wallace, Eugene and Moens, 2004)

Fuel Type	Density (g/cm^3)	Average Net Heating Value (Btu/gal)	% Difference from No. 2 Petro Diesel
No. 2 Petro Diesel	0.85	129 500	
Pure Biodiesel (B100)	0.88	118 296	8.65 %
Blend Diesel (B20)	0.856	127 259	1.73 %
Blend Diesel (B2)	0.851	129 276	0.17 %

Energy content of petro diesel can vary up to 15%. The energy content of biodiesel is much less variable than that of petro diesel. The feedstock utilized has a greater effect on the energy content of biodiesel than a particular processing method.

Pure biodiesel contains about 8% less energy per gallon than No. 2 petro diesel or 12.5% less energy per pound. This difference results from the slightly higher density of biodiesel than petro diesel, 0.88 kg/L versus 0.85 kg/L. As the ratio of biodiesel to petro diesel becomes lower, any difference between the biodiesel and petro diesel becomes less significant. B20 and B2 have 1.7% and 0.17% less energy per gallon from the petro diesel respectively and do not exhibit a noticeable difference in performance (Tyson et al., 2004).

Pure biodiesel contains up to 10-12% weight of oxygen, while diesel contains almost 0% oxygen. The presence of oxygen allows more complete combustion, which reduces hydrocarbons (HC), carbon monoxide (CO) and particulate matter (PM) emission. However, higher oxygen content increases nitrogen oxides (NOx) emissions.

The primary reason biodiesel is suitable as an alternative fuel for petro diesel lies in the cetane number. The cetane number indicates the ignition quality of a diesel fuel. It measures a fuel's ignition delay, which is a period between the start of injection and start of combustion (ignition) of the fuel. Fuels with a higher cetane number have shorter ignition delays, providing more time for the fuel combustion process to be completed. The term "cetane number" is derived form a straight chain alkane with 16 carbons ($C_{16}H_{34}$), hexadecane or cetane which is shown in Figure (2.1).

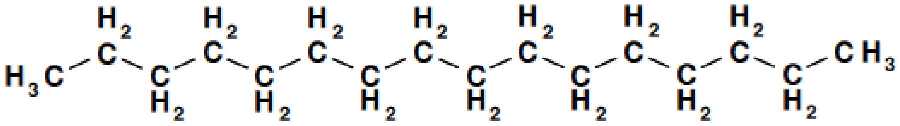


Figure 2.1: Hexadecane

This long unbranched hexadecane is the high quality standard on the cetane scale and has been assigned as having a cetane number of 100. On the other hand, highly branched alkanes are low quality compounds on the cetane scale and have low cetane numbers. Biodiesel's long chain fatty acids methyl ester are similar to long chain alkanes with number of carbons ranging from 14 to 22 (Figure 2.2). This makes biodiesel suitable for alternative diesel fuel (Gerpen, Shanks and Pruszko, 2004).

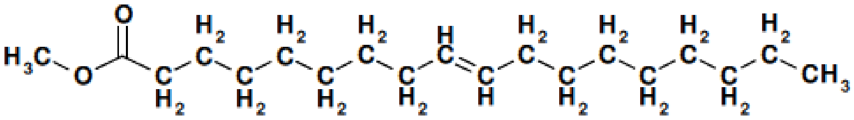


Figure 2.2: Fatty acid methyl ester

From table below, many other hazardous by-products of the combustion of diesel fuel are reduced.

Table 2.2: Average biodiesel emissions compared to conventional diesel according to EPA

Emission Type	B100	B20
Total Unburned Hydrocarbons	-67%	-20%
Carbon Monoxide	-48%	-12%
Particulate Matter	-47%	-12%
NO_x	+10%	+2% - -2%
Sulphates	-100%	-20% (estimated from B100)

This EPA (Environmental Protection Agency) study shows biodiesel is a much safer alternative to diesel fuel as proven by the reduced emissions in the majority of categories. The only category in which biodiesel had higher emissions was Nitrogen Oxides or No_x. However, the lack of sulphates present in biodiesel allow for nitrogen oxide reduction technologies or fuel additives to be used that could not be used otherwise if burning diesel fuel. This substantial reduction in the amount of emissions produced makes biodiesel an extremely attractive alternative to traditional biodiesel fuel.

2.3 Non-edible Oil

The example of non-edible oil use for biodiesel production includes Jatropha, Rubber seed, Castor and Pongamia plunata. The most commonly use was Jatropha Curcas which widely use in India and Indonesia because of its easy availability growth in arid, semiarid and wasteland (Ghadafi, 2008). Castor oil has long been used as lubricant in engines but only recently has research on the use of Castor oil has a biofuel started (Nielsen, Hill and Jongh, 2011). The oil yield for major non-edible and edible oil sources are shown in Table 2.3.

Table 2.3: Oil yield for major non-edible and edible oil sources (Shirame et al., 2011)

Type of oil	Oil yield (kg oil/ha)	Oil yield (wt %)
Non-edible oil		
Jatropha	1590	Seed: 35-40 Kernel: 50-60
Rubber seed	80-120	40-50
Castor	1180	53
Pongamia plunata	225-2250	30-40

Edible oil		
Soybean	375	20
Palm	5000	20
Rapeseed	1000	37-50

From the table, it showed that the oil yield for non-edible oil is higher compared with edible oil.

2.4 Castor oil

Castor oil is obtained from pressing castor beans (the seeds of a plant which has the botanical name Ricinus communis of the family Eurphorbiacae. This is done by either one or a combination of mechanical pressing or solvent extraction. The oil is a pale yellow, viscous, non-volatile and non-drying with a bland taste. It finds uses as a purgative, a plastic and textile finishing material, in paints and varnishes, a feedstock to the transesterification process for the production of biodiesel as well as in the beauty industry as a cosmetic and hair oil. Castor oil has an advantage over other mineral oil in that it is biodegradable, eco-friendly and renewable resource (Ogunniyi, 2006).

Castor oil is a triglyceride in which 80-90% of fatty acid chains are ricinoleic acid. No other vegetable oil contains so high a proportion of fatty hydroxy acids (Shrirame, Panwar and Bamniya, 2011). Oleic, linoleic acids and saturated fatty acids are the other significant components which 2-4% oleic acid, 3-6% linoleic acid and 1-5% saturated fatty acids (Pena, Romero, Luz Martinez, Ramos, Aldo Martinez and Natividad, 2009). Ricinoleic acid, a monounsaturated, 18-carbon fatty acid, is unusual in that it has a hydroxyl functional group on the twelfth carbon. This functional group causes ricinoleic acid (and castor oil) to be unusually polar. It is the hydroxyl group which makes castor oil and ricinoleic acid valuable as chemical feedstocks. In Malaysia, there also castor plant which is at Kuching, Sarawak but the uses of castor oil is not widely applied. Its fruits are produced in typical clusters, each pod containing well developed seeds bearing sufficient oil (47-49%).Castor oil has excellent solubility in methanol and hence theoretically ideal oil for transesterification to biodiesel, requiring a minimum amount of catalyst and heating which can reduce costs production (Bello and Makanju, 2011).

Castor grows well under hot and humid tropical conditions and has a growing period of 4 to 5 months. Castor oils unsaturated bond, high molecular weight (298), low melting point (5^oC) and very low solidification point (-12^oC to -18^oC) make it industrially useful, most of all for the highest and most stable viscosity of any vegetable oil (Shrirame et al., 2011). The characteristics of Malaysian castor seed oil are shown in Table 2.4. The fatty acids composition of castor oil is shown in Table 2.5.

Table 2.4: Characteristics of Malaysian Castor seed oil (Salimon, Noor, Nazrizawati, Firdaus and Noraishah, 2010)

Parameters	**Value**
Lipid content (%)	43.3
Moisture content (%)	0.2
Iodine value (mg/g)	84.5
Acid value (mg/g)	4.9
% free fatty acid	3.4
Peroxide value (meq/kg)	10.2
Saponification value (mg/g)	182.9
Unsaponificable value (mg/g)	3.4
Viscosity	332
Refractive Index at 25^oC	1.47
Average molecular weight	937.7

Table 2.5: Fatty acids composition of Malaysian Castor seed oil (Salimon et al., 2010)

Fatty acid	**Percentage**		
	Malaysia	**Brazil**	**India**
Palmitic	1.3	0.7	-
Stearic	1.2	0.9	1.0
Oleic	5.5	2.8	-
Linoleic	7.3	4.4	4.3
Linolenic	0.5	0.2	-
Ricinoleic	84.2	90.2	94.0
Saturated fatty acids (SFA)	2.5	1.6	1.0
Unsaturated fatty acids (UFA)	97.5	97.6	98.3

From an energy point view, Castor oil is the best vegetable oil for producing biodiesel (Castor methyl ester or Castor ME) because it does not require heat and the consequent energy that is needed when other vegetable oils are transformed into biodiesel. Long storage times are unproblematic under airtight conditions. Biodiesel made from Castor oil still has a relatively high viscosity. In Brazil, Castor ME was found too viscous to be used as such and is blended with biodiesel from other vegetable oils (Nielsen, Hill and Jongh, 2011). Furthermore, Castor oil tends to have same characteristics as other vegetable oils; however it's only produce a little glycerol. Castor oil has only 5.1-6.1% of glycerol. Meanwhile the ester produced from the castor oil is more than the other vegetable oils, which is between 84-92% (Zuhdi, Gerianto, Hashimoto and Dan, 1998).

2.5 Production of Biodiesel

Ma and Hanna (1999) have examined experimentally four primary ways to produce biodiesel. There are direct use and blending, microemulsions, thermal cracking (pyrolysis) and transesterification. They stated that a continuous transesterification process is one choice to lower the production cost. The foundations of this process are shorter reaction time and greater production capacity. The recovery of high quality glycerol is another way to lower production cost. Because little water is present in the system, the biodiesel glycerol is more concentrated. Unlike the traditional soap glycerol recovery process, the energy required to recover biodiesel glycerol is low due to the elimination of the evaporation process. In addition, the process also is simpler than soap glycerol recovery since there is a negligible amount of soap in biodiesel glycerol. This implies that the cost of recovering high quality glycerol from biodiesel glycerol is lower than that soap glycerol and that the cost of biodiesel fuel can be lowered is if a biodiesel plant has its grown recovery facility. Moreover, biodiesel is particularly useful in mining and marine situations where lower pollution levels are important. Transesterification is the technological route more used for biodiesel production and can be applied on a small scale as in laboratories or in industry, producing millions of gallons of biofuel. Although the esterification also results in biodiesel and is recommended when the raw material is composed of oils rich in free fatty acid, this technique is applied commercially in few industries.

Pena et., al (2008) developed the transesterifiction process, which added an inert co-solvent to the base catalyzed methanolysis of castor oil to speed up the reaction. The addition co-solvent which is hexane (10-20% v/v at 6:1 methanol/oil molar ratio) gave the result of a two-phase reaction in which methanolysis occurs only in the methanol phase. Because of miscibility restrictions, the oil concentration is low in the alcohol phase, and this causes the reaction to be slow. Besides that, to conduct the reaction in a single phase and increase the miscibility of oil, it is suggested to use co-solvents like tetrahydrofuran (THF), 1,4-dioxane and diethyl ether.

2.5.1 Direct Use and Blending

The direct use of vegetable oils in diesel engine is not favourable and problematic because it as many inherent failings. Even though the vegetable oils have familiar properties as biodiesel fuel, it required some chemical modification before can be used into the engine. It has only been researched extensively for the past couple of decades, but has been experimented with for almost hundred years. Although some diesel engine can run pure vegetable oils, turbocharged direct injection engine such as trucks are prone to many problems. Energy consumption with the use of pure vegetable oils was found to be similar to that of diesel fuel. For short term use, ratio of 1:10 to 2:10 oil to diesel has been found to be successful (Ma et al., 1999). Furthermore, they 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.

2.5.2 Micro-emulsion Process

Schwab, Bagby and Freedman (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 except for the lower cetane number and energy content. All micro-emulsions with butanol, hexane and octanol meet the maximum viscosity requirement for biodiesel specification.

2.5.3 Thermal Cracking (Pyrolysis)

Sonntag (1979) defined pyrolysis as the conversion of one substance into another by means of heat or heating 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 path and the variety of reaction products that may be obtained from the reaction occur. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. The first pyrolysis of vegetable oil was conducted in an attempt to synthesis petroleum from vegetable oil (Ma et al., 1999). Besides that, Mahanta and Shrivasta (2008) stated that the pyrolyzate had lower viscosity, flash point and pour point then diesel fuel and equivalent calorific values. 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°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 (Ma et a., 1999).

