Transesterification of Castor Oil to Biodiesel by using Mg-Al Hydrotalcites as a Catalyst

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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NURUL FARHAH BT YAACOB

CERTIFICATION OF APPROVAL

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by

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`ABSTRACT

Production of biodiesel via transesterification of castor oil using metal oxides as as solid catalysts is investigated. Finding a suitable catalyst that is active, selective and stable under the high free fatty acids (FFA > 0.5 %) is the major challenge. In this study, castor oil has been chosen as feedstock because it is readily available in Malaysia and non food. Castor oil is constituted mainly by triglycerides which consist of three fatty acids molecule in one molecule of glycerol. These triglycerides are converted to the corresponding alkyl ester and glycerol by transesterification with short chain alcohols; typically methanol. Heterogeneously catalyzed offers advantages over the homogeneous catalyst. Usage of homogeneous catalyst for transesterification is problematic because it can produce large amounts of unwanted soap by product, which create problem in product separation. Biodiesel production costs could certainly be reduced by using a heterogeneous catalyst for transesterification reaction instead of a homogeneous catalyst. This heterogeneous process provides higher quality esters and glycerol, which are more easily separated and further expensive refining operations are not needed. In this study,hydrotalcite derived Mg-Al mixed oxide which is a heterogeneous catalyst will be use as catalyst. The effect of reaction parameters in transesterification reaction is observed through conducting an experiment. Gas Chromatography (GC) and Gas Chromatography Mass Spectrometry (GCMS) have been used to analyze biodiesel product.

Keywords: Biodiesel, transesterification, Mg-Al hydrotalcite, castor oil

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TABLE OF CONTENT

LISTOF FIGURES

LIST OF TABLES

NOMENCLATURE

General alphabet notation:

Mg –Al	=	Magnesium-aluminium
Na_2CO_3	=	Sodium Carbonate
FFA	=	Free Fatty Acids
CO	=	Carbon monoxide
CO_2	=	Carbon dioxide
SO_2	=	Sulfur dioxide
NaOH	=	Sodium hydroxide
XRD	=	X-Ray Diffraction
SEM	=	Scanning Electron Microscope
GC	=	Gas Chromatography
HPLC	=	High Liquid Performance Chromatography
˚C	=	Degree Celsius
˚	=	Degree
M	=	Molarity
V	=	Volume
m	=	mass

Greek symbol

Θ	=	Angle
Þ	=	Density
Λ	=	Wavelength

CHAPTER 1
INTRODUCTION

1.1 Background of Study

Biodiesel has become very attractive as a biofuel because of its environmental benefits. It has less air pollutants per net energy than diesel and is 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 [1]. Biodiesel is produced from renewable sources with high energetic efficiency.

Pure biodiesel fuel contains no petroleum fuels and emits virtually no sulfur, aromatics or particulates and is thus a safer alternative to petroleum diesel. Biodiesel can be used in all convectional diesel engines, delivers comparable performance (though with slightly lesser energy), and engine durability to petroleum diesel and requires virtually no modifications in fuel handling and delivery systems [2].

Generally, biodiesel is obtained by the transesterification of oil triglycerides. These triglycerides are converted to the corresponding alkyl ester and glycerol by transesterification of oil triglycerides. These triglycerides are converted to the corresponding alkyl ester and glycerol by transesterification with short chain alcohols, typically methanol. The transesterification of vegetable oils constitutes an efficient method that provides a fuel (biodiesel) with chemical properties close to the mineral diesel fuel. The overall process is normally a sequence of three consecutive steps, which are reversible reactions. First diglyceride is obtained from triglycerides; second, monoglyceride is produced from diglyceride and in the last step, glycerine obtained from monoglycerides. In all these reactions esters are produced [1].

They are two main factors that affect the cost of biodiesel, the cost of raw materials and the cost of processing. Processing cost could be reduced through simplified operations [7]. In order to lower the costs and make biodiesel competitive with petroleum based diesel, less

expensive feed stocks such as waste fats or inedible type oils, could be used. In this study, castor oil which is inedible oil has been chosen as a feedstock.

The raw materials are converted to biodiesel through a chemical reaction involving alcohol and catalyst. Alternatively, it is a good strategy to discover some vegetable oils that are not used in the food chain (no edible), as it is the case of castor oil. Castor oil is a nontraditional raw material for production of biodiesel. This vegetable oil is comprised entirely of triglycerides of ricinoleic acid in which the presence of hydroxyl group at C-12 imparts several unique chemical and physical properties. Thus, castor oil and its derivatives are completely soluble in alcohols at room temperature. Castor oil ethanolysis and methanolysis were carried out in the presence of enzyme, basic and acid catalyst [3].

Homogenous alkaline catalysts in the transesterification such fats and oils cannot directly being used due to the presence of large amounts of free fatty acids. If this catalyst is being used, the free fatty acids (FFAs) concentration should be less than 0.5 %(w/w) to avoid the formation of high soap concentrations as a consequence of the reaction of FFAs with the basic catalyst[7]. This will result problematic in separation of the product. Thus, heterogeneous catalyst is being used because it is easily removed from the reaction mixture. The use of heterogeneous catalysts makes separation of the product easier and produces neither corrosion nor emulsion. In the methanolysis experiments using Mg-Al hydrotalcite catalysts for biodiesel,the best ester conversions of soybean oil and glyceryl tributyrate were below 80%.So it is important to increase the ester conversion for the reduction of production cost[4].

