CHARACTERISATION OF BIODIESEL PRODUCED FROM CASTOR OIL

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CHARACTERISATION OF BIODIESEL PRODUCED FROM CASTOR OIL

MOHAMAD NADZRIE BIN LARY

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering (Gas Technology)

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JANUARY 2014

SUPERVISOR'S DECLARATION

I hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering (Gas Technology).

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I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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Dedication

To my hardworking supervisor, lecturers and staffs, my loving parents, supportive siblings and friends

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Praise to The Almighty for His guidance, I can complete my undergraduate research project on time to pursue my Bachelor Degree. Huge thanks dedicated to my supervisor, Assoc. Prof. Dr. Ghazi Faisal Najmuldeen, and his Master student, Mardhiana binti Ismail for all their guidance, support and advice during completing my research. Special thanks for my loving and supportive family for their support and bless throughout this research being accomplish. Not forget to all of my friends, especially Gas Technology students for all shared knowledge, support and helping hand given to me. Lastly, thanks also to those who helped me directly or indirectly during my research.

ABSTRACT

Ricinus communis L., or also well-known as castor bean plant which belong to *Euphorbiacceae* family, contain 35% - 55% of oil when extracted. This castor oil contained high value of fatty acid or ricinoleic, which make transesterification process become easier due to high solubility in methanol. Castor oil also reported slowly becoming one of valuable chemical feedstocks because of its special characteristic. Besides, production of biodiesel also gained from castor oil.

Biodiesel produced from castor oil has been one of important research for current researcher. Many of them successfully produced biodiesel with several methods and different catalyst as the cheapest method still the major target. This research focus on using calcium oxide (CaO) as the catalyst which is a type of heterogeneous catalyst. Usage of heterogeneous catalyst seem to help a lot in saving the production cost. To ensure the product can be used or not, the produced biodiesel will be characterized and compare with the standards and result from previous researcher on castor oil. ASTM D6751 standards is the reference during the characterisation part take place.

ABSTRAK

Ricinus communis L., atau lebih dikenali sebagai pokok castor yang terdiri daripada kumpulan tumbuhan keluarga *Euphorbiacceae*, mengandungi 35% - 55% minyak apabila di extrak. Minyak castor ini mengandungi asid lemak dan asid ricinoleic yang tinggi, membuatkan proses transesterifikasi lebih mudah kerana kelarutan yang tinggi dalam methanol. Minyak castor juga dilaporkan mula menjadi stok bahan mentah yang berharga disebabkan oleh keistimewaan sifatnya. Malahan, pengeluaran biodiesel juga diperolehi daripada minyak castor.

Biodiesel yang dihasilkan daripada minyak castor telah menjadi salah satu kajian yang penting bagi penyelidik masa kini. Ramai di Antara mereka yang telah Berjaya menghasilkan biodiesel melalui pelbagai kaedah dan pelbagai pemangkin, namun kaedah yang termurah masih menjadi sasaran utama. Kertas kerja ini memfokuskan atas penggunaan kalsium oksida sebagai pemangkin yang merupakan sejenis pemangkin heterogen. Penggunaan pemangkin heterogen membantu dalam penjimatan kos penghasilan. Untuk memastikan hasil penghasilan boleh digunakan, biodiesel yang dihasilkan akan dipastikan ciri-ciri menepati piawai dan dibandingkan dengan hasil penyelidik seblemun ini. Piawaian ASTM D6751 akan digunakan sebagai rujukan semasa pencirian dilakukan.

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CHAPTER 1

INTRODUCTION

1.1 Motivation and problem statement

The World Energy Forum 2012 suggested the fossil-oil would be distinct in less than ten decades. Searching for new and renewable energy is the most essential nowadays in order to retain the usage of fuel-engine equipment and transportation. Biofuel, such as biodiesel is one of the alternative idea to replace fossil fuel in current situation. Biodiesel can be mixed with petro fuel and give lower exhaust emission. In addition, it is very important to have green energy as it could help having better and clean environment. Furthermore, using bio-plant lead to good sustainability because crop can be plant and grow at almost everywhere without having extinction, also the price of biofuel is much cheaper than fossil-based oil.

Castor Bean and Castor Oil

Biodiesel can be produced from various type of vegetable oil. One of it is castor oil which extracted from castor bean. Ricinus communis L. or famously known as castor bean plant is a type of plant that belong to Euphorbiacceae family. This plant originally found in Africa but also could be found wild in the tropical and subtropical countries all around the world. Due to wild conditions of this plant, its well-adapted to arid conditions and anti-cyclonic condition which also able to stand long period of drought (Ferrero, 2006). Nowadays it widely grown on large and wide scale as commercial crop for its oil. The oil content inside the bean were approximately in range from 35% - 55%, depending of the seed and environment of the seed being planted. Handling of this bean must give a great care because fungus could grow on the beans if expose to certain temperature and humidity.

Castor oil is colourless to pale yellow and without any taste or odour. Chemically, it is triglyceride contained approximately 90% of fatty acid or ricinoleic. Others than that, it also contain of oleic and linoleic acids. Ricinoleic acid, a monounsaturated with 18-carbon fatty acid has hydroxyl functional group on the twelfth carbon. Due to this unusual cases make castor oil and ricinoleic acid becoming one of valuable chemical feedstocks (Chakrabarti and Ahmad, 2008). Besides that, biodiesel produced from castor oil is low cost compared to production of biodiesel from other oils regarding to its solvability in alcohol transesterification could occur without usage of many excess heating equipment (Conceicao, et al., 2007).

Biodiesel

Recently, biodiesel getting high demand, and getting higher interest when the production is involving lower and cheaper cost. It define as any diesel equivalent ester produced by transesterification process from biological material which are edible and non-edible oil. Chemically, biodiesel knows as “Free Fatty Acid Methyl Ester” (Sreenivas, 2011). Biodiesel is biodegradable and nontoxic fuel. Forero (2006) conclude in his journal that castor oil biodiesel can be used as petroleum diesel additive that improving in both environmental and flow of the petroleum fuel. In August 10, 1983, about hundreds years ago, Rudolf Diesel first to test peanut oil as fuel for his engine. Biodiesel does not contain any petroleum, but it can be blend with any level of petroleum diesel to produce biodiesel blend (Deshpande, et al., 2012). However, pure biodiesel cannot be injected to diesel engine vehicle and need several modification need to be done to the diesel engine in order fit the requirement to use the pure biodiesel. Furthermore, it also can lead to corrosion in vehicle material and later fuel system blockage, filter clogging, seal failures and deposits at injection pumps. Use in internal combustion could cause engine durability problems. All those problem occurs when we inject pure biodiesel inside the diesel engine vehicles (Atabani, et al., 2012).