2.5.4 Transesterification Process

Transesterification or alcoholysis is the displacement of alcohol from an ester by another in a process similar to hydrolysis, except than alcohol is used instead of water (Srivatava and Prasad, 2000). This process has been widely used to reduce the high viscosity of triglycerides. The transesterification reaction is represented by the general equation as in the following equation. Transesterification is one of the reversible reactions and proceeds essentially by mixing the reactants. However, the presence of a catalyst (a strong acid or base) will accelerate the conversion.

$$\text{Triglycerides + Methanol} \xrightleftharpoons{\text{Catalyst}} \text{Glycerol + Methyl Ester}$$

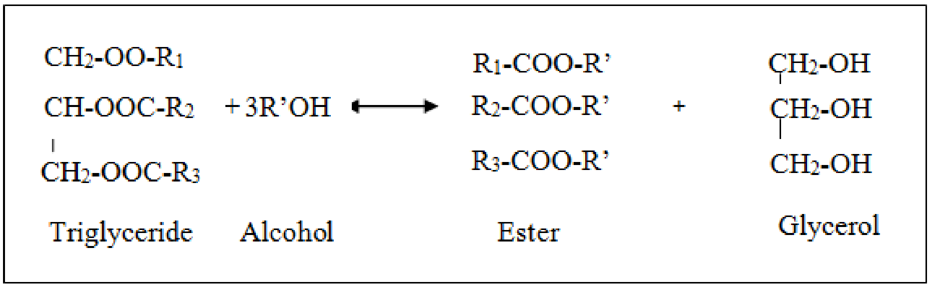


Figure 2.3: Transesterification of triglycerides with alcohols

Transesterification of triglycerides with methanol and aid of catalyst produce methyl ester and glycerol. The glycerol layer settles down at the bottom of the reaction vessel. The step wise reactions are reversible and a little excess alcohol is used to shift the equilibrium towards the formation of ester. In presence of excess alcohol, the forward reaction is first order reaction and the reverse reaction is found to be second order reaction. It was observed that transesterification is faster when catalyzed by alkali (Freedman et al., 1986).

2.6 Base-Catalyzed Transesterification

The base-catalyzed transesterification of vegetable oils to form alkyl ester is faster than the acid-catalyzed reaction. The base-catalyzed reaction proceeds rapidly at ambient temperature depending on the boiling point of the alcohol. For the current process to produce biodiesel, the vegetable oil transesterification is catalyzed by alkali hydroxide dissolved in methanol. The homogeneous catalysis reduces the mass transfer residence, which leads to the good reaction efficiency. However, a large amount of wastewater is discharged from the process because it is necessary to wash the homogeneous catalyst off the produced biodiesel. Moreover, the washing operation involves formation of stable emulsion. These are the problems causing the costly production of biodiesel. One of the solutions for the problems mentioned above is to utilize the heterogeneous catalytic reaction for biodiesel production and quicklime (calcium oxide) seems to promise the solid base catalyst (Kouzu, Tsunomori, Yamanaka and Hidaka, 2010). Quicklime is easy to get and inexpensive. For utilizing quicklime as the solid base catalyst, we must not only evaluate the catalytic activity but also understand a mechanism on the heterogeneous catalytic reaction.

For typical base catalyzed alcoholysis of oils and fats, the catalyst is first dissolved in the alcohol such as methanol or ethanol and then mixed with oil. The solubility of alcohol in oil varies depending on the size of the alkyl group of the alcohol and the reaction temperature. The solubility of methanol in oil is fairly low at room temperature, even at moderate temperature such as $60^{o}C$ (Mao, 1995). Therefore, very vigorous mixing is employed to initiate the first phase of the reaction. The triglyceride is converted stepwise to diglyceride, monoglyceride and finally to glycerol. The glycerol starts to form after addition of alcohol and slowly settles at the bottom of the reaction vessel by gravity. The lower glycerol-rich phase containing a small amount of alcohol and probably some monoglyceride is separate for purification. The upper fatty ester-rich phase contains the remainder of glycerol, most of the unreacted alcohol, catalyst and mono-,di- and triglycerides. The excess alcohol is removed by distillation and the ester-rich phase is washed with distilled water. Soap is usually a by-product. The base-catalyzed transesterification is exothermic (Feugo and Gros, 1949). They reported that a rise of 1 to $2^{o}C$ above the reaction temperature occurs immediately after the addition of catalyst solution to the oil. After 4 or 5 minutes, the temperature returns to the original reaction temperature and then remains constant throughout the reaction.

From the previous researched, Kawashima et., al (2009) was examined the activated CaO (quicklime) catalyst in order to develop an effective catalyst for the FAME production process. They found that CaO activated with methanol was an efficient catalyst for high-yield transesterification reaction. The optimal reaction conditions were 0.1 g of CaO and 3.9 g of methanol added to 15 g of rapeseed oil and activation at 25°C for 1.5 hours, which resulted in approximately 90% yield of methyl ester within a reaction time of 3 hours at 60°C.

2.7 Solvent

Actually, there are many types of alcohols such as methanol and ethanol that can be used in the transesterification. Short-chain alcohols such as methanol, ethanol and butanol are the most commonly used as a solvent. Therefore, selection of the alcohol is depends on cost and performance consideration. Ethanol can be produced from agricultural renewable resources, thereby attaining total independence from petroleum based alcohols. For example, if methanol is used, the resulting biodiesel is fatty acid methyl ester (FAME) which has proper viscosity, boiling point and high cetane number (Gryglewicz, 1999). But, methanol is the most common alcohol because of it has lower price compared to other alcohols. Handling methanol might be considered an exception to that generality.

2.8 Process Variables Affecting Transesterification

The yield of biodiesel production from transesterification process affected by several conditions such as reaction temperature, type and concentration of catalyst and molar ratio of alcohol to vegetable oil, type of alcohol and others.

The research to examine the activated CaO catalyst in order to develop an effective catalyst for the biodiesel production process was studied by Kawashima et., al (2009). They found that CaO activated with methanol was an efficient catalyst for high-yield transesterification reaction. The optimal reaction conditions were 0.1 g of CaO and 3.9 g of methanol added to 15 g of rapeseed oil and activation at 25°C for

1.5 hours, which resulted in approximately 90% yield of methyl ester within a reaction time of 3 hours at 60°C.

Base catalyzed alcoholysis of fats or oil usually performed near the boiling point of the alcohol or at elevated temperature in order to improve the rate of reaction. However, room temperature is considered to be the optimum due to safety and energy consumption cost. Nye and Southwell (1984) conducted methanolysis and ethanolysis of rapeseed oil with 1 wt% NaOH at 6:1 methanol/oil molar ratio and 24°C. They successfully produced "substantial" amounts of methyl ester and ethyl ester of rapeseed oil in an hour.

Besides that, Encinar et., al (2010) was studied about operation variables which is catalyst types (sulphuric and phosphoric acids, potassium hydroxide and potassium methoxide), catalyst concentration (2, 3 and 4 wt. % in acid catalysts; 0.5, 1.0 and 1.5 wt. % in basic catalysts), methanol/oil molar ratio (3:1, 6:1, 9:1 and 12:1) and temperature (25, 35, 45, 55 and 65°C). Reaction time (3 h) and agitation rate (700 rpm) were fixed as common parameters in all experiments. The most suitable catalyst for this process proved to be basic catalyst which is potassium methoxide. Potassium hydroxide achieved similar results but its methyl esters contents slightly lower. The best molar ratio of methanol was 9:1, for both acid and basic catalyst. The temperature variable exerted a positive influence on the reaction rate, although not significant. The final concentration of methyl ester was almost the same for all temperatures.

Moreover, Chakrabarti et., al (2008), studied about the transesterification of castor oil under various conditions which is amount of methanol and catalyst (KOH), temperature and reaction time. From the result, the reaction mixture containing 65 ml of methanol along with 2.4 g of catalyst took a good start in half an hour at 30°C. In this reaction, amount of glycerine removed as well as ester content produced was considerably increased with rise in temperature of mixture up to 70^{o}C by extending time period (180-360 minutes). The removal of glycerine increased by two and half times and ester content by four times, respectively.

CHAPTER 3

METHODOLOGY

3.1 Flow Diagram of Experiment

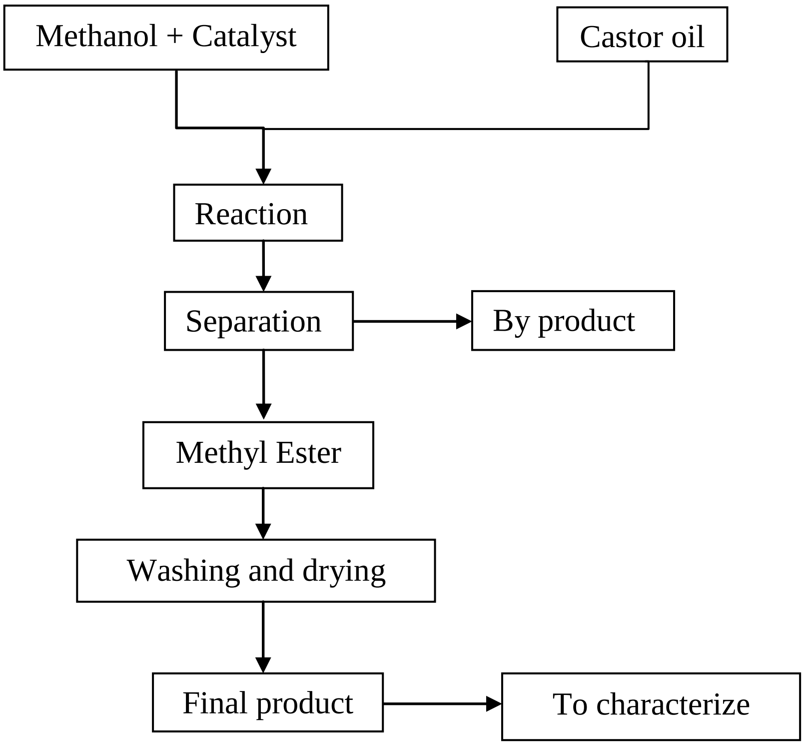


Figure 3.1: Flow diagram of transesterification process

3.2 Method Descriptions

The detailed description of the materials, equipments and methods was discussed.

a) Material

  - Raw material.
  - Alcohol selection.
  - Drying agent.

b) Equipment

  - Hot plate magnetic stirrer.
  - 250 ml 3-necked round bottomed flask equipped with a reflux condenser and thermometer.
  - 250 ml separating funnel.
  - Centrifuge.
  - Rotary evaporator.

c) Research method

  - Collecting sample.
  - Performing experiment.
  - Product analysis.

3.2.1 Material

i. Raw material

The raw material use in this research was pure Castor oil.

ii. Alcohol selection

Price is the main factor in determining which alcohol as a solvent used in the production process. Ethanol (C_2H_3OH) and methanol (CH_3OH) are the two most common options. The high quality methanol is cheaper than ethanol and therefore, methanol is used on nearly all biodiesel operations including in this research.

iii. Drying agent

Anhydrous magnesium sulphate ($MgSO_4$) is used as a drying agent to remove excess water from the product. This is because the presence of water will cause a cloudy product.

3.2.2 Equipments

A few types of equipment are required in this experiment in order to achieve the production of biodiesel by using calcium oxide as a basic catalyst.

i. Hot plate magnetic stirrer

This equipment is one of the major equipment for this experiment. It is used to prepare water bath, warm up the oil and heat distilled water for washing.

ii. **Three-necked round bottomed flask with reflux condenser and thermometer**

To heat and stirred the mixtures of methoxide and oil.

iii. **Separating funnel**

To separate two layers of glycerine and biodiesel.

iv. **Centrifuge**

To remove excess catalyst from the product.

v. **Rotary evaporator**

To recover excess methanol from the product.

3.2.3 Research Method

i. **Collecting sample**

The pure castor oil used in this research was collected from Indian market at Kuantan, Pahang Darul Makmur.

ii. **Preparation of samples**

In the laboratory, two sets of different ratios of methanol to oil were prepared. The ratios of methanol to oil were:

a. 3:1 (60 ml : 20 ml)
b. 4:1 (80 ml : 20 ml)

In order to have 1.0 % CaO for every 20 ml of oil used, 0.2 gram of calcium oxide (CaO) was added into methanol to produce methoxide solutions. These solutions were prepared in a 250 ml beaker and stirred without heat up around 30 minutes to activate the catalyst. The calcium oxide did not fully dissolved in the methanol because of it type of heterogeneous catalyst.

iii. Performing experiment

In this research, three experiments for each set of parameters with a total of six experiments are done as shown in the table below:

Table 3.1: Sets of samples for experiment for each parameter

Ratio (methanol: oil)	Time (min)
3:1	60
	120
	180
4:1	60
	120
	180

The temperature for the experiment was fixed to 60°C.