In the present work,calcined Mg-Al hydrotalcite were adopted for transesterification of castor oil with methanol.

1.2 Problem statement

Traditionally, vegetable oils including canola, soybean and corn are used as feedstocks for biodiesel production. However, increasing concerns of food shortage throughout the world due to usage of edible oils for biodiesel production that conflict with human consumption has developed a contradictory situation of food vs fuel. In this study, castor oil has been chosen as feedstock. Castor oil is non-food oil and low-cost feedstocks

High free fatty acids (FFA) feedstocks react with the catalyst and easily form soaps. Convectional operation for production of biodiesel usually takes place in two steps. The first step is acid esterification where the free fatty acids (FFAs) content of the oil reduces to less than 2%.The second step is alkali transesterification where the products of first step are converting to monoesters and glycerol.

This study is conduct to combine the two steps transesterification process (acid esterification followed by alkali transesterification) to single step of transesterification to produce biodiesel from high free fatty acids (FFAs) feedstocks .Finding a suitable catalyst that is active, selective and stable under the high FFA content is the major challenge. The use of homogenous base catalysts for transesterification is problematic because the alkali can produce large amounts of unwanted soap by product, which creates serious problems of product separation and ultimately decreases substantially the yield. Heterogeneous catalysts are easily removed from the reaction mixture, making the purification step easier.

1.3 Objectives & Scope of the study

The objectives of this research are:

- To study reaction kinetic of castor oil transesterification to biodiesel.
- To study on influence of reaction parameters which are molar ratio of catalyst and effect of time and temperature for transesterification reaction on production of biodiesel from castor oil

The whole project would start with the knowledge gathering and theoretical studies. The study on single step of transesterification of biodiesel of high free fatty acids (FFA) to biodiesel is to be completed within approximately one year time frame (two semesters).The project can be divided into two phase. The scope of phase 1 is to study on the theoretical parts on the properties of feedstock, catalyst, alcohol selection and reaction parameters of castor oil transesterification. The method to carry out the experiment also had been study in phase 1.

For 2^{nd} phase, experiment will be carried out to correlate theoretical knowledge with practice. The product will be further analyzed. Meanwhile, further research and development would be continuously practiced to ensure satisfactory results are achieved.

CHAPTER 2
LITERATURE REVIEW

2.1 Introduction of Biodiesel Production

Nowadays, petroleum products derived from crude oil and natural gas are important world energy resources. These resources are limited and non renewable. If these resources continue to be consumed at the current rate, their shortage can be expected .Moreover, the widespread use of petroleum based fuels causes environmental problems, especially the global warming and pollution .Consequently, there has been a considerable interest in the development of some alternative energy[3,5,20]. Biodiesel is a promising nontoxic and biodegradable renewable fuel comprised of mono-alkyl esters of long chain fatty acids, which are derived from vegetable oils or animal fats [11].It is a viable alternative fuel for diesel engine due to its non toxicity, biodegradability and low emission.

Biodiesel is oxygenated and essentially free of sulfur making it a cleaner burning fuel than petroleum diesel which reduced emissions of sulfur, carbon monoxide, unburnt hydrocarbons and particulate matter [11].

Traditionally, vegetable oils including canola, soybean, and corn are used as feedstock for biodiesel production. However, increasing concern of food shortage throughout the world due to usage of edible oils for biodiesel production that conflicts with human consumption has developed a contradictory situation of food vs fuel. Inedible oils meet the requirement for these considerations because they are inedible and can be grown in waste land with low fertilizer and pesticide inputs. Therefore, it is crucial to developed environmentally friendly processes with low cost feedstock containing high net energy ratios [14].

The high cost of vegetable oils, especially edible oils, is the main barrier for expansion of biodiesel applications. Reducing the cost of the feedstock is necessary for biodiesel's long-term commercial viability. One way to reduce to reduce the cost of this fuel is to use less expensive feedstock including waste cooking oils and vegetable oils that are inedible and/or require low harvesting costs [14].

2.2 Castor oil as a feedstock

A variety of oils both edible and non edible oils can be used to produce biodiesel but most are derived from edible oils such as sunflower, soybean, and palm oil. Since the prices of edible vegetable oils are high, the less expensive raw materials containing free fatty acids, such as non-edible crude oils, waste food oils, animal fats and byproducts of the refining vegetable oils, are preferred.

Figure 1: Castor Beans

However, the free fatty acid content in the oil has significant effect on the transesterification of glyceride with alcohol using an alkaline catalyst. These free fatty acids react with the alkaline catalyst to produce soaps. These free fatty acids react with the alkaline catalyst to produce soaps, which inhibit the separation of the product from glycerin and wash water. In addition, soap increases the viscosity of the reactants and results in the lower yield of methyl ester [5].

The sulfur content of commercial diesel fuels causes a decrease in its lubricity, causing possible damage to the engine and fuel injection systems. Biodiesel can be used as an additive in diesel fuel increasing lubricity. Castor oil has shown a better performance as an additive with more effective lubricity than oils that do not contain any hydroxylated fatty acids. The hypothesis was that the hydroxylated fatty acids of ricinoleic acid in castor oil which represent approximately 90 % of oil composition give it better performance as a lubricity enhancer that other common vegetable oil esters. Besides the use as an additive in diesel fuel, castor oil is highly valuable for industrial purposes due to this chemical composition. However, depending on the reaction conditions, the products obtained by transesterification of castor oil do not form two liquid phases. Glycerol showed low solubility in the biodiesel phase. The solubility was considered temperature insensible [16].