Transesterification

For producing biodiesel, transesterification process is one of the most suitable method to be used because castor oil has high viscosity relatively to vegetable oils. Gerpen and Knothe (2005) wrote that there are possible four methods to reduce the high viscosity of vegetable oils to enable their use in common diesel engines without having any operational problems. The four methods are blending with petrodiesel, pyrolysis, microemulsification and transesterification. We are focusing on transesterification process because it was found that up to 85% of ester could be obtained (Chakrabarti and Ahmad, 2008). In the transesterification process, triglyceride component inside the castor oil will react with alcohol with presence of catalyst, then will produced glycerol and methyl ester.

Catalyst

From most of the experiment that has been conducted by previous researcher, same reaction used using homogenous catalyst such as potassium and sodium hydroxide, sodium and potassium alkoxides. Besides, by using those catalyst shows the reaction is faster than acid catalyst such as sulfuric acid, hydrochloric and sulfonic acid (Fukuda et al., 2001; Ma and Hanna, 1999). Although having aimed reaction by using the homogenous catalyst, there main disadvantages of the aforementioned homogeneous catalysts that is the undesirable production of both, glycerol and soap. This will increase the production cost as also the catalysts consumed thus reducing the efficiency of the catalyst (Romero, et. al, 2011). In the other hand, usage of heterogeneous catalyst inside the biodiesel production could save the production cost. Advantages of using heterogeneous catalyst are it does not leave neutralization salts in the glycerol produced and can be retained in the reactor by filtration. Regarding to the circumstances, induction to the heterogeneous catalyst could help reducing the cost compare by using the homogeneous catalyst. Neutralization salt in the glycerol does not leave by the heterogeneous catalyst and retained in the reactor by filtration process. Furthermore, number of separation can be decrease as additional neutralization stage does not required (MacLeod, et al., 2007). In addition, heterogeneous catalyst is less corrosive, and can be used in fixed-bed reactor, that much more safe, cheaper, and more friendly to environment (Dossin, et al., 2006).

Problem Statement

High interest and high demand for biodiesel in the world market has increase the interest among researcher to find the best method for producing the biodiesel. Furthermore, biodiesel with much lower and cheaper cost has been the major target among the researcher as most of investor targeting on much lower cost but high grade biodiesel. Biodiesel itself does not contain any petroleum but can be blend with the petroleum fuel. Several automotive modification will be needed to be done before the pure biodiesel can be used with the automotive engine.

By using castor oil, with considering the current production and plantation of the castor plant, castor has capability to contribute toward production of biodiesel which is renewable energy. This research aiming to produce biodiesel through transesterification reaction with the use of heterogeneous catalyst. Compared to previous research where homogeneous catalyst has been used to enhance the reaction, this research would introduce the use of heterogeneous catalyst because of the price as heterogeneous catalyst is much cheaper than homogeneous catalyst, and efficiency of homogeneous will decrease as the catalyst was consumed by the reaction.

1.2 Objectives

The target of this research are:

- To produce biodiesel from castor oil transesterification using calcium oxide (CaO) catalyst.
- To characterise the biodiesel produced from castor oil.

1.3 Research Scope

The following are the scope of this research:

i) Experimental work on producing biodiesel through transesterification process with heterogeneous catalyst.

ii) Experimental analysis and characterisation analysis of produced biodiesel.

1.4 Main contribution of this work

The following are the contributions of this work:

- Biodiesel as substitute fuel to replace petroleum diesel
- Producing low cost biodiesel

1.5 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides an introduction of the thesis and what will be do along the research paper. This chapter explaining the detail explanation on the selection of castor oil as the main component of the transesterification process, and the origin of the oil. To produce the desired biodiesel, transesterification reaction will be used with the reason of the usage of heterogeneous inside the reaction. The selection of ratio of methanol-catalyst and oil for the transesterification process do affect the result of the produced biodiesel. Besides, the catalyst weight percentage also need to be considered.

Chapter 3 review the research methodology for this experiment. The castor oil will need to undergo transesterification process to produced targeted biodiesel. The transesterification is one of the best method to produce biodiesel from feedstock vegetable oil. To ensure transesterification is run on the best condition, several suggestion used based on suggested by previous researcher. The best of 6:1 molar ratio between methanol-catalyst and oil ratio is used, under system temperature of 60-70 ^{o}C and around 200rpm of stirrer speed. After the reaction is complete, the product will need to be separation using separation funnel, then centrifuge then rotary to remove any excess catalyst, methanol and water vapour during the experiment is being done. Then it will undergo characterisation process. Characterisation is important to determine the specification of the product and contain of the produce biodiesel. The characterisation process is through standard method of ASTM to obtain the result.

Chapter 4 will show the result obtain from the experimental product of produced biodiesel from castor oil. This chapter will discuss the result obtain and comparing to other research result on the production of biodiesel produced from castor oil.

Chapter 5 is the final chapter on the conclusion and the recommendation on this paper, and possible future work that could be done on continuing this research.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

This paper presents the experimental studies of biodiesel transesterification process and its characterization. In the transesterification process, a heterogeneous catalyst which is calcium oxide (CaO) use rather than normal homogeneous catalyst. Mixture of methanol-catalyst and oil will be selected and used the best molar ratio for the transesterification process. Production of this transesterification process will lead to production of biodiesel, an alternative to conventional fossil based diesel (Fjerbaek, et. al., 2008). Production of biodiesel using heterogeneous catalyst is less cost as the catalyst efficiency not decrease in large number as usage of heterogeneous catalyst, and will not require additional neutralization process (Romero, et. al., 2011, MacLeod, et. al., 2007). In this experiment, castor oil will be used in the process. Castor oil obtained from extracted castor bean, which contain large percentage of oil.

2.2 Introduction

This paper presents production of biodiesel produced from castor oil through transesterification process by using CaO as catalyst. The produced biodiesel later being characterise to determine either the produced biodiesel is according to the standards.