1. Reaction of methoxide with Castor oil

A sample of 20 ml oil were poured into a 3-necked round bottomed flask and pre-heated up to 60°C on the hotplate. A higher reaction temperature can decrease the viscosities of oils and result in an increased reaction rate and a shorter time. Depending the oil used, the optimal temperature ranged from 60°C to 65°C (Encinar et al., 2010). Carefully, the methoxide was poured into the heated oil according to the ratio selected in Table 3.1. Stirring speed was set up at 400 rpm. It increased the intact area between oil and calcium oxide methanol solution.

2. Separation of glycerine and biodiesel

After the transesterification process was completed, the hot mixture from 3-necked round bottomed flask was poured into the separating funnel for settling. The products which were Castor oil methyl ester and glycerine were settled for at least 12 hours.

3. Washing

When the top layer was decanted from the bottom layer, the top layer may contain unreacted catalyst, methanol and residual glycerol. These impurities were removed by hot water treatment. The ester layer was washed with 45^{o}C of hot distilled water. The water was poured in carefully and gently to avoid emulsifying. The water washing method was continued (4-6 times) until the water layer becomes clear. For this process equal amount of hot distilled water was used to remove the impurities.

4. Centrifuge

After the methyl ester layer was washed, it may still contain unreacted catalyst. Hence, the methyl ester was centrifuged at -5^{o}C and 3000 rpm in 10 minutes. The unreacted catalyst was settled at the bottom of centrifuge tube.

5. Removal of excess methanol

The ester layer was heated in a flask placed in a rotary evaporator. The temperature and the speed were set up at 80^{o}C and 60 rpm. Methanol was evaporated and condensed in the centre tube condenser and collected. The biodiesel product was left in a rotary flask.

6. Drying

After the completion of purification process the biodiesel may contain some amount of water. This should be removed because the water content is responsible for growth of biological organisms and it also increases the acid value of fuel. Hence the ester layer was reacted with some amount of anhydrous magnesium sulphate and it was settled for 12 hours. Finally, the dried biodiesel formed with very clear fuel.

3.2.4 Product Analysis

The product was analysed with Gas Chromatography Mass Spectrometry (GC-MS) in order to determine the compositions contained in the product. The fatty acid methyl esters (FAMEs) contents were determined by gas chromatography, model GC−6890N coupled with mass spectrometer, model MS−5973 MSD (mass selective detector). Separation was performed on a capillary column DB-5MS (30 m ×0.32 mm, 0.25µm of film thickness). The carrier gas was helium with flow rate of 1.5 mL/min. The column temperature was programmed from 120-300 °C at the rate of 10 °C/min. A sample volume of 1.0µL was injected using a split mode, with the split ratio of 1:10. The mass spectrometer was set to scan in the range of m/z 50-550 with electron impact (EI) mode of ionization.

CHAPTER 4

RESULTS AND DISCUSSION

This chapter presents all the results obtained with the best biodiesel yield based on reaction time and ratio of methanol to oil of biodiesel produced by using the method described in Chapter 3.

4.1 Biodiesel Yields

In this research, the parameters that are taken into consideration are reaction time and methanol: oil ratio. The temperature was fixed at 60^oC and the agitation speed was set at 400 rpm. The percentage yields for all samples at different parameters were shown in Table 4.1 below:

Table 4.1: Biodiesel yield

Ratio (methanol: oil)	Time (min)	Total Product (g)	Yield (%)
3:1	60	9.4917	48
	120	12.9393	65
	180	16.2163	82
4:1	60	11.2825	57
	120	15.5833	79
	180	12.2846	62

4.2 Yield Comparisons

4.2.1 Effect of methanol: oil ratio

The effect of methanol/oil ratio can be seen in the graphs below.

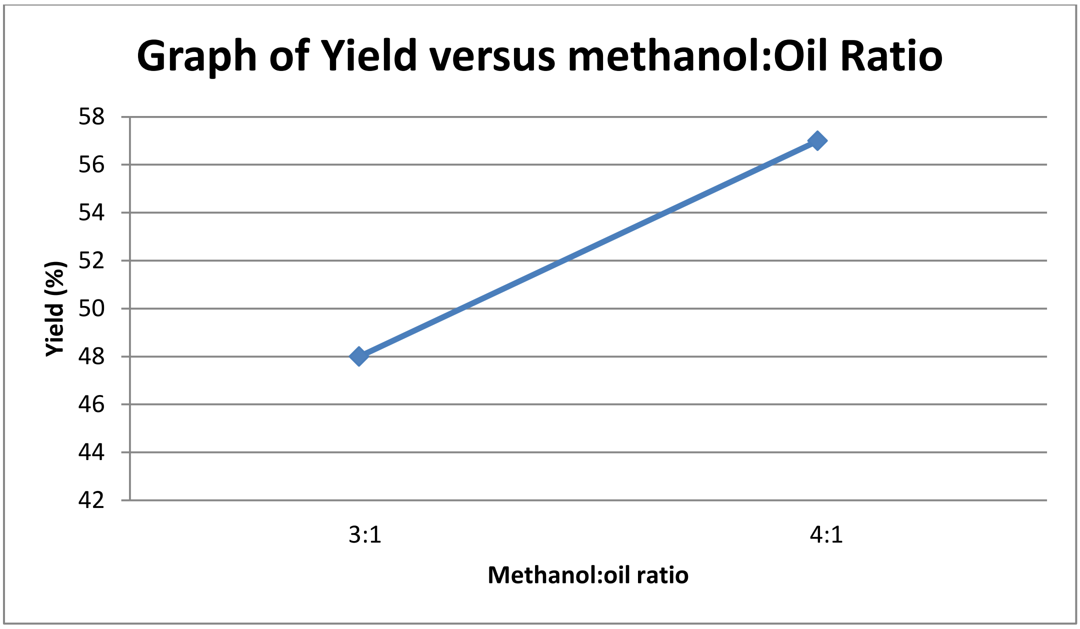


Figure 4.1: Effect of methanol/oil ratio to biodiesel yield at 60 minutes

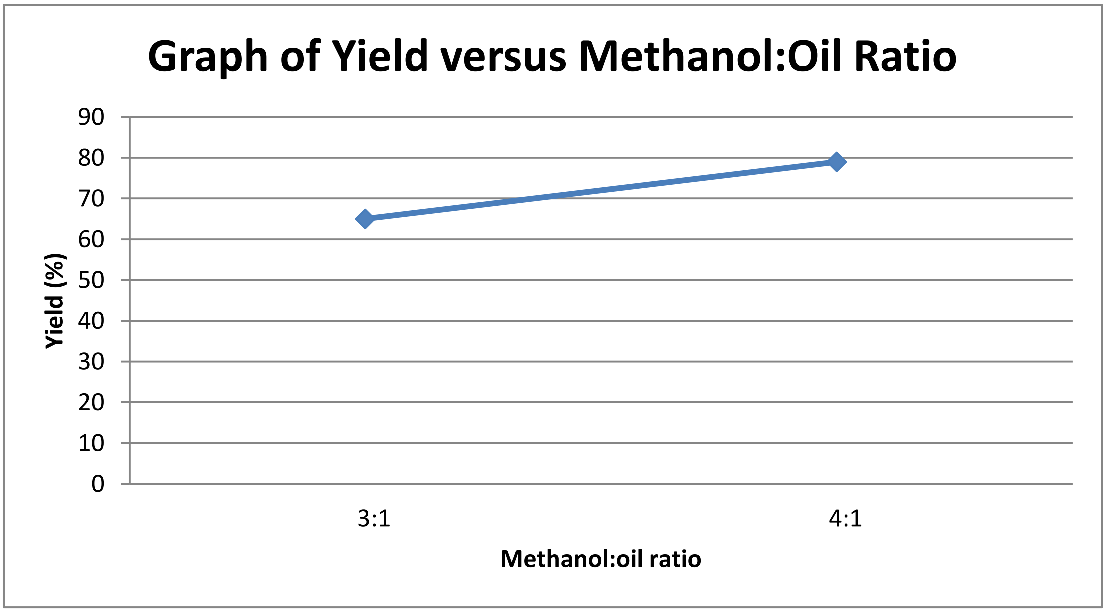


Figure 4.2: Effect of methanol/oil ratio to biodiesel yield at 120 minutes

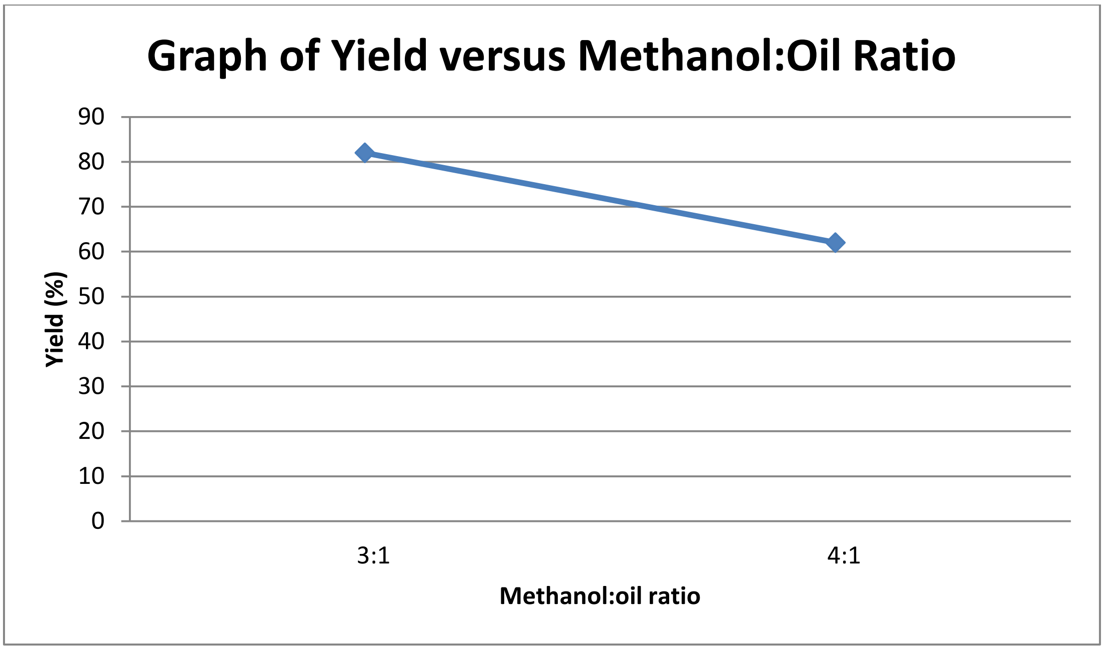


Figure 4.3: Effect of methanol/oil ratio to biodiesel yield at 180 minutes

Figure 4.1and 4.2 were shown that the biodiesel yield increased when the methanol/oil ratio were increased. These graph different compared with Figure 4.3 which the biodiesel yield were decreased with increases of methanol/oil ratio. The biodiesel achieved the higher yield (82%) at 3:1 of methanol/oil ratio compared with 4:1 of methanol oil ratio which the yield is 79%.

4.2.2 Effect of reaction time

The effect of reaction time toward the percentage yield of biodiesel can be seen in the graphs below.

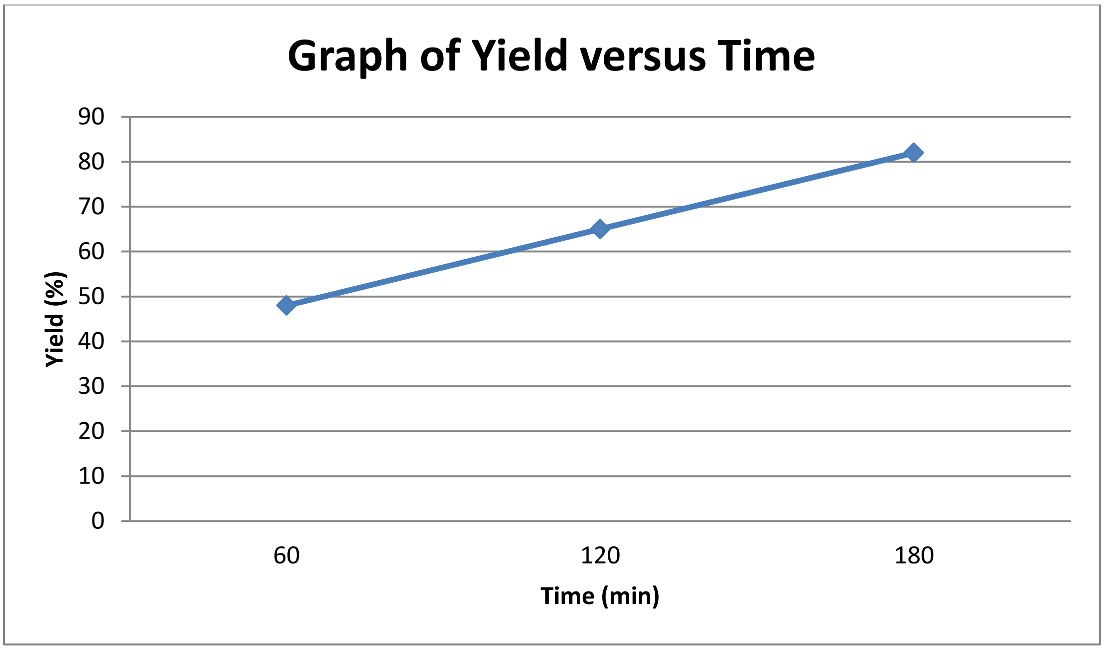


Figure 4.4: Effect of reaction time to biodiesel yield at 3:1 of methanol/oil ratio