Castor oil is a nontraditional raw material for production of biodiesel. It is inedible, inexpensive and environmentally friendly. This vegetable oil is comprised almost entirely (90 % wt) of triglycerides of ricinoleic acid in which the presence of hydroxyl group at C-12

imparts several unique chemical and physical properties. Thus, castor oil and its derivatives are completely soluble in alcohols at room temperature [3, 26].

It has been thought to be an alternative source of biodiesel because it's unique chemical and physical properties [1]. Typical of vegetable oils and most fats, castor oil is a triglyceride of various fatty acids. Its uniqueness stems from the very high (87-90 wt %) content of ricinoleic acid, $C_{18}H_{34}O_3$, structurally cis-12 hydroxyoctaeca-9-enoic acid, CH_3 $(CH_2)_5CH$ (OH) CH2CH=CH $(CH_2)_7COOH$, an eighteen-carbon hydroxylated fatty acid having one double bond. Castor oil, sometimes described as a triglyceride of ricinoleic acid, is one of the few commercially available glycerides that contain hydroxyl functionality in such a high percentage of one fatty acid [12]. Castor oil is a viscous, pale yellow nonvolatile and non-dry oil. It has a good shelf life and it does not turn rancid unless subjected to excessive heat. The presence of ricinoleic acid, which is a complex fatty acid that contains both a double bond and a hydroxyl group, can impart increased lubricity to the castor oil and its derivatives as compared to other vegetable oils and makes of it a prime candidate as an additive for diesel fuel [1].

The difficulty to separate both phases (biodiesel and glycerol) is evident on the castor oil transesterification process. The phase separation between the ester (biodiesel) and the glycerol was obtained with neutralization of the products using co solvents or extraction by polar solvent. [3]

Castor oil is the only significant oil composed mainly of the glyceride of a hydroxylated fatty acid. Ricinoliec acid cannot be distilled unless special precautions are taken via derivative formation to protect the hydroxyl group. It is distinguished from other triglycerides by its high specific gravity, viscosity and hydroxyl value. Another unique feature is alcohol solubility, one volume of castor oil dissolves on two volumes of 95% ethyl alcohol at room temperature, and the oil is miscible in all proportions with absolute ethyl alcohol [12].

Table 1: Fatty Acid Composition of Castor Oil

Fatty acid	Composition (%)
ricinoleic acid	87
linoleic acid	5
oleic acid	4
palmitic acid	2
estearic acid	1
linoleic acid	1

Table 2 :Castor Oil Properties

Properties	Value
free fatty acid (%)	0.63
flash point (C)	230
viscosity at 40 C (mm 2/s)	227
water content (ppm)	367
iodine value (g I2/100 g sample)	85.5

Standards for industrial quality castor oil as specified by the ASTM are given in table 3.

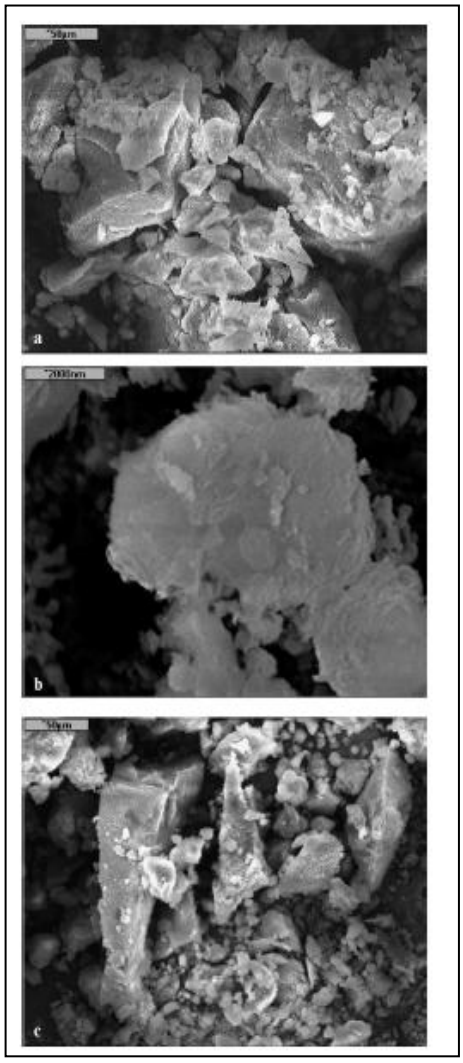
Table 3: Industrial Castor Oil Standards

Property	**Value**
acid value,max	2
clarity	clear
Gardner color,max	2
hydroxyl value	160-168
loss on heating ,wt % max	0.2
refractive index ,25 C	1.4764-1.4778
saponification value	176-184
solubility in alcohol	complete
specific gravity 25/25C	0.957-0.961
unsaponifiable matter,wt % max	0.7
viscosity,mm^s	6.5-8.0
iodine value	84-88

2.3 Catalyst Selection

The transesterification reaction can be carried out using both homogeneous (acid or base) and heterogeneous (acid, base or enzymatic) catalysts. Homogeneous base catalysts provide much faster reaction rates than heterogeneous catalysts, but it is considerably more costly to separate homogeneous catalyst from the reaction mixture. Heterogeneous catalyst has many advantages such as being noncorrosive, being environmentally and presenting fewer disposal problems. These catalysts are also much easier to separate from liquid products, and they can be designated to give a higher activity and selectivity and to have longer catalyst lifetimes. Many types of heterogeneous catalysts, such as alkaline earth metal compounds supported on alumina or zeolite, can catalyze many types of chemical reactions. In transesterification of vegetable oils to biodiesel, most supported alkali catalysts and anion exchange resins exhibit a short catalyst lifetime because the active ingredients are easily corroded by methanol [32].