2.3 Selection of Castor Oil

Castor oil is a product obtained from the extraction of castor bean or also known as castor seed. Scientifically, castor bean named as Ricinus communis L. is a type of plant that belong to Euphorbiacceae family. Castor oil is a type of vegetable oil gained from planted crop and currently widely planted at some countries. The table 2.3-1 shows different type of oil producing crop and their yield per acre. The advantages of using vegetable oil as sources of fuel are ready availability, renewability and nature-portability. Despite of the advantages, there are also disadvantages such as higher viscosity, the reactivity of the unsaturated carbon chained and lower value of volatility. These disadvantages can be overcome with several methods during the process of producing the biodiesel itself.

Figure 2-3-1: Castor plant

Figure 2-3-2: Castor bean

Table 2.3-1: Edible and non-edible oil producing crops and their yield

Oil Producing Crop/Plant	Yield (Lb Oil/Acre)
Palm	4585
Coconut	2072
Sunflower	734
Soybean	344
Cottonseed	250
Jatropha	1458
Castor bean	1089
Rubber seed	199

The oil contain from this bean approximately in range of 35% - 55%. This percentage of oil can be consider as high value in number as the oil is extracted from bean itself, depending on the environment the seed being planted. With high contain of ricinoleic acid, a monounsaturated with 18-carbon fatty acid and hydroxyl group on the twelfth carbon, up to 90%, this make the castor oil become one of most valuable chemical feedstocks nowadays (Chakrabarti and Ahmad, 2008).

Table 2.3-2: Fatty acid composition of castor oil (Conceicao, et. al., 2007)

Fatty Acid	Composition (%)
Ricinoleic Acid	90.2
Linoleic Acid	4.4
Oleic Acid	2.8
Estearic Acid	0.9
Palmitic Acid	0.7
Dihidroxiestrearic Acid	0.5
Licosanoic Acid	0.3
Linoleic Acid	0.2

Based on table 2.3-2, Conceicao, et. al., show that ricinoleic acid is the highest acid contain in the castor oil. Other acid such as linoleic, oleic, estearic, palmitic, dihidroxiestrearic, licosanoic and linoleic only contain less than 5% of the total composition inside the castor.

By containing high value of ricinoleic acid and hydroxyl group, is another reason why castor oil has high viscosity and density (Scholz and da Silva, 2008). Researcher start focus to castor oil due on advantages given by the oil itself. Transesterification of castor oil is characterized by its stability and solubility which affect the reaction. Furthermore, this oil favour the transesterification as it soluble in the methanol. Results obtained by previous researcher showed that temperature slightly affect the reaction, but the catalyst amount affect more specifically (de Lima de Silva et. al., 2009).

Since almost more than 95% of biodiesel create from edible oil, as castor is one type oil plant which produce edible oil, converting these type of oil into biodiesel also mean creating new alternative automotive fuel. Although this is one of positive to create better future, this also will bring negative issue to the earth as when the large-production of edible could bring global imbalance between the food supply and market demand. People more tend to compete to joint into the market demand rather than food supply because more profit could be gain in this situation. More destruction and deforestation could happen and the forest being cleared to create oil crop plantation purpose. Due to this issue can bring us into depletion of edible oil supply around the world in exchange of biodiesel production as the substitute fuel (Deligiannis, et. al).

2.4 Biodiesel and Transesterification Process

Biodiesel is one type biofuel which getting high demand, due to depleting volume of fossil fuel left inside the earth. Recently, the prices of crude oil keep hiking, and environmental concern make biodiesel became major focus to many researcher. Biodiesel can be produced from renewable biological sources such as vegetable oil and animal fats. Rudolf Diesel was the first one to test peanut oil as fuel for his engine about hundred years ago. In order to produce biodiesel, there are four methods to reduce the high viscosity of vegetable oils that are blending with petrodiesel, pyrolysis, microemulsification and transesterification (Gerpen and Knothe, 2005). Biodiesel can be produced from various type of vegetable oil such as palm oil, coconut oil, sunflower, soybean, rubber, etc. Special interest shown to vegetable oil because it reduce particulate emission relatively compare to petroleum diesel (Sreenivas, et. al., 2011). Petroleum diesel or diesel engine is one of major air pollutant. This could affect the ozone layer and give the greenhouse effect. Carbon monoxide produced from exhaust emission could lead to hypoxia and causes further health effect. Hydrocarbon emission are carcinogenic, odorants and irritant, while nitrogen oxide could cause pulmonary diseases.

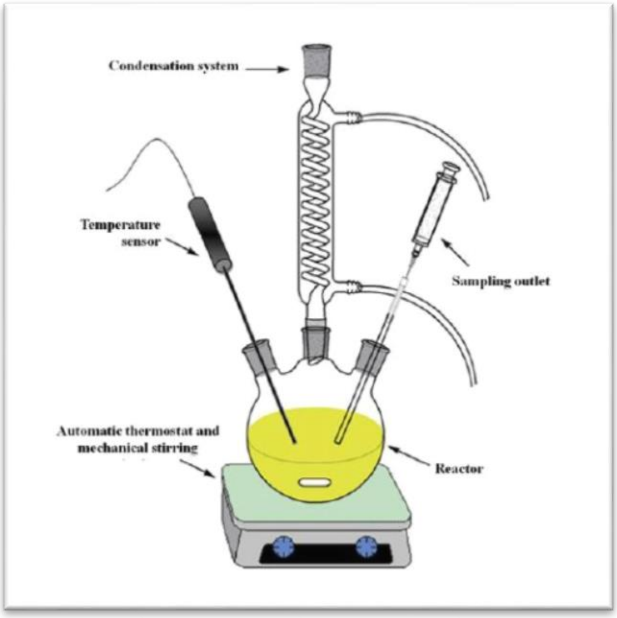

Figure 0-3: Illustration of apparatus set-up of experimental transesterification system (Encinar, et. al., 2010)

In this research, transesterification method will be used as the reaction lead to production of biodiesel. Commonly, this process prepared product of methyl esters because the methanol is the cheapest among other type of alcohol. Basically, the general reaction of this reaction is when the oil is mixed with alcohol, then it will produce alkyl ester and glycerol. The alkyl ester is the desired product which is biodiesel itself. Generally, transesterification process can be done with help of either acid or base catalyst.