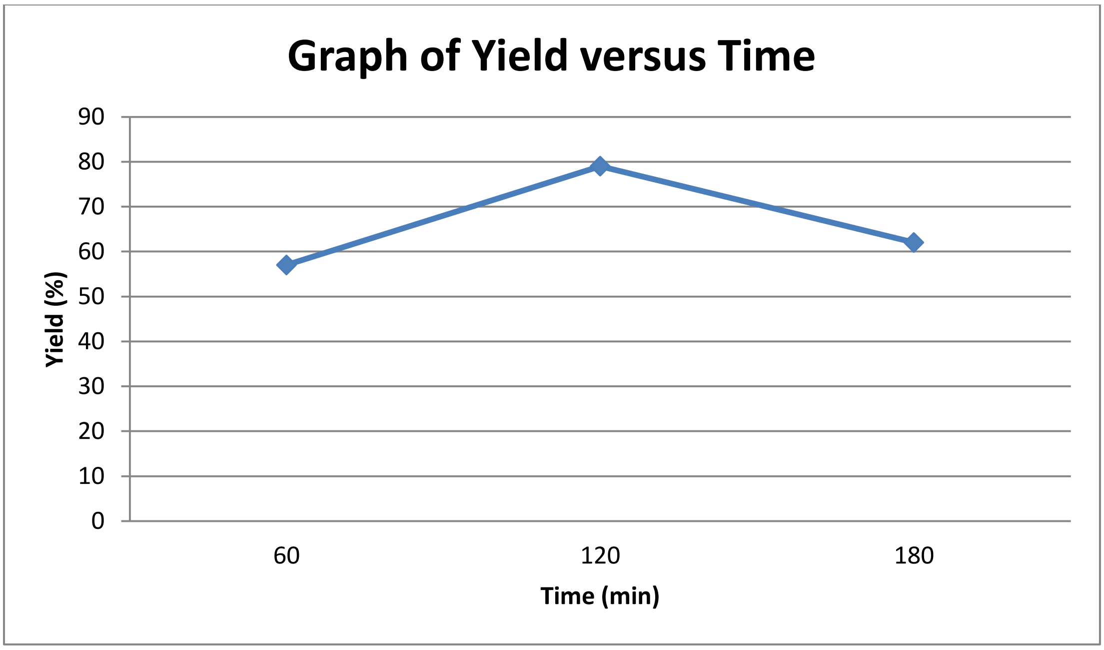


Figure 4.5: Effect of reaction time to biodiesel yield at 4:1 of methanol/oil ratio

Figure 4.4 was shown that the biodiesel yield is proportional with reaction time. Higher biodiesel yield is achieved with increasing of transesterification reaction time which 82% at 180 minutes. While Figure 4.5 was shown that the biodiesel yield increased at 60 and 120 minutes but decreased at 180 minutes.

4.3 Summary

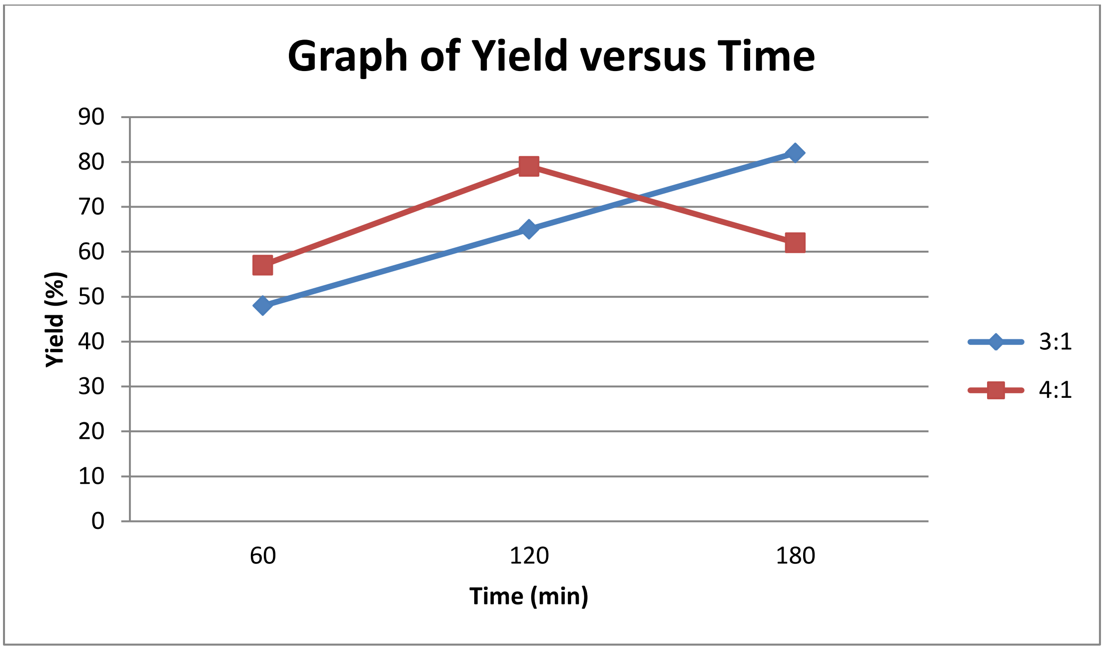
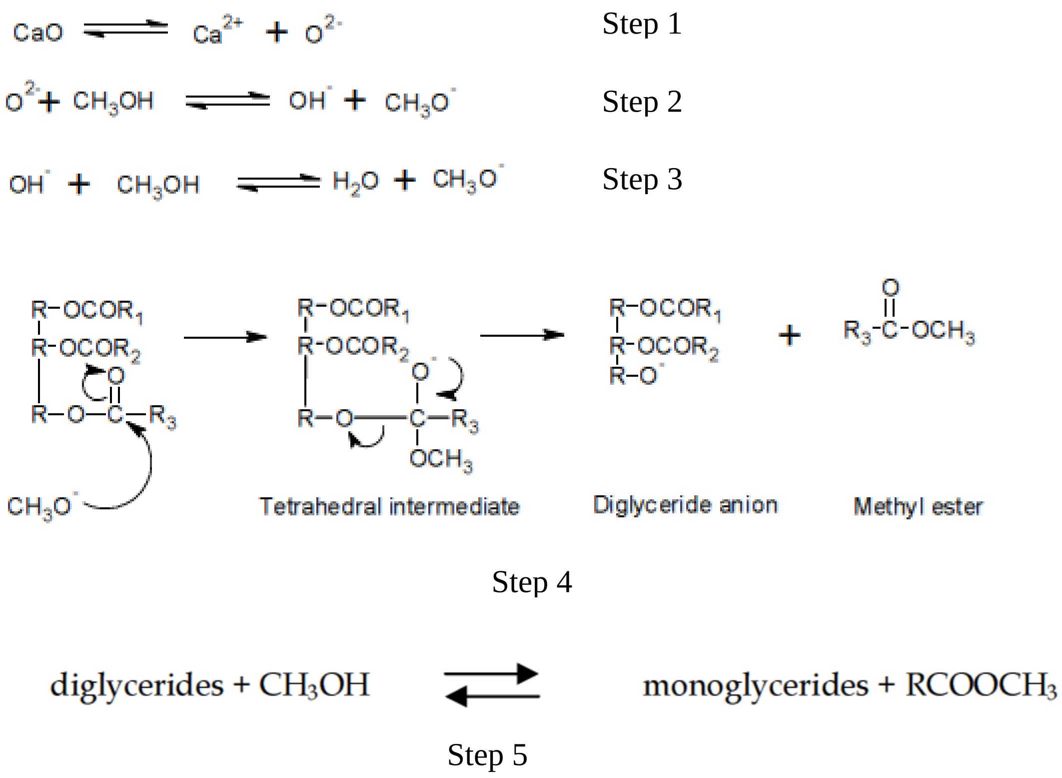


Figure 4.6: Yield comparison based on different of methanol/oil ratio and reaction time

Figure 4.3 shows experimental conditions and obtained results. As mentioned, the transesterification activity also depends on the ratio of methanol to oil. From the transesterification reaction stoichiometry, theoretically 3 mol of alcohol is required for 1 mol of triglycerides to produce 3 mol of fatty acid ester and 1 mol of glycerol. An excess of alcohol is used in biodiesel production to ensure that the oil will be completely converted to the corresponding alkyl esters (biodiesel), hence a higher alcohol: oil ratio can result in a greater alkyl ester yield in a shorter time. Also, biodiesel yield is increased when the alcohol/oil ratio is raised beyond 3 and reaches a maximum. Therefore, it is important to consider that increasing the alcohol amount beyond the optimal ratio will not increase the yield but will increase the cost for alcohol recovery. The results can be observed in Figure 4.6. The effect of methanol/oil ratio on biodiesel production was evident since the increasing the methanol/oil ratio from 3:1 to 4:1, increased the biodiesel yield from 65% to 79%. Besides that, from the results it is clear that reaction time affected positively the catalytic activity since the biodiesel yield increased steadily with reaction time achieving in 60, 120 and 180 minutes yields of 48%, 65% and 82% at 3:1 methanol/oil ratio, respectively.

In the presence of heterogeneous catalyst, the reaction mixture constitutes a three-phase system, oil-methanol-catalyst, in which the reaction would be slowed down because of the diffusion resistance between different phases.



$CaO \rightleftharpoons Ca^{2+} + O^{2-}$ Step 1

$O^{2-} + CH_3OH \rightleftharpoons OH^- + CH_3O^-$ Step 2

$OH^- + CH_3OH \rightleftharpoons H_2O + CH_3O^-$ Step 3

Step 4

diglycerides + $CH_3OH \rightleftharpoons$ monoglycerides + $RCOOCH_3$

Step 5

$$\text{monoglycerides} + CH_3OH \rightleftharpoons \text{glycerine} + RCOOCH_3$$

Step 6

Figure 4.7: Mechanism of CaO-catalysed transesterification (Boey et al., 2011)

As shown in Figure 4.7, the mechanism of CaO in transesterification reaction starts with disassociation of CaO and methanol (Step 1and Step 2). Then the formation of methoxide anion resulted from the reaction between methanol and hydroxide ion (Step 3). The anion later attacks carbonyl carbon of triglyceride to form tetrahedral intermediate. Then the rearrangement of the intermediate molecule forms a mole of methyl ester and diglyceride, as shown by Step 4 (Boey et., al). Then the methoxide attacks another carbonyl carbon atom in diglyceride, forming another mole of methyl ester and monoglyceride (Step 5). Finally another methoxide attacks on monoglyceride produces a total of three moles of methyl esters and a mole of glycerol (Step 6).

On the other hand, Gas Chromatography Mass Spectrometry was analysed the composition of product in order to make sure that the product is biodiesel (methyl ricinoleate, $C_{19}H_{36}O_3$). From the GCMS result, the higher peak of the graph is methyl ricinoleate which mean that the sample containing most of methyl ricinoleate composition. The molecular weight of methyl ricinoleate is 312.4873 g/mol. On the other hand, methyl ricinoleate also called as 12-hydroxy-cis-9-octadecenoic acid methyl ester, methyl 12-hydroxyoleate or ricinoleic acid methyl ester. The melting and boiling points are -29^oC and 170^oC. Table below shown the summary of product analysis:

Table 4.2: Summary of product analysis by GCMS

Ratio (Methanol:oil)	**Time (min)**	**Area Pct of Methyl Ricinoleate (%)**
3:1	60	57.1868
	120	73.5235
	180	73.6488
4:1	60	70.3081
	120	72.8757
	180	69.7089

where:

Area Pct = % of the total measured area in the total ion chromatogram

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this research, the main objective is to use heterogeneous catalyst quicklime for possible high yield production biodiesel from Castor oil. The obtained result shown the high yield production biodiesel from Castor oil is 82% which the reaction conditions were 180 minutes (3 hours) and 3:1of methanol/oil ratio with 0.2 g CaO (1 wt%) at 60^oC. Hence, the objective of this research is achieved.

5.2 Recommendations

There are few recommendations needed to improve this research in order to get better results and outcomes:

i. Further study can be done by using mixer with higher temperature than 60^oC to decide if it will gives better yield.

ii. The biodiesel can be characterized such as it flash point, density, kinematic viscosity, cetane number, cloud point, pour point and saponification value.

iii. Add other parameters such as type of catalysts and reaction temperature in order to get the best yield and optimum condition.