The most commonly used technology for fats and oils transesterification is based on the use of batch reactors, in which a basic homogeneous catalyst is used. The use of homogeneous catalysts requires extensive conditioning and purification step for the reaction products to separate the catalysts. In contrast, heterogeneous catalysts are easily removed from the reaction mixture, making the purification step easier. Biodiesel production costs could certainly be reduced by using a heterogeneous catalyst for transesterification reaction instead of a homogeneous catalyst. This heterogeneous process provides higher quality esters and glycerol, which are more easily separated and further expensive refining operations are not needed [8, 16]. Heterogeneous solid base catalysts, able to catalyze the transesterification of alkyl esters could solve these problems, they can be easily separated from the reaction mixture without the use of solvent, and they are easily regenerated and have a less corrosive character ,leading to safer ,cheaper and more environment friendly operations[8].



2.3.1 Hydrotalcite catalyst

Hydrotalcite like compounds (HTLCs) consist of brucite like layers with positively charged metal oxide or hydroxide layers with anions located intestinally. [15]The hydrotalcite has attracted much attention during the development of new environmentally friendly catalysts. Their chemical composition can be represented by the general formula $[M^{2+}_{(1-x)} M^{3+}_{x} (OH)_2]^{X+} (A_{x/n})^{n-}.y\ H2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations respectively, A^{n-} is an n-valent anion, and x usually has a value between 0.25 and 0.33. [17] Outside of these limits the high density of Mg^{2+} or Al^{3+} octahedral will lead to the formation of Mg $(OH)_2$ and Al $(OH)_3$ respectively. The basic sites in the alkali earth oxides component can originate from O^{2-} (strong basicity), O- species near hydroxyl groups (medium strength) and OH groups (weak).The addition of Al^{3+} alters the acid: base sites which are of moderate Lewis acidicity and only medium basicity.[18]

Figure 2: Images of hydrotalcite catalyst

Thermal decomposition of hydrotalcites is often practiced to obtain high surface area and well dispersed multimetallic mixed oxide catalysts. This treatment is also intermediate in the fictionalization of the clay by intercalation of anions in the interlayer. This approach makes use of the memory effect a unique property by which the oxide is retropotactically transformed into the original hydrotalcite structure in aqueous solutions or humid atmospheres. In this manner, the compensating anion in the as-synthesized hydrotalcite is first decomposes and the calcined product is reconstructed in aqueous solutions containing the desired anion [16].

2.4 Influence of Co-Solvent

The biodiesel samples were analyzed according to the European Standard EN 14214. The use of hexane as co-solvent can improve the yield of methyl ester in the transesterification reaction of castor oil. Besides, the co-solvent makes the metyl ester content very close to the EN 14214 specifications. The use of co-solvent increases the reaction rate by making the oil soluble in methanol, thus increasing contact of the reactants. This is in agreement with a kinetic study that clearly indicates that the reaction rate constant for transesterification increases markedly when the solvent is added. However, the increase of hexane beyond 15% v/v lightly decreases the methyl ester content. On the other hand, the presence of co-solvent helps to separate the phases (biodiesel and glycerol) more easily. The critical separation of the glycerol rich phase still occurs and is faster than in the co-solvent free system .Besides, when hexane is used as co-solvent the formation of soap of significantly reduced [1].

During early stages, the transesterification reaction is limited by the low solubility of oil in alcohol especially in methanol. In consequence, it has been shown that it reaches substantial completion within a few minutes. The primary concerns with this method are the additional complexity of recovering and recycling the co-solvent, although this can be simplified by choosing co-solvent with a boiling point near that of the alcohol being used. To perform the reaction in single phase, co-solvents like tetrahydofuran(THF),1,4-dioxane and diethyl ether have been tested[1].

2.5 Transesterification Reaction

Biodiesel is monoalkyl esters of long chain fatty acids derived from vegetable oils or animals' fats. It is produced through a chemically reversible reaction called transesterification or alcoholysis which has been widely used to reduce the high viscosity of triglyceride [5, 16].

The transesterification reaction can be expresses by the following general equation.

$$\text{Triglyceride} + 3\ \text{ROH} \rightarrow 3\ \text{R'CO}_2\text{R} + \text{Glycerol}$$

The reaction is carried out in the presence of catalyst [5].

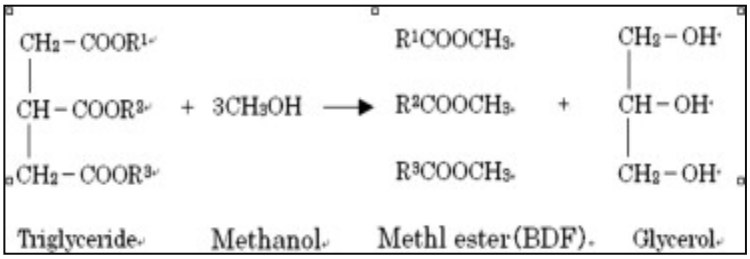


Figure 3: Overall reaction of triglyceride transesterification.