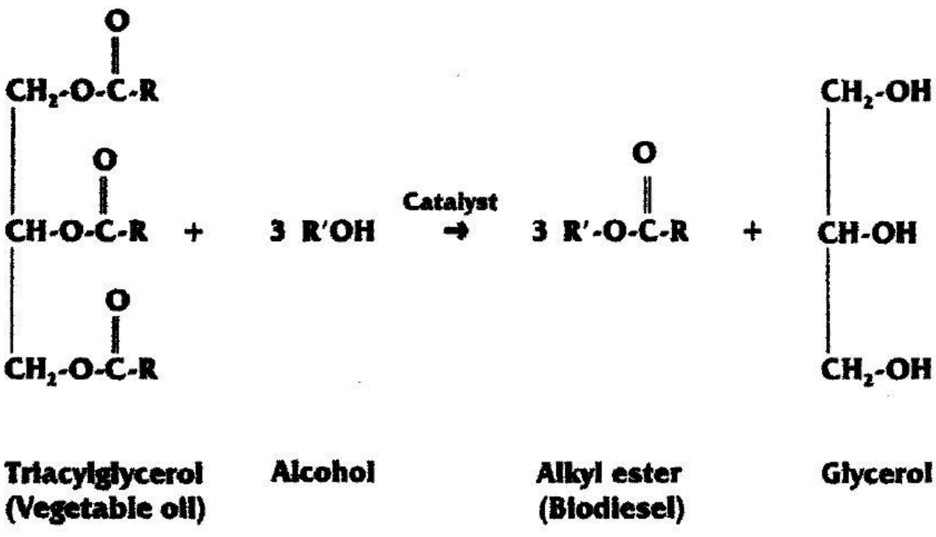

Figure 2-4-4: Transesterification process reaction

2.5 Catalyst

Presence of catalyst during the transesterification process is very essential to increase the rate of reaction. Currently, most of biodiesel produced are using homogeneous catalyst. The fact that homogeneous catalyst cannot be reused is the major disadvantage and reduce the efficiency of the transesterification process. Due to this problem, an addition and further washing stage need to imply, where an additional cost will be needed from the production cost. An approach by using heterogeneous has been done, but despite of all effort, the heterogeneous catalyst for the biodiesel production still have not use at industry level yet. This research will introduce the usage of a type of heterogeneous catalyst which is calcium oxide (CaO). The heterogeneous acid and basic catalyst can be classified as Bronsted or Lewis catalysts, where its character will determine the transesterification reaction rate (Romero et al., 2011). Various research has been done determined that different catalyst used will need different parameter such as catalyst weight and temperature, which affect the final result of the experiment and the production of biodiesel.

2.6 Characterisation

To make sure the product can be use and blend normally, it must be characterise and follow the standards. The importance of characterisation is to determine contain and the specification of the oil produced. There are a lot of standard set by the standards council and almost every country have their own standards. ASTM D6751 has been choose to be reference in this thesis. In the ASTM D6751 standards, several specification are being highlighted to ensure the produced biodiesel can be use and blend with petrodiesel. In this thesis, only several major specification highlighted due to time constraint and based on the availability of the test equipment inside the laboratory.

Figure 2-6-5: Table of ASTM D6751 standards

Biodiesel Standards		USA
Specification		ASTM D 6751-07b
Applies to		FAAE
Density 15°C	g/cm^3	
Viscosity 40°C	mm^2/s	1.9-6.0
Distillation	% @ °C	90%,360°C
Flashpoint (Fp)	°C	93 min
CFPP	°C	
Cloud point	°C	* report
Sulphur	mg/kg	15 max
CCR 100%	%mass	0.05 max
Carbon residue (10%dist.residue)	%mass	
Sulphated ash	%mass	0.02 max
Oxid ash	%mass	
Water	mg/kg	500 max
Total contamination	mg/kg	
Cu corrosion max	3h/50°C	3
Oxidation stability	hrs;110°C	3 hours min
Cetane number		47 min
Acid value	mgKOH /g	0.5 max
Methanol	%mass	0.2 max or Fp <130°C
Ester content	%mass	
Monoglyceride	%mass	
Diglyceride	%mass	
Triglyceride	%mass	
Free glycerol	%mass	0.02 max
Total glycerol	%mass	0.24 max
Iodine value		
Linolenic acid ME	%mass	
C(x:4) & greater unsaturated esters	%mass	
Phosphorus	mg/kg	10 max
Alkalinity	mg/kg	
Gp I metals (Na,K)	mg/kg	5 max
GpII metals (Ca,Mg)	mg/kg	5 max
PAHs	%mass	
Lubricity / wear	μm at 60°C	

2.7 Summary

This thesis will proved that the usage of heterogeneous catalyst during transesterification process will produce biodiesel according to standards. Besides, castor oil also can be a major source in producing biodiesel, as substitute for petrofuel in the future.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Overview

In this thesis, transesterification process is the major process use in the experiment. The ratio of methanol-catalyst and oil used is 6:1 ratio, as be found the best ratio suggested in producing castor oil. The reaction will be done in a batch reactor for several hours, then later separated in a separation funnel. The unused catalyst will later be removed and oil will be centrifuged before rotary to ensure the biodiesel produced are free from any unwanted component and only pure biodiesel will be kept.

3.2 Introduction

In this experiment, the best value for the methanol-catalyst and oil ratio will be obtained. The important to find the exact ratio is to maximize the efficiency of the process. The high efficiency of the process means the more to perfect process we could obtained from the experiment and faster the reaction will be react. To run in small scale experimental test, the raw feedstock which is castor oil will be mix with the mixture of methanol and catalyst inside a reactor, then being left for couple of hours to ensure the reaction is completely react. When the reaction complete, the product will be left in a separation funnel for a night to separate the catalyst and produced oil. After the separation, the oil centrifuged to remove any excess catalyst inside the oil then later rotary to remove any excess methanol or water vapour.

3.3 *Chemicals*

Chemicals use in this study will be obtained from University Malaysia Pahang Chemical Engineering Laboratory. Alcohol that will be used for the transesterification process is methanol, while the catalyst that is calcium oxide also will be gained from the laboratory.

3.4 *Castor Oil*

Castor oil is a type of oil can be get by extracting the castor bean. Due to time constraint based on provided time on conducting this experiment, castor oil will be bought from the market to save time, and the grade of castor oil used was only technical grade oil, not purified castor oil.