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APPENDICES

APPENDIX A.1

CALCULATION

Methanol/oil Ratio	Time (min)	Empty Flask (g)	Flask + FAME (g)	FAME (g)	Average FAME (g)	Yield (%)
3:1	60	48.9014	58.4223	9.5209	9.4917	48
		48.8822	58.3447	9.4625		
	120	51.8482	64.7880	12.9398	12.9393	65
		51.8212	64.7600	12.9388		
	180	49.9418	66.1439	16.2021	16.2163	82
		49.9520	66.1824	16.2304		
4:1	60	51.2370	62.5292	11.2922	11.2825	57
		51.2633	62.5361	11.2728		
	120	51.5385	67.1479	15.6094	15.5833	79
		51.6025	67.1597	15.5572		
	180	51.9031	64.1882	12.2851	12.2846	62
		51.8746	64.1586	12.2840		

Yield = $\frac{\mathrm{m_{FAMEl}}}{\mathrm{m_{oill}}} \times 100\%$

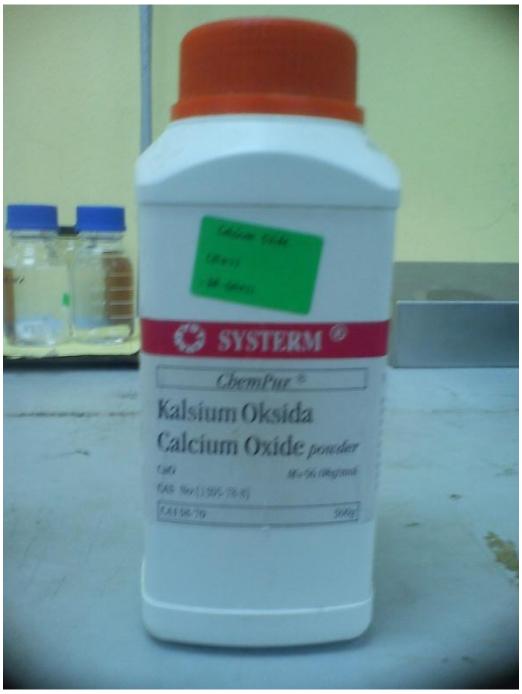
where : $\mathrm{m_{oil}}$ = 19.8271 g

APPENDIX A.2

PRODUCTION PROCESSES

Appendix A.2.1: Castor oil (150 ml)

Appendix A.2.2: Methanol, CH_3OH (99.5%)



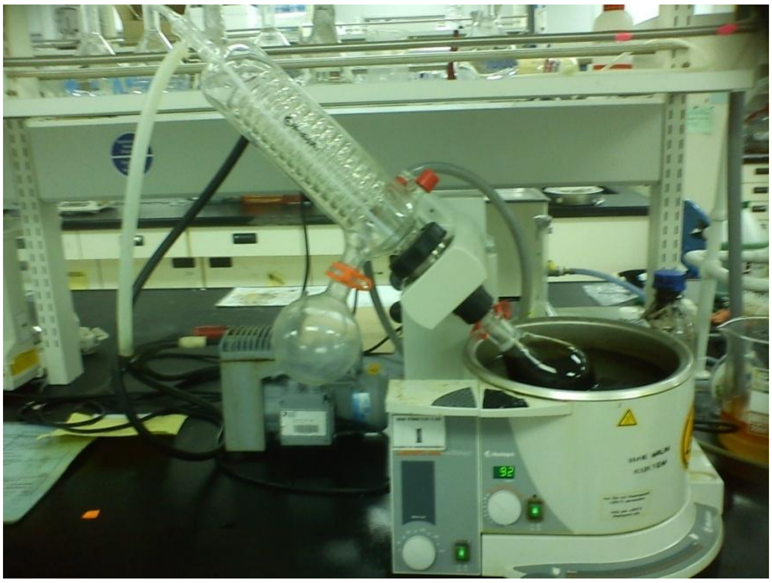
Appendix A.2.3: Calcium oxide (quicklime)

Appendix A.2.4: Mixing of methanol and catalyst for produce methoxide

Appendix A.2.5: Mixing of Castor oil and methoxide (Transesterification process)

Appendix A.2.6: 24 hours settling in a separating funnel

Appendix A.2.7: Biodiesel washing



Appendix A.2.8: Thermal oil rotary evaporator

Appendix A.2.9: Anhydrous $MgSO_4$ (drying agent)

Appendix A.2.10: Mixing drying agent with biodiesel

Appendix A.2.11: pH meter to check pH value of biodiesel

Appendix A.2.12: Biodiesel from Castor oil

APPENDIX A.3

PRODUCT ANALYSIS

Appendix A.3.1: Gas Chromatography Mass Spectrometry

Appendix A.3.2 : GCMS Methodology

Methodology

The fatty acid methyl esters (FAMEs) contents were determined by gas chromatography, model GC−6890N coupled with mass spectrometer, model MS−5973 MSD (mass selective detector). Separation was performed on a capillary column DB-5MS (30 m ×0.32 mm, 0.25μm of film thickness). The carrier gas was helium with flow rate of 1.5 mL/min. The column temperature was programmed from 120-300 °C at the rate of 10 °C/min. A sample volume of 1.0μL was injected using a split mode, with the split ratio of 1:10. The mass spectrometer was set to scan in the range of m/z 50-550 with electron impact (EI) mode of ionization.

Appendix A.3.3: GCMS results

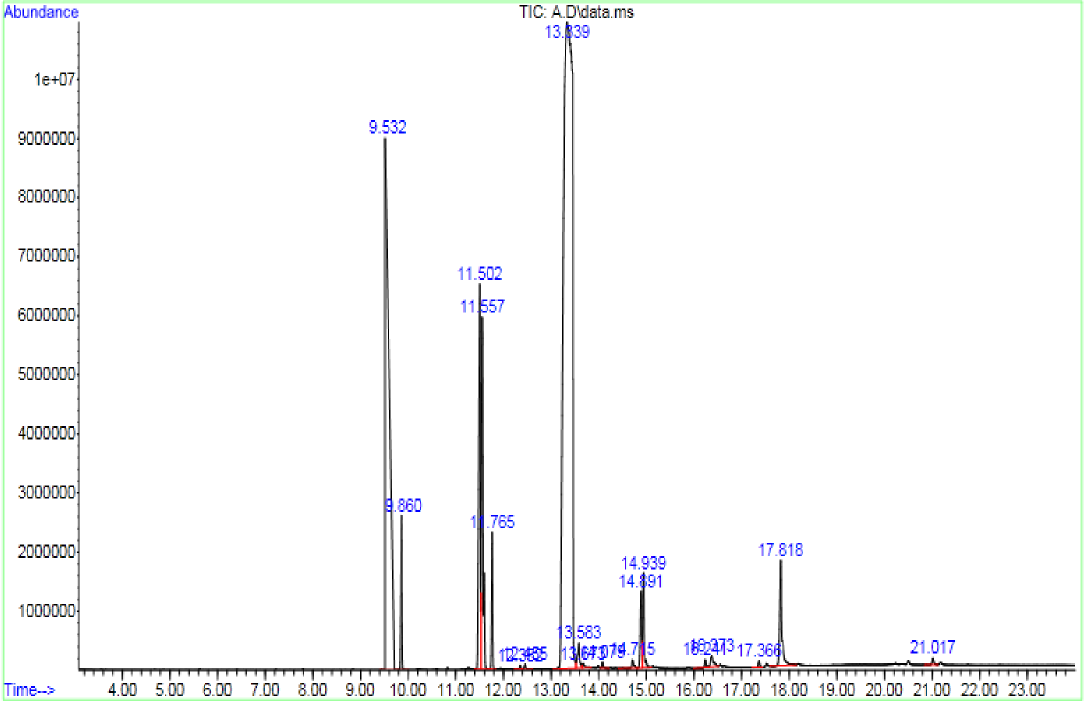
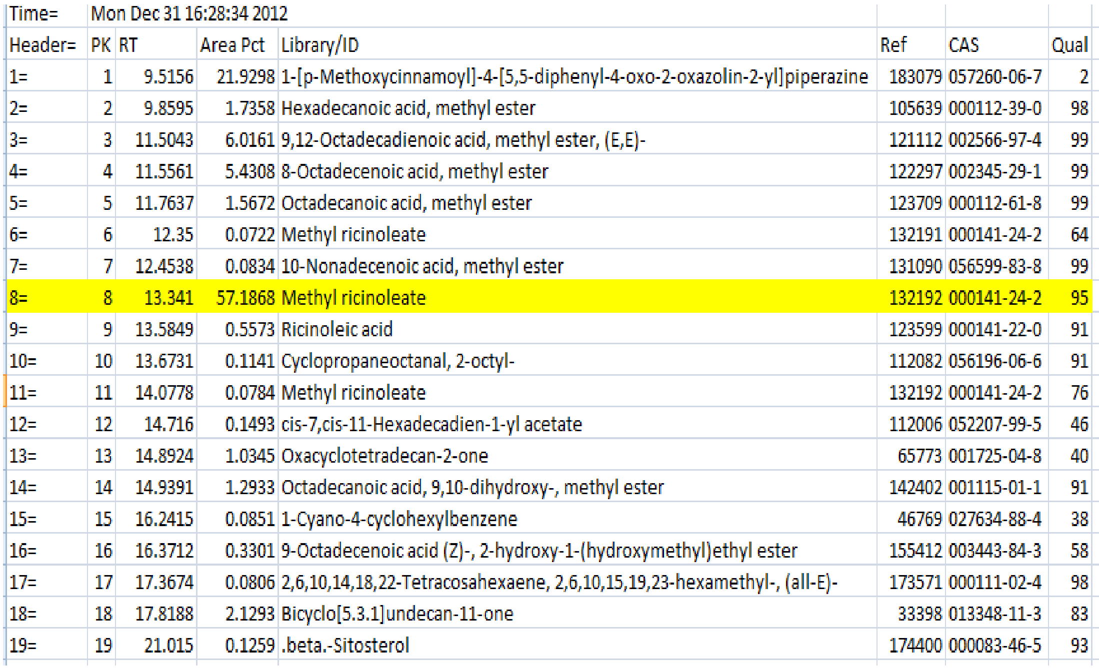


Figure A.3.1: Reaction conditions; 3:1 methanol/oil ratio, 60 min, 1 wt%, 60^{o}C



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1=	1	9.5156	21.9298	1-[p-Methoxycinnamoyl]-4-[5,5-diphenyl-4-oxo-2-oxazolin-2-yl]piperazine	183079	057260-06-7	2
2=	2	9.8595	1.7358	Hexadecanoic acid, methyl ester	105639	000112-39-0	98
3=	3	11.5043	6.0161	9,12-Octadecadienoic acid, methyl ester, (E,E)-	121112	002566-97-4	99
4=	4	11.5561	5.4308	8-Octadecenoic acid, methyl ester	122297	002345-29-1	99
5=	5	11.7637	1.5672	Octadecanoic acid, methyl ester	123709	000112-61-8	99
6=	6	12.35	0.0722	Methyl ricinoleate	132191	000141-24-2	64
7=	7	12.4538	0.0834	10-Nonadecenoic acid, methyl ester	131090	056599-83-8	99
8=	8	13.341	57.1868	Methyl ricinoleate	132192	000141-24-2	95
9=	9	13.5849	0.5573	Ricinoleic acid	123599	000141-22-0	91
10=	10	13.6731	0.1141	Cyclopropaneoctanal, 2-octyl-	112082	056196-06-6	91
11=	11	14.0778	0.0784	Methyl ricinoleate	132192	000141-24-2	76
12=	12	14.716	0.1493	cis-7,cis-11-Hexadecadien-1-yl acetate	112006	052207-99-5	46
13=	13	14.8924	1.0345	Oxacyclotetradecan-2-one	65773	001725-04-8	40
14=	14	14.9391	1.2933	Octadecanoic acid, 9,10-dihydroxy-, methyl ester	142402	001115-01-1	91
15=	15	16.2415	0.0851	1-Cyano-4-cyclohexylbenzene	46769	027634-88-4	38
16=	16	16.3712	0.3301	9-Octadecenoic acid (Z)-, 2-hydroxy-1-(hydroxymethyl)ethyl ester	155412	003443-84-3	58
17=	17	17.3674	0.0806	2,6,10,14,18,22-Tetracosahexaene, 2,6,10,15,19,23-hexamethyl-, (all-E)-	173571	000111-02-4	98
18=	18	17.8188	2.1293	Bicyclo[5.3.1]undecan-11-one	33398	013348-11-3	83
19=	19	21.015	0.1259	.beta.-Sitosterol	174400	000083-46-5	93