The transesterification reaction is completed via a transition state, in which ring formation consisting of the carbon of the carboxyl and alkoxy groups appears, even if a long-chain alcohol is used as a reactant.The properties of the biodiesel fuel are strongly influenced by the structure and concentration of the fatty acid esters, which depend on the source, such as palm, soybean, corn or sunflower. Normally, the triglyceride consists of one glycerol and various types of fatty acid esters which vary in carbon chain length and in number of unsaturated bonds. Therefore, a transesterification reaction can be rather complex. A typical transesterification of a triglyceride ,consisting of consecutive reversible reactions, where R^1, R^2 and R^3 represent long-chain alkyl groups[21] .The overall process is normally a sequence of three consecutive steps, which are reversible reactions. The triglyceride is converted stepwise to a diglyceride, a monoglyceride and finally, to glycerol by removal of an alkyl in each step [14, 17, and 21].Transesterification reaction of castor oil takes place at a significantly lower temperature when compared to other vegetable oils [16].

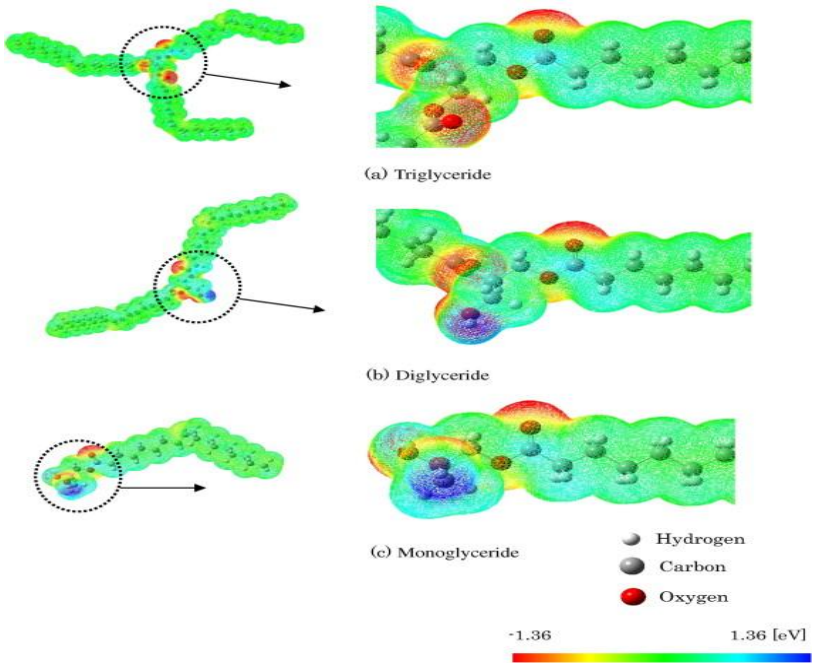


Figure 4: Structure of triglyceride, diglyceride and monoglyceride

2.5.1 Effect of molar ratio of alcohol to oil

The stoichiometric ratio for the reaction requires 3 mol of alcohol and 1 mol of triacyglycerol to yield 3 mol fatty acid ester and 1 mol of glycerol. However, because of the reversibility if the reaction, an excess of alcohol is usually needed to force the equilibrium to the product side .In practice, 6 mol of alcohol and 1 mol of triacyglycerol are use to raise the product yield. Hence, the reaction rate depends on ethanol solubility in the oil phase [23].The stoichiometric ratio alcohol/oil has been identified as a crucial variable and has been studied in the range of 1:1 and 6:1.An excess of alcohol has been recognized to improve the reaction toward the desired product [1].

2.5.2 Effect of Temperature

The transesterification process is generally carried out at 40.15 C to 70.15 C, because the reaction temperature is limited by the boiling point of the alcohol. Because of the low mutual solubility of vegetable oil and ethanol at atmospheric pressure, the reaction mixture is usually mechanically stirred to enhance mass transfer. Solvent reuse would also lead to water accumulation in ethanol, affecting the initial stage of the reaction. One factor of particular

importance in the alcoholysis process is the degree of mixing between the alcohol and the triacyglycerol phases [23].

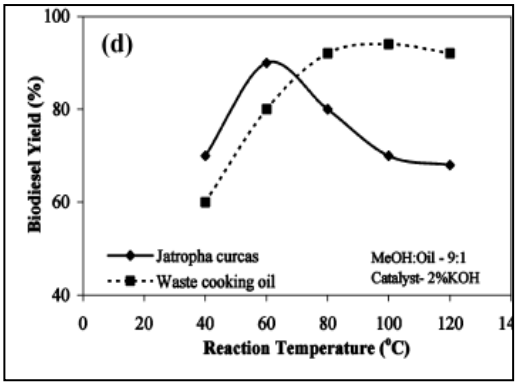


Figure 5: Reaction temperature effect for jatropha curcas

As shown in the above figure, the reaction temperature effect on the yield was studies in the temperature range of 40 – 100 C for jatropha curcas oil at atmospheric pressure. The maximum yield was obtained at a temperature of 60 C for jatropha oil. A decrease in yield was observed when the reaction temperature was above 60 C. Other researchers have achieved optimum yield at temperature above 60 and 70 C while using refined linseed oil and brassica carinata oil respectively. The reaction temperature for processing jatropha oil should be maintained below 60 C because saponification of glycerides by the alkali catalyst is much faster than the alcoholysis at temperature above 60 C [1].