3.5 *Production of Biodiesel through Transesterification Reaction*

The transesterification process of this experiment was done by using 6:1 methanol-catalyst and oil ratio. This ratio proven as the best ratio in producing biodiesel from vegetable oil feedstock. The feedstock oil used in this experiment is castor oil. Castor oil is one type of oil which very viscos due to high number of carbon chain. From 6:1 methanol-catalyst and oil molar ratio, the volume of castor oil, methanol and catalyst used being calculated. The catalyst used is only 1% weight of total mass of methanol and castor oil.

The reactor used in this experiment is round glass reactor, attach with thermometer to ensure inside reactor temperature and stirrer. This reactor is set-up in a fume hood, due to reactive material which was methanol is being used in this experiment. The oil inserted into the reactor with stirrer speed of 200rpm and the reactor was heated up to 100^{o}C to remove and excess water or vapour inside the oil because the oil used in this experiment was technical oil, and the oil was kept inside air-conditioning room, considering the cold air will cause production of water inside the oil storage. After the oil heated to remove the excess water, the methanol and catalyst mixed to obtained methanol-catalyst mixture before pour into the reactor. The stirrer speed was maintain at 200rpm while the reaction temperature was maintain at 65-68^{o}C. Then the reaction left for minimum of 2(two) hours to ensure complete reaction between the mixture of methanol-catalyst and oil completely react.

After the reaction completed, the product will be inserted into separation funnel, then left for minimum of 12 hours, or at the best of 24 hours to separate the unreacted catalyst and biodiesel.

Figure 3.5-1: Separation of mixture catalyst and biodiesel

After the catalyst removed, the biodiesel and some mixture of biodiesel-catalyst will be centrifuged at speed of 5000rpm for 7-10 minutes. The purpose to centrifuge the biodiesel and mixture of biodiesel-catalyst was to completely remove the catalyst from the biodiesel to obtain only biodiesel product at the end. After centrifuge process, the biodiesel will enter last stage, inserted into the rotary evaporator. The biodiesel was rotary at system temperature of 95ºC and speed of 200rpm to remove any excess methanol and water inside the biodiesel to obtain only pure biodiesel at the end before getting characterise. The characterisation of biodiesel obtain will be discuss at the next chapter.

Figure 3.5-2: Rotary evaporator system to remove excess methanol and water vapour

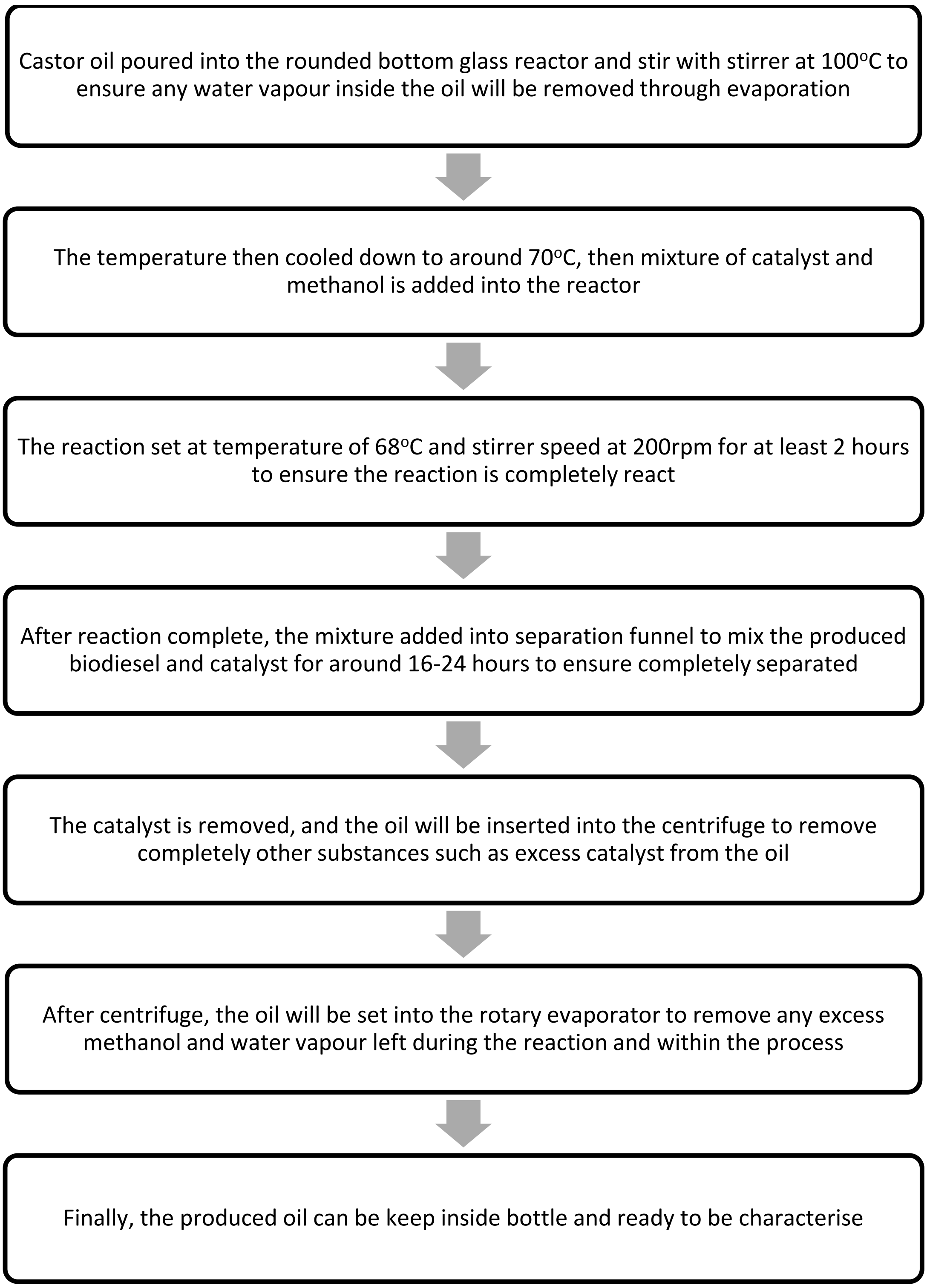

Figure 03.5-3: Flowchart for production of biodiesel with castor oil

3.6 Characterisation of Biodiesel

The characterisation need to be done in proper way to obtain best result. The result are best taken with their average value to ensure the value is consistent with best value obtain. The biodiesel produce will be inspected by visual appearance, acid value/acid number using Metrohm 785 DMP Titrino with 728 Stirrer, Acid Number Potentiometric Titrator, kinematic viscosity at 40^{o}C using Polystat Temperature Controller with Bath Vessel, Calibrated Viscometer Cannon-Fenske Routine size 350 and stopwatch, cloud point using Koehler Instrument, Cloud and Pour Point Apparatus, flash point using Petrotest PM4, Flash Point Tester, density using Kyoto Electronics DA-130N, Density/ Specific Gravity Meter, and component and acid contain Gas Chromatography – Mass Spectrometer.