Figure A.3.1.1: Result summary

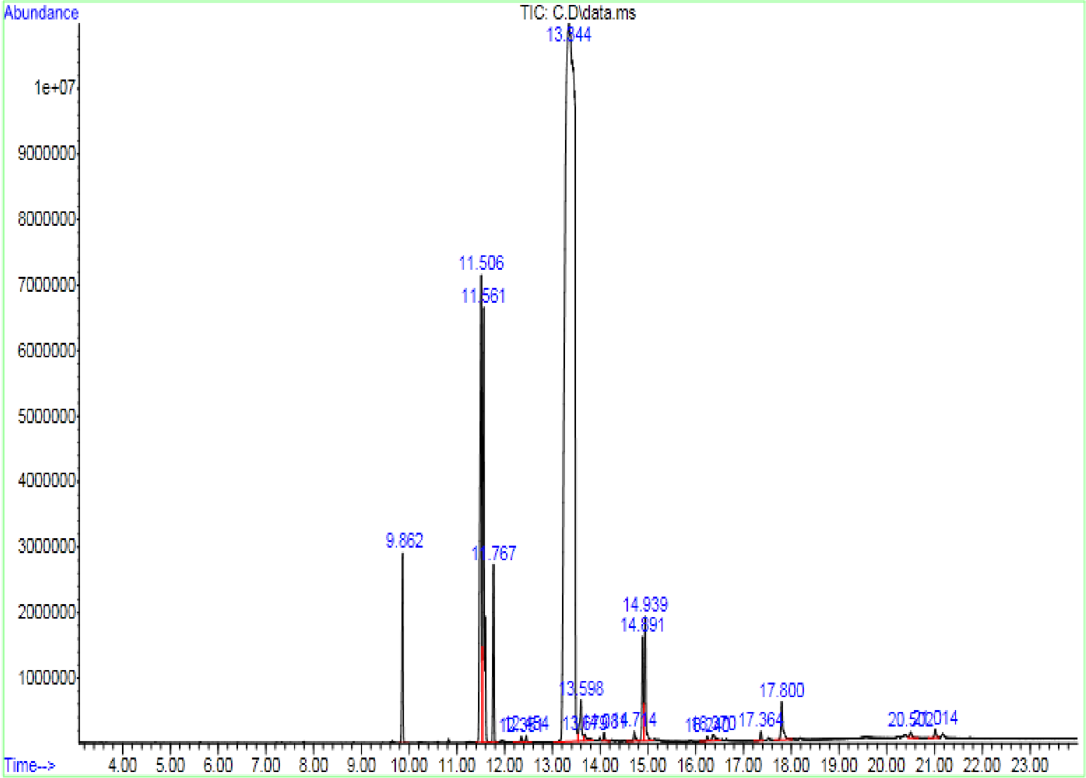
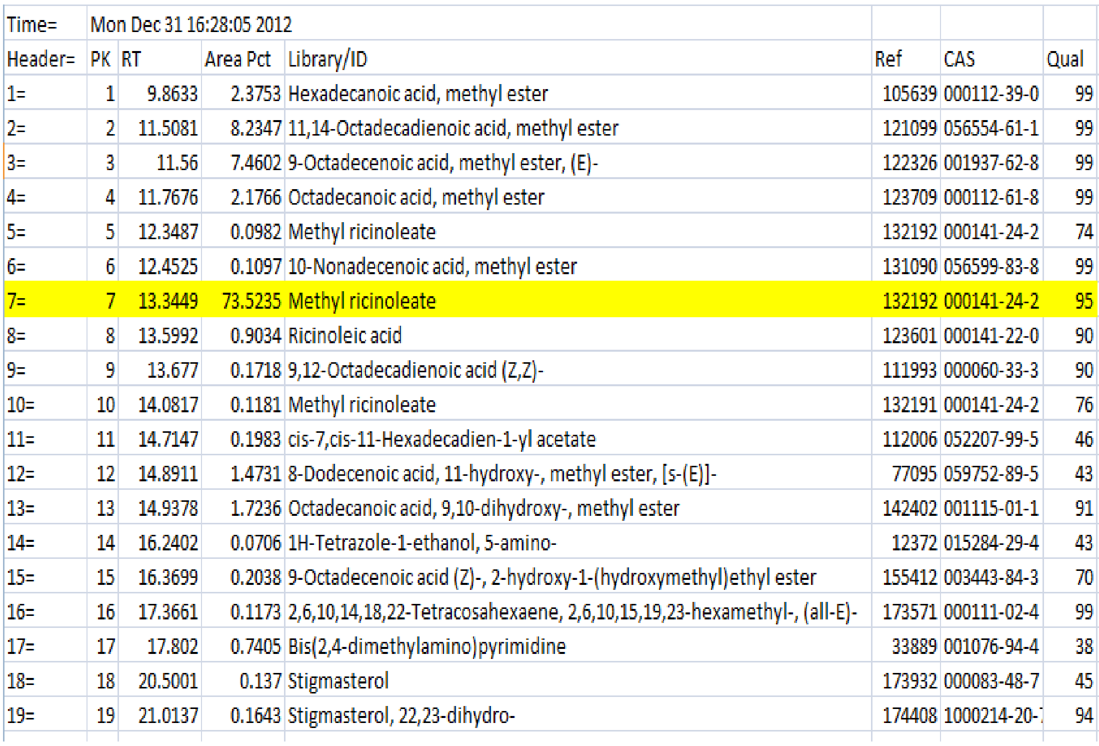


Figure A.3.2: Reaction conditions; 3:1 methanol/oil ratio, 120 min, 1 wt%, 60°C



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2=	2	11.5081	8.2347	11,14-Octadecadienoic acid, methyl ester	121099	056554-61-1	99
3=	3	11.56	7.4602	9-Octadecenoic acid, methyl ester, (E)-	122326	001937-62-8	99
4=	4	11.7676	2.1766	Octadecanoic acid, methyl ester	123709	000112-61-8	99
5=	5	12.3487	0.0982	Methyl ricinoleate	132192	000141-24-2	74
6=	6	12.4525	0.1097	10-Nonadecenoic acid, methyl ester	131090	056599-83-8	99
7=	7	13.3449	73.5235	Methyl ricinoleate	132192	000141-24-2	95
8=	8	13.5992	0.9034	Ricinoleic acid	123601	000141-22-0	90
9=	9	13.677	0.1718	9,12-Octadecadienoic acid (Z,Z)-	111993	000060-33-3	90
10=	10	14.0817	0.1181	Methyl ricinoleate	132191	000141-24-2	76
11=	11	14.7147	0.1983	cis-7,cis-11-Hexadecadien-1-yl acetate	112006	052207-99-5	46
12=	12	14.8911	1.4731	8-Dodecenoic acid, 11-hydroxy-, methyl ester, [s-(E)]-	77095	059752-89-5	43
13=	13	14.9378	1.7236	Octadecanoic acid, 9,10-dihydroxy-, methyl ester	142402	001115-01-1	91
14=	14	16.2402	0.0706	1H-Tetrazole-1-ethanol, 5-amino-	12372	015284-29-4	43
15=	15	16.3699	0.2038	9-Octadecenoic acid (Z)-, 2-hydroxy-1-(hydroxymethyl)ethyl ester	155412	003443-84-3	70
16=	16	17.3661	0.1173	2,6,10,14,18,22-Tetracosahexaene, 2,6,10,15,19,23-hexamethyl-, (all-E)-	173571	000111-02-4	99
17=	17	17.802	0.7405	Bis(2,4-dimethylamino)pyrimidine	33889	001076-94-4	38
18=	18	20.5001	0.137	Stigmasterol	173932	000083-48-7	45
19=	19	21.0137	0.1643	Stigmasterol, 22,23-dihydro-	174408	1000214-20-	94

Figure A.3.2.1: Result Summary

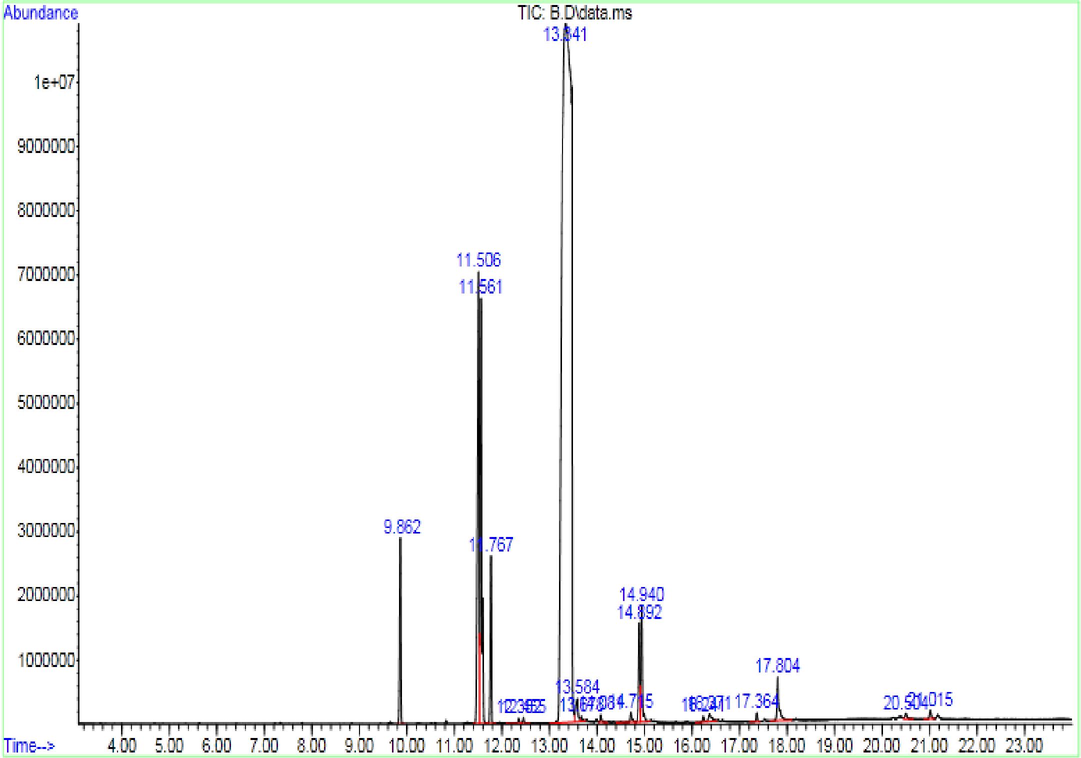
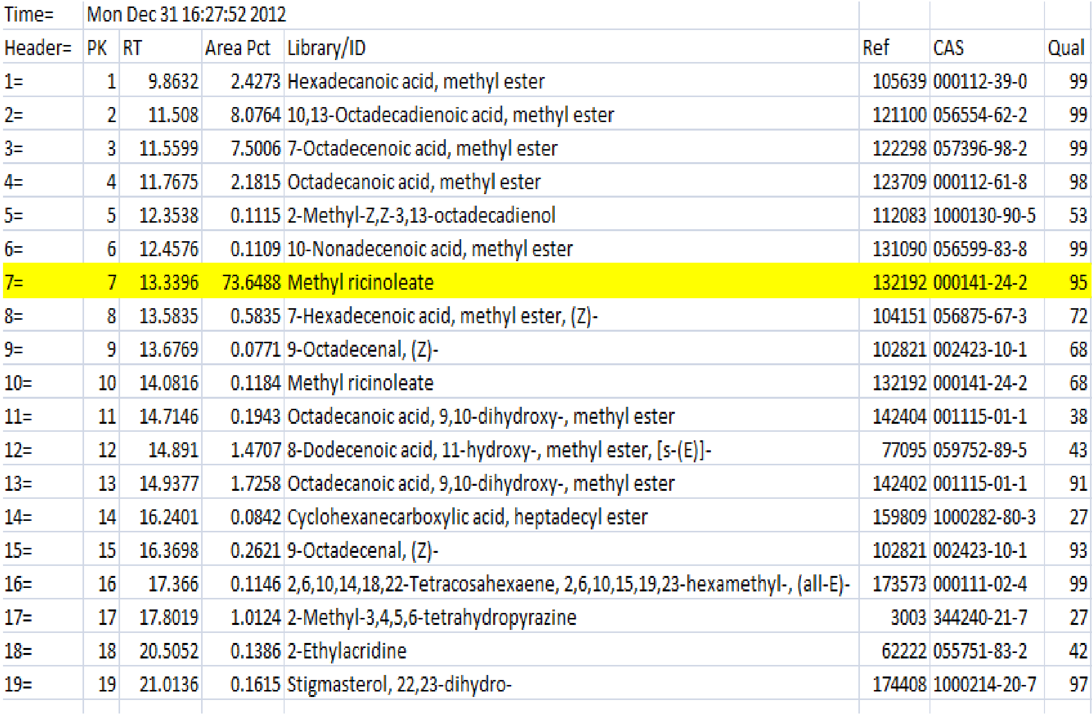