2.5.3 Effect of reaction time on the conversion

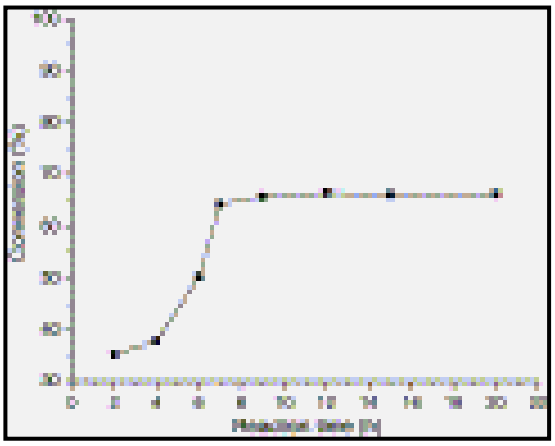


Figure 6: Influence of reaction time on the conversion.

Reaction conditions: methanol/oil molar ratio 15:1, catalyst amount 7.5% and methanol reflux temperature

The conversion vs reaction time is presented in figure 6.It can be seen that the conversion increases steadily with the reaction time and then reached a plateau value representative of a nearly equilibrium conversion .A nearly maximum conversion of 65% is obtained after 9 hour reaction time [24].

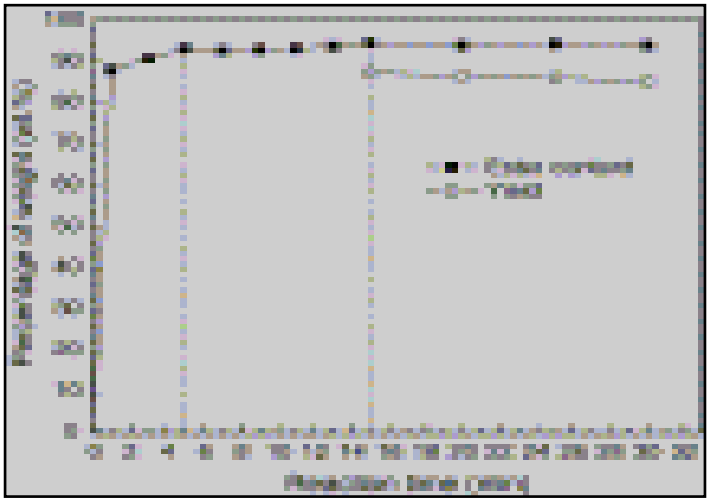


Figure 7: Effects of reaction time on ester content.

The results showed that the reaction was very fast in the first few minutes, a product of more than 90% ester content was formed within the first 5 min. After that (the time of a clear phase being formed), the reaction slowed down and entered a slow rate stage till the reaction equilibrium was reached eventually. As can be observed, the ester content increased with reaction time at the beginning, reached a maximum at a reaction time of 15 min at 70°C, and then remained relatively constant with increasing further the reaction time. Based on this, the product yield under the case of a reaction time larger than 15 min was examined. The results indicated that an extension of the reaction time from 15 min to 30 min had no significant effect on the conversion of triglycerides, but led to a reduction in the product yield, the yield of the product with the same ester content decreased from 87.5% to 85.3%, dropped by about 2%. This is because longer reaction enhanced the hydrolysis of esters (reverse reaction of transesterification), resulted in a loss of esters as well as causing more fatty acids to form soap. More visible soaps were observed experimentally with gradually extending the reaction time.

Accordingly, it can be concluded that the reaction time was also a controlling factor of product yield and extending the reaction time had a negative effect on the product yield. The optimal reaction time for the transesterification of used frying oil is 15 min at 70 °C with the maximum mixing degree currently available, which is similar to that of neat Canola oil[25].

2.6 Glycerol

Glycerol or glycerin (1, 2, 3- propanetriol) has a particular combination of chemical and physical properties and it is physiologically harmless. Glycerol is a colorless, odorless and sweet-tasting hygroscopic liquid. Glycerol is a reactive molecule that undergoes various reactions.It is easily oxidized yielding glyceric acid,tartronic acid,ketomalonic(or mesoxalic) acid and dihydroxyacetone. These are useful compounds as such and as intermediates. Today, glycerol has over 2000 different applications ,in cosmetics ,pharmaceutics, foods and drinks, tobacco ,paper ,inks and printing colors, the production of phthalic and maleic alkyl resins and cross linked polyesters and as a hydraulic agent[16,20].

2.6.1Glycerol from Biodiesel Production

The glycerol obtained from the transesterification is separated from the biodiesel gravity. Owing to the low solubility of glycerol in the esters, this separation generally occurs quickly and may be accomplished with either a settling tank or a centrifuge. The glycerol stream from the separator contains only about 50% glycerol including some of the excess alcohol, soap and most of the catalyst. In this form glycerol has little value and disposal may be difficult because the methanol content requires glycerol to be treated as hazardous waste.

The first step in the purification of the raw glycerol is to split the soaps with acids into free fatty acids and salts. The free fatty acids are not soluble in glycerol in glycerol and will rise to the top, where they can be recycled. The salts remain mainly with glycerol (some may precipitate out).The glycerol stream is then neutralized with caustic soda. A vacuum flash process or another type of evaporator removes the excess methanol. At this point glycerol should have a purity of 80-85%.It is often most cost effective to purify the raw glycerol and sell the so-called crude glycerol to industrial glycerol refiners. The refining of the crude glycerol raises the purity to 99.5 – 99.7 % by vacuum distillation [11].

2.7 Analysis method

Mg-Al hydrotalcite were characterize by X-Ray Diffraction (XRD), Fourier Transform Infrared Spectoscopy(FTIR) and Scanning Electron Microscope(SEM).