3.6.1 Acid Value

The acid value will be inspected by using the Metrohm 785 DMP Titrino with 728 Stirrer.

Figure 3.6-4: Acid Number Potentiometric Titrator

The biodiesel will be weigh then diluted in 50 mL of ethanol inside a beaker then stir using magnetic stirrer above the 728 Stirrer. The mixture will be mix for about 10 minutes to ensure it become homogeneous. Acid Number (AN) mode will be recall from the memory, then by entering the weight of the weigh biodiesel from the beginning, the test will begin until EP1 mode ended. The AN will be obtain directly from the system with the amount of KOH being titrated. To ensure the result are correct, the acid number also can be calculated manually by using equation:

$$Acid\ Value = \frac{mL\ KOH\ \times N\ \times 56.1}{\frac{w}{t}\, of\ sample\ in\ grams}$$

N is the normality of the titrant, depending of the sample weight.

3.6.2 Kinematic Viscosity

The kinematic viscosity of an oil must be consider as important specification in producing biodiesel and also in the later stage of blending. The kinematic viscosity at 40^{o}C using Polystat Temperature Controller with Bath Vessel, Calibrated Viscometer Cannon-Fenske Routine size 350 and stopwatch.

Figure 3.6-5: Kinematic Viscosity tester

The produced biodiesel will be pour into the Cannon Fenske tube then dip inside the jar at 40^{o}C for a few minutes to ensure the oil temperature is stable at 40^{o}C. Once the oil heated for few minutes, the oil will be pull up to the above upper level mark, the release back the pressure. The stopwatch will start as the oil reach the first upper mark then stop when reach the lower mark. To calculate the kinematic viscosity, the time will be added into the formula as stated below:

$$Kinematic\ Viscosity\ \left(\frac{mm^2}{s}\right) = efflux\ time\ \times viscosity\ constant$$

3.6.3 *Cloud Point*

The cloud point value tested using the Koehler Instrument Cloud and Pour Point Apparatus. Only cloud point obtain from this experiment and pour point still have not appeared after few hours. The experiment cannot run much longer due to time limit on using certain apparatus inside the laboratory.

Figure 3.6-6: Cloud and Pour Point Apparatus

3.6.4 Flash Point

The flash point is the lowest temperature at which fuel emits enough vapours to ignite. Biodiesel have high flash point, while normal conventional diesel has much lower than biodiesel. The flash point was tested using the flash point tester, Petrotest PM4 in a closed cup test.

Figure 3.6-7: Petrotest PM4 flash point tester

3.6.5 Density

Density is density of component compared to the density of water, with unit of weight per unit volume. Density is very important especially in later stage as the density needed to calculate the conversion and the viscosity properties. The density of the produced biodiesel inspected using the Kyoto Electronics DA-130N, Density/ Specific Gravity Meter. The density function mode selected from the menu with unit of g/m^3 before the sample suck into the apparatus to get the reading of the sample. The sample then flush and the reading taken again to obtain the average density reading of the sample.

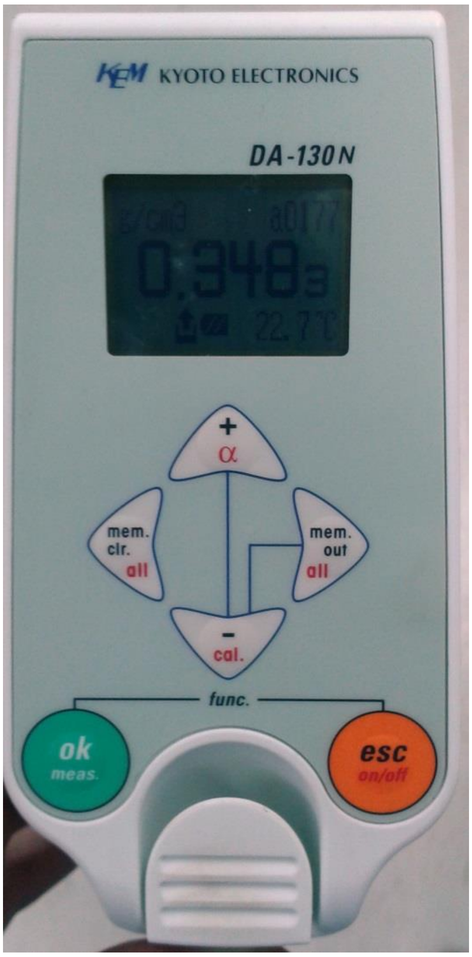

Figure 3.6-8: Kyoto Electronics DA-130N, Density/ Specific Gravity Meter

3.7 Summary

The biodiesel produced based from transesterification process of 6:1 molar ratio of methanol-catalyst and oil. The mixture than reacted inside the reactor, then separated and centrifuged before getting rotary, where the pure biodiesel will produced at the end. To obtain only pure biodiesel is very important to ensure best quality of biodiesel is produced before being characterise to know the specification of the biodiesel.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Overview

This chapter will discuss the result of the characterisation of biodiesel produced from castor oil through the transesterification process earlier. From the result, the quality of the produced oil can be determine. Furthermore, based on the result also can determine exactly either the experiment has gone through correct process and experiment as the targeted production or not. This experiment has shown successful product of biodiesel has been obtain, and the quality is based on biodiesel characteristic that has been done. The oil can later then submitted to other party to continue and test the oil for further blending process before can approve as automotive oil to be used in the automotive engines.

4.2 Results and Discussion

The biodiesel obtained produced from castor oil through transesterification process by using molar ratio of 6:1, methanol-catalyst and oil molar ratio. To ensure the product of best quality biodiesel produce, almost half of the reactor must be filled in with the combination of methanol-catalyst and oil based on calculated ratio. When the reactor vessel contain less than half of the mixture, high possibility of the reaction will not completely reaction will happen. This because of the consideration of the stirrer effect with the temperature inside the vessel and the heat supply outside the reactor. Table 4.2-1 show the result based on the average value tested based on characterisation using the specific equipment for testing certain specification.