Figure A.3.3: Reaction conditions; 3:1 methanol/oil ratio, 180 min, 1 wt%, 60°C



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2=	2	11.508	8.0764	10,13-Octadecadienoic acid, methyl ester	121100	056554-62-2	99
3=	3	11.5599	7.5006	7-Octadecenoic acid, methyl ester	122298	057396-98-2	99
4=	4	11.7675	2.1815	Octadecanoic acid, methyl ester	123709	000112-61-8	98
5=	5	12.3538	0.1115	2-Methyl-Z,Z-3,13-octadecadienol	112083	1000130-90-5	53
6=	6	12.4576	0.1109	10-Nonadecenoic acid, methyl ester	131090	056599-83-8	99
7=	7	13.3396	73.6488	Methyl ricinoleate	132192	000141-24-2	95
8=	8	13.5835	0.5835	7-Hexadecenoic acid, methyl ester, (Z)-	104151	056875-67-3	72
9=	9	13.6769	0.0771	9-Octadecenal, (Z)-	102821	002423-10-1	68
10=	10	14.0816	0.1184	Methyl ricinoleate	132192	000141-24-2	68
11=	11	14.7146	0.1943	Octadecanoic acid, 9,10-dihydroxy-, methyl ester	142404	001115-01-1	38
12=	12	14.891	1.4707	8-Dodecenoic acid, 11-hydroxy-, methyl ester, [s-(E)]-	77095	059752-89-5	43
13=	13	14.9377	1.7258	Octadecanoic acid, 9,10-dihydroxy-, methyl ester	142402	001115-01-1	91
14=	14	16.2401	0.0842	Cyclohexanecarboxylic acid, heptadecyl ester	159809	1000282-80-3	27
15=	15	16.3698	0.2621	9-Octadecenal, (Z)-	102821	002423-10-1	93
16=	16	17.366	0.1146	2,6,10,14,18,22-Tetracosahexaene, 2,6,10,15,19,23-hexamethyl-, (all-E)-	173573	000111-02-4	99
17=	17	17.8019	1.0124	2-Methyl-3,4,5,6-tetrahydropyrazine	3003	344240-21-7	27
18=	18	20.5052	0.1386	2-Ethylacridine	62222	055751-83-2	42
19=	19	21.0136	0.1615	Stigmasterol, 22,23-dihydro-	174408	1000214-20-7	97

Figure A.3.3.1: Result summary

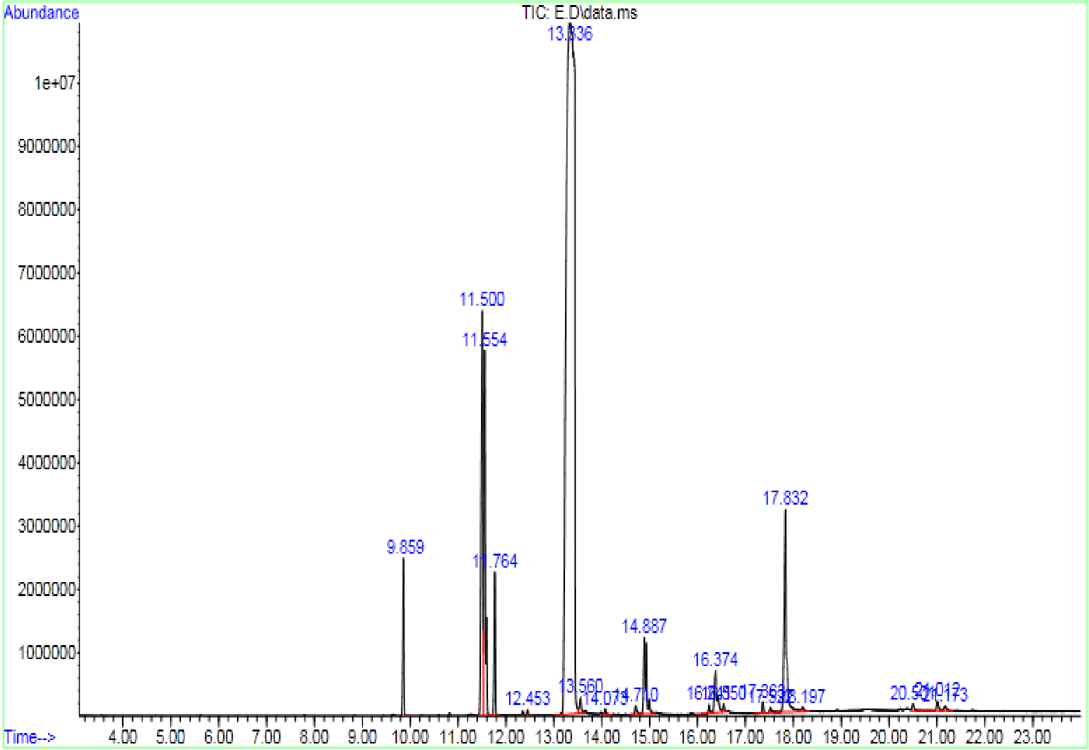
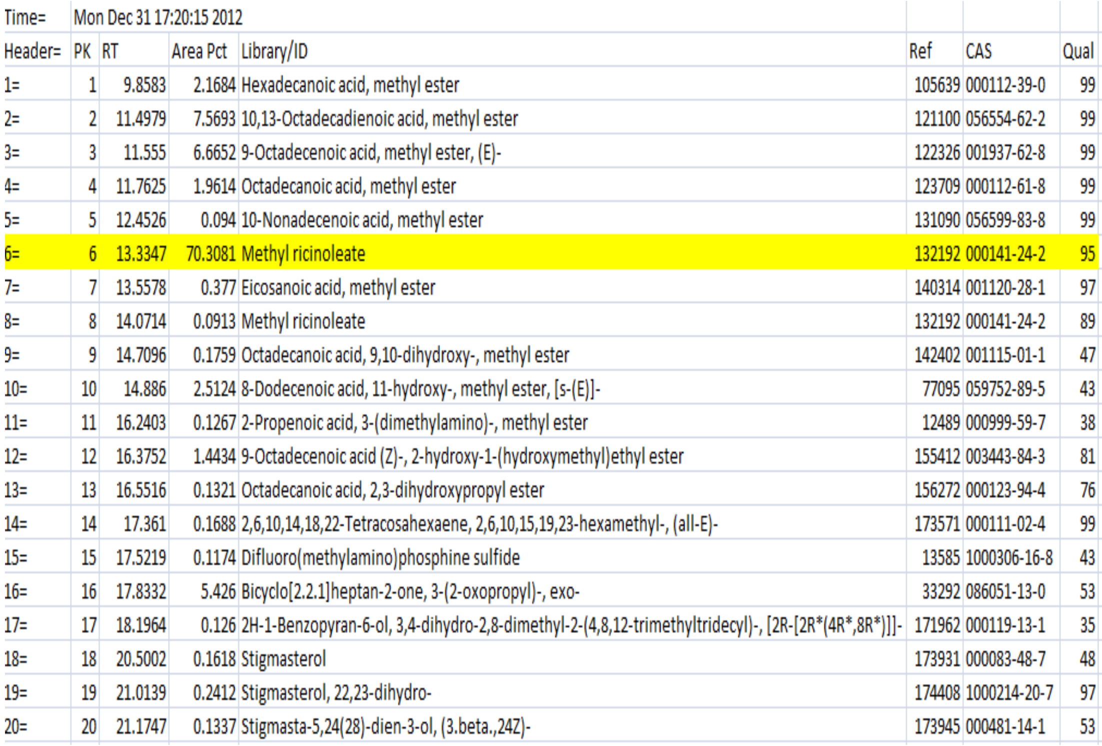


Figure A.3.4: Reaction conditions; 4:1 methanol/oil ratio, 60 min, 1 wt%, 60°C



Time=	Mon Dec 31 17:20:15 2012						
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1=	1	9.8583	2.1684	Hexadecanoic acid, methyl ester	105639	000112-39-0	99
2=	2	11.4979	7.5693	10,13-Octadecadienoic acid, methyl ester	121100	056554-62-2	99
3=	3	11.555	6.6652	9-Octadecenoic acid, methyl ester, (E)-	122326	001937-62-8	99
4=	4	11.7625	1.9614	Octadecanoic acid, methyl ester	123709	000112-61-8	99
5=	5	12.4526	0.094	10-Nonadecenoic acid, methyl ester	131090	056599-83-8	99
6=	6	13.3347	70.3081	Methyl ricinoleate	132192	000141-24-2	95
7=	7	13.5578	0.377	Eicosanoic acid, methyl ester	140314	001120-28-1	97
8=	8	14.0714	0.0913	Methyl ricinoleate	132192	000141-24-2	89
9=	9	14.7096	0.1759	Octadecanoic acid, 9,10-dihydroxy-, methyl ester	142402	001115-01-1	47
10=	10	14.886	2.5124	8-Dodecenoic acid, 11-hydroxy-, methyl ester, [s-(E)]-	77095	059752-89-5	43
11=	11	16.2403	0.1267	2-Propenoic acid, 3-(dimethylamino)-, methyl ester	12489	000999-59-7	38
12=	12	16.3752	1.4434	9-Octadecenoic acid (Z)-, 2-hydroxy-1-(hydroxymethyl)ethyl ester	155412	003443-84-3	81
13=	13	16.5516	0.1321	Octadecanoic acid, 2,3-dihydroxypropyl ester	156272	000123-94-4	76
14=	14	17.361	0.1688	2,6,10,14,18,22-Tetracosahexaene, 2,6,10,15,19,23-hexamethyl-, (all-E)-	173571	000111-02-4	99
15=	15	17.5219	0.1174	Difluoro(methylamino)phosphine sulfide	13585	1000306-16-8	43
16=	16	17.8332	5.426	Bicyclo[2.2.1]heptan-2-one, 3-(2-oxopropyl)-, exo-	33292	086051-13-0	53
17=	17	18.1964	0.126	2H-1-Benzopyran-6-ol, 3,4-dihydro-2,8-dimethyl-2-(4,8,12-trimethyltridecyl)-, [2R-[2R*(4R*,8R*)]]-	171962	000119-13-1	35
18=	18	20.5002	0.1618	Stigmasterol	173931	000083-48-7	48
19=	19	21.0139	0.2412	Stigmasterol, 22,23-dihydro-	174408	1000214-20-7	97
20=	20	21.1747	0.1337	Stigmasta-5,24(28)-dien-3-ol, (3.beta.,24Z)-	173945	000481-14-1	53

Figure A.3.4.1: Result Summary

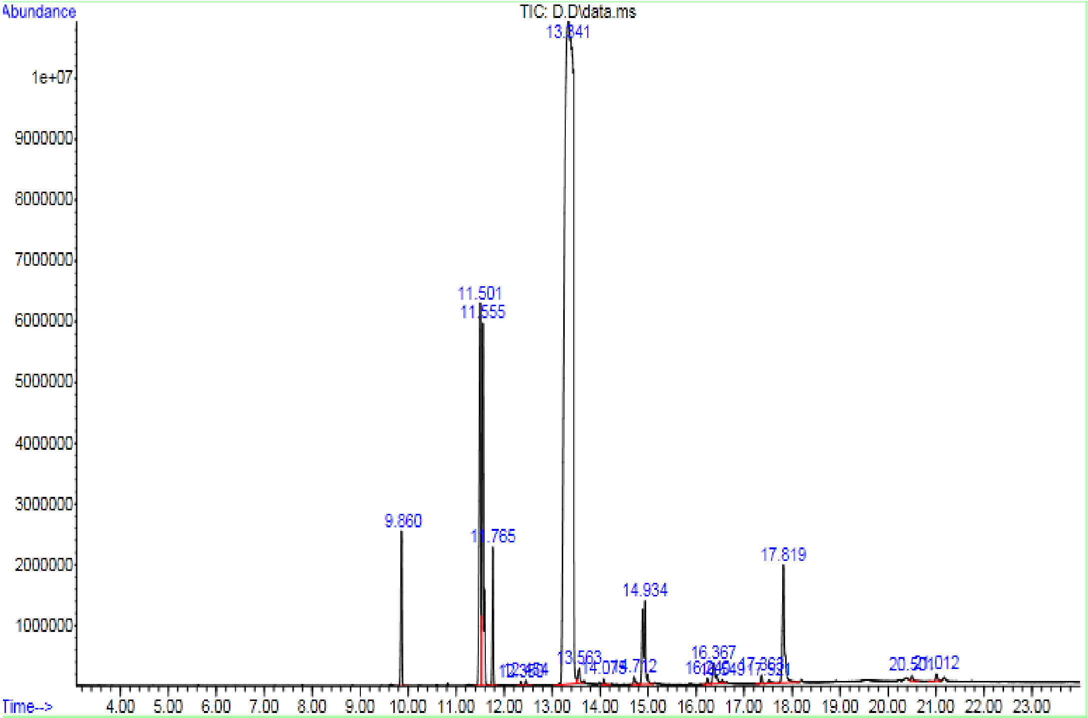
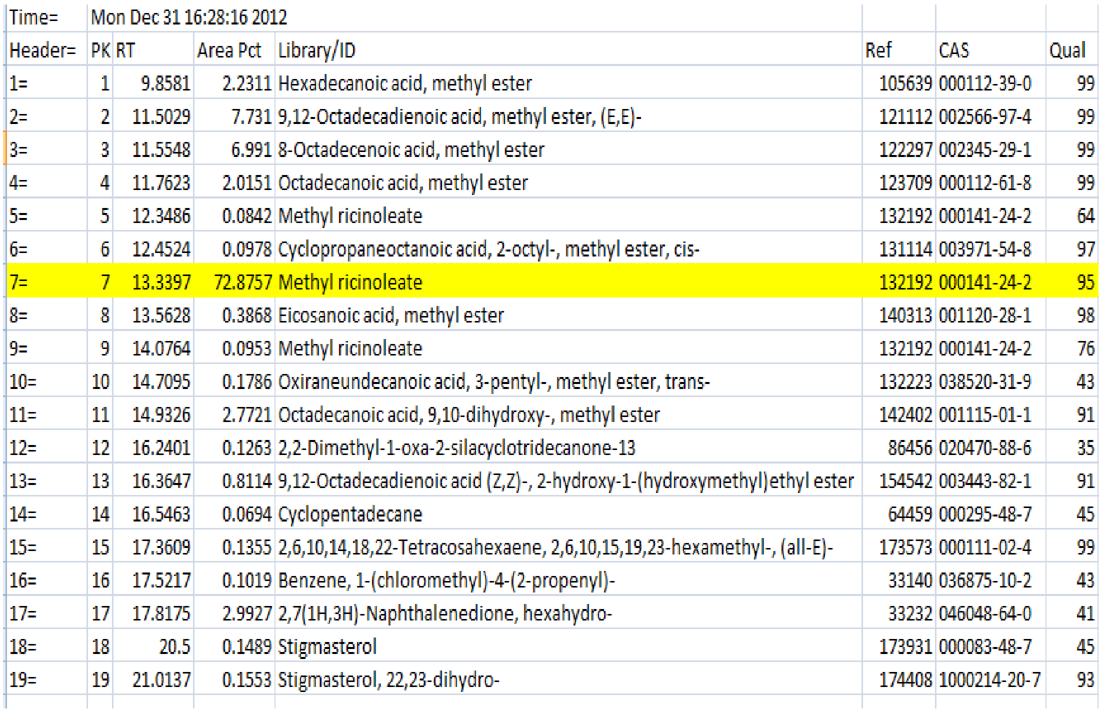