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. An FTIR spectrometer simultaneously collects spectral data in a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time. FTIR technique has made dispersive infrared spectrometers all but obsolete (except sometimes in the near infrared) and opened up new applications of infrared spectroscopy [28].

Scanning Electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity [27].

Biodiesel production from castor oil will be analyzed by using Thin Layer Chromatography (TLC), Gas Chromatography (GC) and Gas Chromatography Mass Spectrograph (GCMS).

TLC is a chromatography technique used to separate mixtures.The figure shown changes in product compositions with reaction time during the transesterification of the oils and the distribution of various components in the reaction system can be clearly seen. When the reaction time reached 15 min, no triglyceride (main component of raw oil) was left in the product mixture, indicating complete conversion; only traces of mono-, di-glycerides and free fatty acid could be seen in the TLC analysis [25].

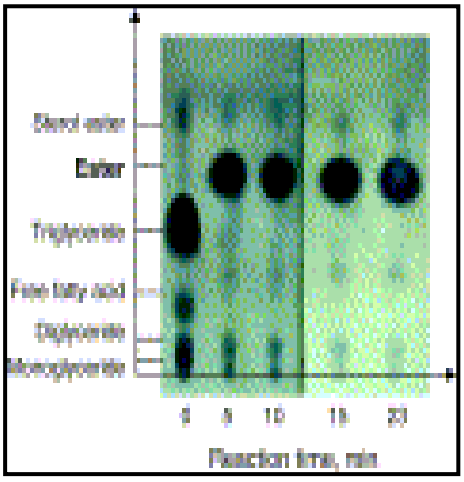


Figure 8: Sample of TLC analysis

Gas chromatography (GC), is a common type of chromatography used in analytic chemistry for separating and analyzing compounds that can be vaporized without decomposition. Typical uses of GC include testing the purity of a particular substance, or separating the different components of a mixture (the relative amounts of such components can also be determined). In some situations, GC may help in identifying a compound [30].

Gas chromatography-mass spectrometry (GC-MS) is a method that combines the features of gas-liquid chromatography and mass spectrometry to identify different substances within a test sample [31].

CHAPTER 3

METHODOLOGY

3.1 Chemicals

Chemical	Purity/Assay	Supplier
Magnesium nitrate	99.00%	SYSTERM
Aluminium nitrate	98.50%	R&M Chemical
Sodium carbonate	98.50%	SYSTERM
Castor Oil	None	R&M Chemical
Methanol	99.90%	R&M Chemical
Hexane	96.00%	MERCK
Diethy ether	99.00%	CheMAR
Acetic acid	99.80%	MERCK

3.2 Experimental Set Up

Equipments that were used in the experiment are listed below:

Equipment	Quantity
250 ml beaker	5
500 ml beaker	2
50 ml buret	1
Retort stand	2
Pipette	2
Thermometer	1
Stopwatch	1
Hot plate stirrer	1
250ml, 3-necked round bottomed flask with reflux condenser	1

Electromantle solid state stirrer	1
Oven	1
Furnace	1

3.3 Experimental Methods

3.3.1Catalyst preparation

Hydrotalcites with various Mg-Al molar ratios were prepared by coprecipitation.In the method, two solutions, A and B were heated to 50 with continuous stirring.Solution A (200ml) was prepared by mixing Mg and Al metal nitrates in the desired molar ratios. Solution B was prepared by dissolving sodium carbonate in 100 ml distilled water.After the reaction, the precipitates were filtered, washed thoroughly with distilled water until the filtrate showed no presence of carbonate. The filtrate was dries at 100 For 24 hours. Part of the samples was calcined at 773 K for overnight for further characterization analysis.The dried and calcined catalyst will be characterized with X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) [4, 22].

3.3.1.1 Flowchart of catalyst preparation

Catalyst will be prepared in this experiment. There are 2 steps of preparation catalyst which are:

1) Preparation of Mg-Al hydrotalcite by coprecipitation.
2) Preparation of hydrotalcite Mg-Al mixed oxide.

3.3.1.2Preparation of Mg- Al hydrotalcite by coprecipitation

Magnesium nitrate hexahydrate (33.56g) and aluminium nitrate nonahydrate (16.43g) are dissolved in 100 ml distilled water to make solution (A) in 500 mL beaker

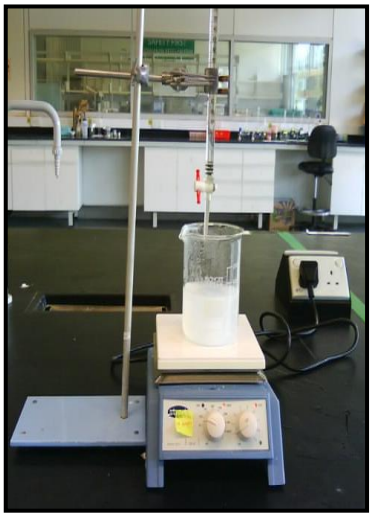


Figure 9: Titration of magnesium and aluminium nitrate to sodium carbonate.

10% excess of theoretical requirement of Na_2CO_3 which is 30.96 g Na2 CO3.10 H20 is dissolved in distilled water to make 0.5 MNa_2CO_3 solutions (B).

A solution of Na_2CO_3 solution is prepared in 500 ml beaker. After that, the solution is stirred.

The solution (A) and solution (B) from the respective burets are put drop by drop into the beaker. The precipitation solution is maintained at 50 is continuous stirring.