Table 4.2-1: Comparison of Critical Parameters between ASTM D6751 Standards, Biodiesel Report (Sanford, et. al., (2009)) and Experimental Results

Properties	Units	ASTM D6751	Biodiesel Report (Sanford, et. al. (2009))	Experimental Results
Visual Appearance	-	-	Clear (1)*	Clear (1)*
Flashpoint (Closed Cup)	^{o}C	93 min	>160	110
Cloud Point	^{o}C	*report	-13.4	-5
Acid Value/ Acid Number	mmKOH/g	0.50 max	0.996	0.26
Density	g/m^3	-	0.8990	0.9568
Kinematic Viscosity at $40^{o}C$	mm^2/s	1.9 – 6.0	15.250	59.2779

Based on six (6) properties discuss in table 4.2-1, the experimental results show that the result obtain qualified with the ASTM standard except the kinematic viscosity at $40^{o}C$. This was expected as the castor oil molecular compound consist of carbon 18 (C-18) molecule which show that the oil is very viscos. When the molecule is consist of much higher number of carbon molecule, more higher the viscosity of the oil will be obtain. The biodiesel report column is an example of experimental result on produced biodiesel from castor oil by Sanford, et. al., in their paper. The result are much more different from the experimental result because the experiment was done by using technical grade castor oil, compare by experiment done by Stanford was done by using refined castor oil. Refined castor is much better compare to technical grade because the oil has been refined from technical grade and any side substances has been removed, where only pure, better castor oil produced. But compare with the ASTM standard, the technical grade castor oil gave the nearest to the biodiesel B-100 standard.

In other research by Conceicao et. al. about castor oil biodiesel, it is shown that castor oil have high viscosity, and reduced after undergo the transesterification process. The density is around 0.9 value and the flash point is 120^{o}C for the biodiesel.

Table 4.2-2: Physical-chemistry properties of diesel, castor oil and biodiesel (Conceicao, el. al., 2007)

Analyses	Castor oil	Biodiesel	Diesel
Viscosity (mm^2/s)	239.39	13.75	3.2
Sulfur (%)	0	0.0001	0.20
Density 15^{o}C (g/cm^3)	0.9573	0.9245	0.8503
Density 20^{o}C (g/cm^3)	0.9584	0.9245	0.8465
ASTM Colour	Yellow	Yellow	Red
Flash Point (^{o}C)	310	120	37
Copper Corrosion	1	1	1

From table 4.2-2, research by Conceicao, et. al., proved that castor oil is very viscos oil at viscosity of 239.39 mm^2/s before being processed into biodiesel through transesterification process. Comparing this research with the experimental result on table 4.2-1, the viscosity is around 59.2779 mm^2/s while Conceicao obtain at 13.75 mm^2/s. The colour obtain was also yellow, and the flash point obtain for 110^{o}C from the experimental result and 120^{o}C from the Conceicao experiment. Standford and Conceicao both obtain very low viscosity for biodiesel produced possibly because of the use of refined castor oil in the experiment. Refined castor will give much better result as the oil has been refined compared to the technical oil.

The produced biodiesel also inserted into the GC to check the molecule contain inside it. The picture result obtain from the GC-MS show in the figure 4.2-1:

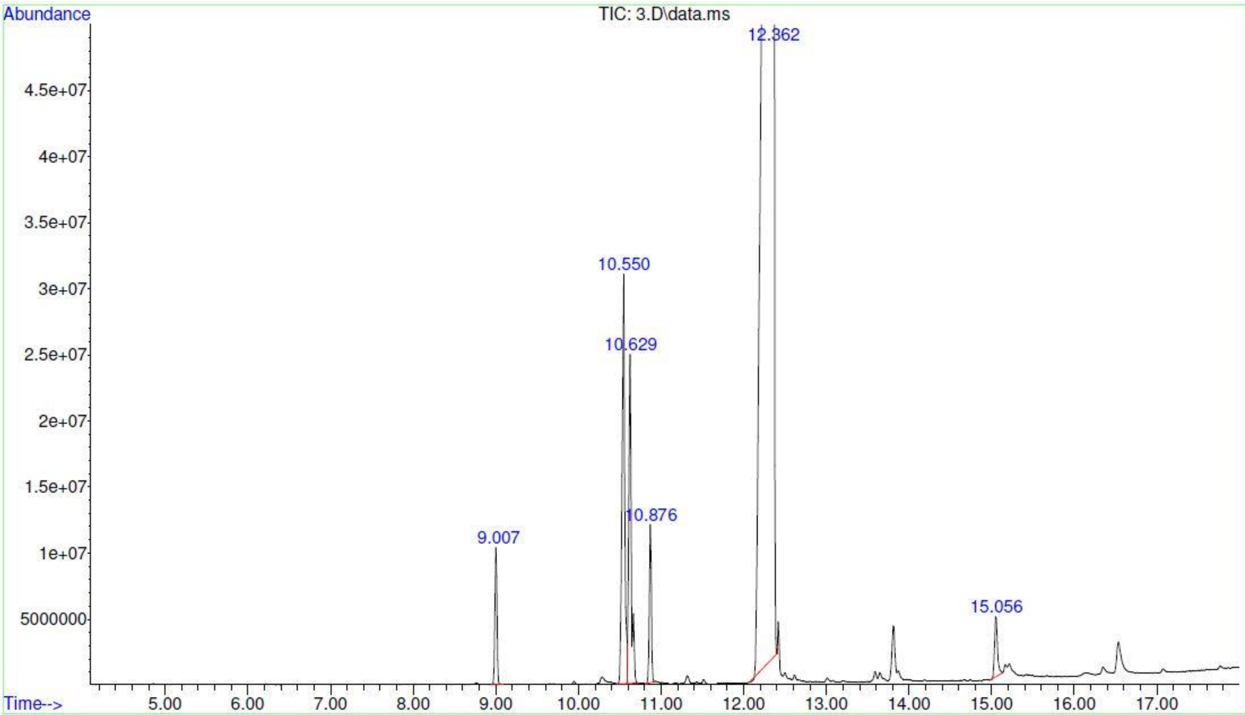

Figure 4.2-1: Result obtain from Gas Chromatography for produced biodiesel

The biodiesel was injected into the vial with mixture of 10μL if biodiesel with 900μL of hexane. The column temperature was program at 120°C with increment of 3°C/minute for 57 min where the injector and detector temperature were set at 260°C and 280°C respectively. Separation was performed on capillary DB-5MS (30m x 0.32mm, 0.25μm of film thickness). The carrier gas of helium flow at flow rate of 1.5 mL/minute. The sample volume 1.0μL inject using a split mode, with split ratio of 1:10.