Figure A.3.5: Reaction conditions; 4:1 methanol/oil ratio, 120 min, 1 wt%, 60^{o}C



Time=	Mon Dec 31 16:28:16 2012						
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2=	2	11.5029	7.731	9,12-Octadecadienoic acid, methyl ester, (E,E)-	121112	002566-97-4	99
3=	3	11.5548	6.991	8-Octadecenoic acid, methyl ester	122297	002345-29-1	99
4=	4	11.7623	2.0151	Octadecanoic acid, methyl ester	123709	000112-61-8	99
5=	5	12.3486	0.0842	Methyl ricinoleate	132192	000141-24-2	64
6=	6	12.4524	0.0978	Cyclopropaneoctanoic acid, 2-octyl-, methyl ester, cis-	131114	003971-54-8	97
7=	7	13.3397	72.8757	Methyl ricinoleate	132192	000141-24-2	95
8=	8	13.5628	0.3868	Eicosanoic acid, methyl ester	140313	001120-28-1	98
9=	9	14.0764	0.0953	Methyl ricinoleate	132192	000141-24-2	76
10=	10	14.7095	0.1786	Oxiraneundecanoic acid, 3-pentyl-, methyl ester, trans-	132223	038520-31-9	43
11=	11	14.9326	2.7721	Octadecanoic acid, 9,10-dihydroxy-, methyl ester	142402	001115-01-1	91
12=	12	16.2401	0.1263	2,2-Dimethyl-1-oxa-2-silacyclotridecanone-13	86456	020470-88-6	35
13=	13	16.3647	0.8114	9,12-Octadecadienoic acid (Z,Z)-, 2-hydroxy-1-(hydroxymethyl)ethyl ester	154542	003443-82-1	91
14=	14	16.5463	0.0694	Cyclopentadecane	64459	000295-48-7	45
15=	15	17.3609	0.1355	2,6,10,14,18,22-Tetracosahexaene, 2,6,10,15,19,23-hexamethyl-, (all-E)-	173573	000111-02-4	99
16=	16	17.5217	0.1019	Benzene, 1-(chloromethyl)-4-(2-propenyl)-	33140	036875-10-2	43
17=	17	17.8175	2.9927	2,7(1H,3H)-Naphthalenedione, hexahydro-	33232	046048-64-0	41
18=	18	20.5	0.1489	Stigmasterol	173931	000083-48-7	45
19=	19	21.0137	0.1553	Stigmasterol, 22,23-dihydro-	174408	1000214-20-7	93

Figure A.3.5.1: Result summary

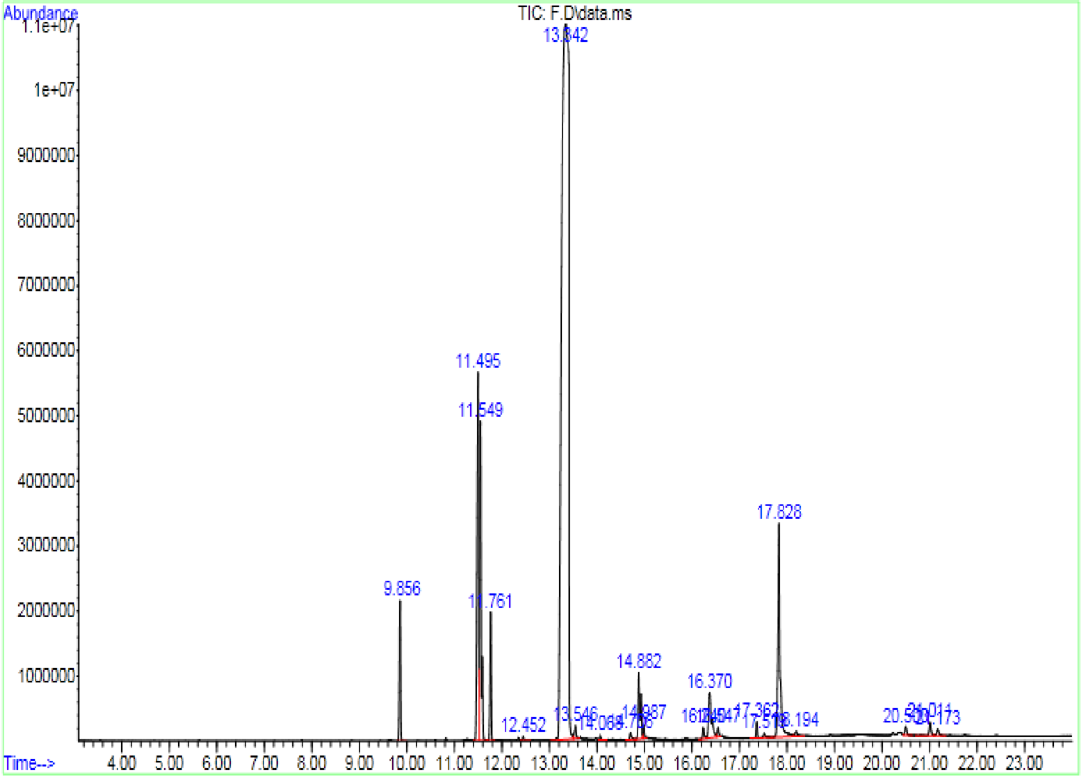
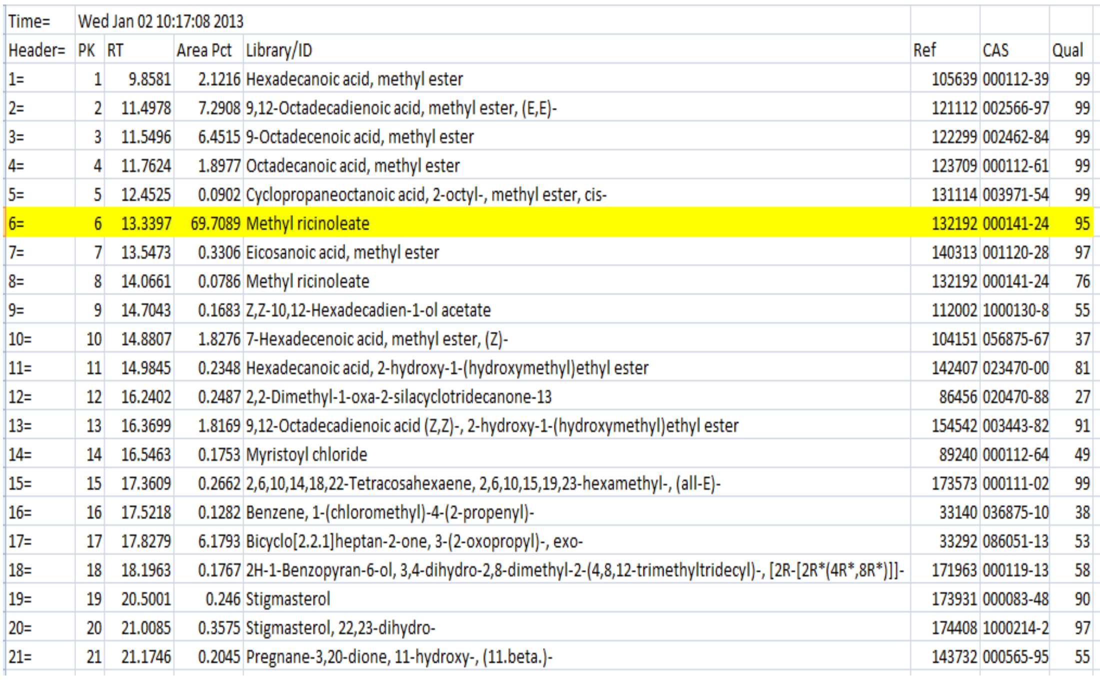


Figure A.3.6: Reaction conditions; 4:1 methanol/oil ratio, 180 min, 1 wt%, 60^{o}C



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2=	2	11.4978	7.2908	9,12-Octadecadienoic acid, methyl ester, (E,E)-	121112	002566-97	99
3=	3	11.5496	6.4515	9-Octadecenoic acid, methyl ester	122299	002462-84	99
4=	4	11.7624	1.8977	Octadecanoic acid, methyl ester	123709	000112-61	99
5=	5	12.4525	0.0902	Cyclopropaneoctanoic acid, 2-octyl-, methyl ester, cis-	131114	003971-54	99
6=	6	13.3397	69.7089	Methyl ricinoleate	132192	000141-24	95
7=	7	13.5473	0.3306	Eicosanoic acid, methyl ester	140313	001120-28	97
8=	8	14.0661	0.0786	Methyl ricinoleate	132192	000141-24	76
9=	9	14.7043	0.1683	Z,Z-10,12-Hexadecadien-1-ol acetate	112002	1000130-8	55
10=	10	14.8807	1.8276	7-Hexadecenoic acid, methyl ester, (Z)-	104151	056875-67	37
11=	11	14.9845	0.2348	Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester	142407	023470-00	81
12=	12	16.2402	0.2487	2,2-Dimethyl-1-oxa-2-silacyclotridecanone-13	86456	020470-88	27
13=	13	16.3699	1.8169	9,12-Octadecadienoic acid (Z,Z)-, 2-hydroxy-1-(hydroxymethyl)ethyl ester	154542	003443-82	91
14=	14	16.5463	0.1753	Myristoyl chloride	89240	000112-64	49
15=	15	17.3609	0.2662	2,6,10,14,18,22-Tetracosahexaene, 2,6,10,15,19,23-hexamethyl-, (all-E)-	173573	000111-02	99
16=	16	17.5218	0.1282	Benzene, 1-(chloromethyl)-4-(2-propenyl)-	33140	036875-10	38
17=	17	17.8279	6.1793	Bicyclo[2.2.1]heptan-2-one, 3-(2-oxopropyl)-, exo-	33292	086051-13	53
18=	18	18.1963	0.1767	2H-1-Benzopyran-6-ol, 3,4-dihydro-2,8-dimethyl-2-(4,8,12-trimethyltridecyl)-, [2R-[2R*(4R*,8R*)]]-	171963	000119-13	58
19=	19	20.5001	0.246	Stigmasterol	173931	000083-48	90
20=	20	21.0085	0.3575	Stigmasterol, 22,23-dihydro-	174408	1000214-2	97
21=	21	21.1746	0.2045	Pregnane-3,20-dione, 11-hydroxy-, (11.beta.)-	143732	000565-95	55

Figure A.3.6.1: Result summary