At the first peak, retention time of 9.011, with area of 1.48%, Hexadecanoic acid (methyl ester) and Pentadecanoic acid (14-methyl-, methyl ester). At the second retention time of 10.550, area of 5.81%, component of 10, 13-Octadecadienoic acid (methyl ester), 9, 12-Octadecanoic acid (methyl ester), and 11, 14-Octadecanoic acid (methyl ester) found. Third peak at retention time of 10.624, area 4.53%, component found were 8-Octadecenoic acid (methyl ester), 9-Octadecenoic acid (methyl ester) and 7-Octadecenoic acid (methyl ester). For the fourth peak, retention time 10.881 and area 1.72%, Octadecanoic acid found. At retention time 12.365, area 85.52% for the fifth peak, Methyl ricinoleate, 9-Octadecenoic acid (12-hydroxy-, methyl ester) and Oxacyclododecan-2-one. At the last peak with retention time of 15.057 and area of 0.94%, Cyclohexanecarxylic (undec-10-enyl ester), Hexanedioic acid (bis (2-methylpropyl)) ester, and 1H-Imidazole-2-methanol.

As determine by the GC test, the acid contain inside the biodiesel has been found and can be summarise as follow:

- Hexadecanoic Acid
- Pentadecanoic Acid
- Octadecanoic Acid

As this is only the GC-MS test, only the component contain inside the biodiesel can be determine.

Several comparison on the castor oil biodiesel have been done, and almost each of the detail was different from each other. One of major cause for this differences between results was the sources of castor oil itself. Castor oil can come from different grade as the technical grade and refined grade. Technical grade is roughly factory produce castor oil, while refined castor is the best oil as the oil has been refined to the best condition and other unwanted substances removed from the original oil. Castor oil also obtained from different place and different countries whom produced the castor. The plantation condition of castor plant also affect the plant quality. From the quality of soil in different countries, seeding rate, use of fertilizer and pesticide are the factor that also affect the plant quality then the oil quality.

4.3 Summary

Based on the result obtain on the experiment test, it can be conclude that the biodiesel produced from castor oil with using the calcium oxide (CaO) catalyst, which is a type of heterogeneous catalyst was successful. The result on the characterisation is discuss earlier in this chapter and can be used for further research on this experiment.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This project focus on the production of biodiesel by transesterification process with the usage of heterogeneous catalyst, and castor oil as the main component for the reaction. The produced biodiesel was not fit with the standard because the castor oil use was only technical grade oil. Normally, for producing best quality of biodiesel, refined feedstock oil will be used. Besides that, the biodiesel produced from different type of vegetable oil will also probably will not 100% fit to the B-100 standards, due to different carbon chain between all type of the vegetable oil. If the vegetable oil contain high number of chain carbon, the oil will be much more viscos compare to other oil.

5.2 Future work

As the product obtained from this research which is the biodiesel, further research can be done by using refined castor oil as the feedstock. As per research which has been done in this paper and previous paper, the best molar ratio for producing biodiesel from castor oil was 6:1 methanol to oil ratio. By using refined castor oil as the feedstock, we could get better performance of oil and better specification of produced biodiesel will be obtained.

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APPENDICES A

Example calculation for the biodiesel production:

Reactor: V = 3L

V_{castor} = 1000mL

n_{castor} = ρ_{castor} x V_{castor} / MW_{castor}
= 1.0784 mol

Based on 6:1 ratio,

$n_{methanol}$ = 6.4704 mol

$V_{methanol}$ = $n_{methanol}$ x $MW_{methanol}$ / $\rho_{methanol}$
= 262 mL

Mass catalyst = 1% of total mass of methanol and castor
= 11.68g

Therefore;

1000mL of castor oil, 262mL of methanol, and 11.68g of Calcium Oxide used in one of the experiment, and all experiment is based on same method of calculation.

APPENDICES B

Result of GC-MS

Pk#	RT	Area%	Library/ID	Ref#	CAS#	Qual
1	9.011	1.48	C:\Database\NIST05a.L			
			Hexadecanoic acid, methyl ester	105639	000112-39-0	99
			Pentadecanoic acid, 14-methyl-, methyl ester	105662	005129-60-2	97
			Hexadecanoic acid, methyl ester	105646	000112-39-0	94
2	10.550	5.81	C:\Database\NIST05a.L			
			10,13-Octadecadienoic acid, methyl ester	121100	056554-62-2	99
			9,12-Octadecadienoic acid (Z,Z)-, methyl ester	121106	000112-63-0	99
			11,14-Octadecadienoic acid, methyl ester	121099	056554-61-1	99
3	10.624	4.53	C:\Database\NIST05a.L			
			8-Octadecenoic acid, methyl ester	122297	002345-29-1	99
			9-Octadecenoic acid, methyl ester, (E)-	122326	001937-62-8	99
			7-Octadecenoic acid, methyl ester	122298	057396-98-2	99
4	10.881	1.72	C:\Database\NIST05a.L			
			Octadecanoic acid, methyl ester	123709	000112-61-8	99
			Octadecanoic acid, methyl ester	123708	000112-61-8	98
			Octadecanoic acid, methyl ester	123700	000112-61-8	98
5	12.365	85.52	C:\Database\NIST05a.L			
			Methyl ricinoleate	132192	000141-24-2	91
			9-Octadecenoic acid, 12-hydroxy-, methyl ester, (Z)-	132216	127062-53-7	87
			Oxacyclododecan-2-one	45712	001725-03-7	14
6	15.057	0.94	C:\Database\NIST05a.L			
			Cyclohexanecarboxylic acid, undec-10-enyl ester	112010	1000279-53-9	27
			Hexanedioic acid, bis(2-methylpropyl) ester	97279	000141-04-8	22
			1H-Imidazole-2-methanol	2973	003724-26-3	18