After the precipitation the slurry is stirred for 2 hours under nitrogen at room temperature, then filtered and dried overnight in an oven.

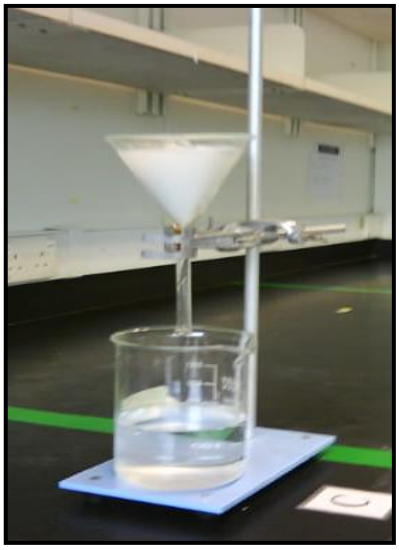


Figure 10: Filtered solution after titration

3.3.1.3 Preparation of hydrotalcite –derived Mg-Al mixed oxide

Hydrotalcite –derived Mg-Al mixed oxide is prepared by calcining the Mg-Al-NO3-HT at 500 C.

3.3.1.4 Catalyst Characterization

The dry precipitate is analyzed by X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) while the the calcined catalyst will be characterized by the same equipment.

Figure 11: Mg Al hydrotalcite before calcined.

3.3.2 Transesterification reaction

Castor oil and an appropriate volume of methanol with calcined Mg-Al hydrotalcite catalyst (1-3%) were placed into 250ml, 3-necked round bottomed flask with reflux condenser equipped with reflux condenser. The reaction mixture was stirred for a period time at 60 C.The samples were taken for each 1 hour to determine the change in transesterifiaction product composition over time.The product will be analyzed by Gas Chromatography (GC) and Gas Chromatography Mass Spectrometer (GCMS).In parallel fashion, each reaction was repeated with different catalyst loading and different mol ratio of catalyst [4, 22].

3.3.2.1 Flowchart of transesterification reaction

In the transesterification of castor oil with alcohol, in the presence of hydrotalcite-derived Mg-Al mixed oxide catalyst, methyl ricinoleate and glycerin are formed. After the reaction complete the reaction product will be analyzed.

The transesterification reaction are performed in 200ml,3-necked round bottomed flask equipped with a reflux condenser, a thermometer, an electromantle solid state stirrer and a heating mantle.

Figure 12: Mixtures of methanol and castor oil

Initially, the3-neck flask is filled with (15ml) castor oil and alcohol (32.2 ml basis 6:1 alcohol to oil ratio) and heated to desired reaction temperature (60 C) with stirring.

Then, hydrotalcite derived Mg-Al mixed oxide catalyst is added to the mixture with difference catalyst loading (0.2g, 0.25g, and 0.3g catalyst).The temperature is maintained at the desired reaction temperature, with continuous stirring. The duration time for the experiment is from 4- 6 hours.

Figure13: Transesterification reaction

Samples of the reaction mixture are pipette out at every30 minute .Water is added to stop the reaction and hexane to separate the product. Samples of result will be analyzed by using Thin Layer Chromatography (TLC), Gas Chromatography (GC) and Gas Chromatography Mass Spectrometer (GCMS).

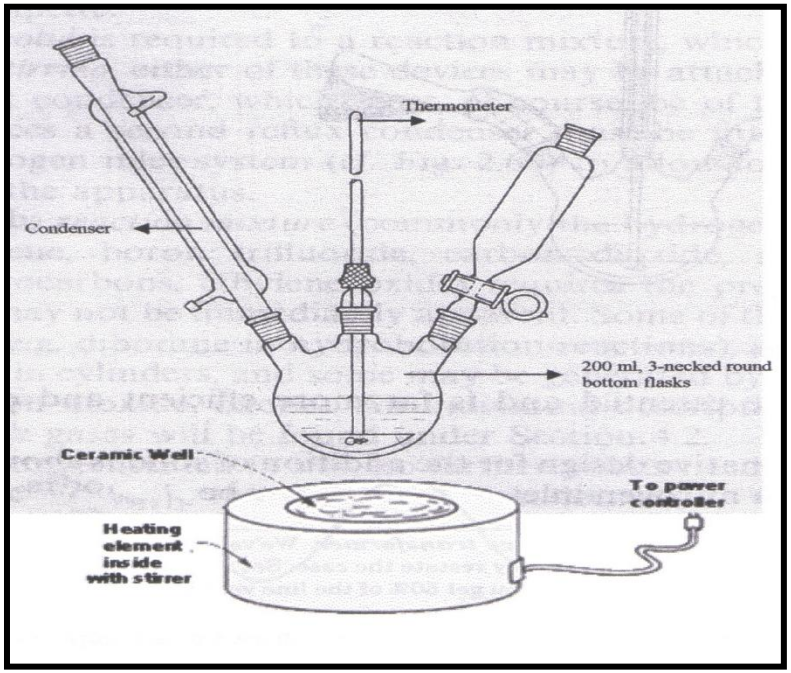


Figure 14 Experimental Set-up for heating and stirring under Reflux

3.4 Analysis Product

Reactants and reaction products are analyzed by Gas Chromatography with TCD using 30m x 0.32 mm ID x 0.1 μm film thickness, SHMADZU GC 2010 with SGE HT-5.Analysis conditions for all reactants and products are set to be the same so that comparison can easily be made. The analysis conditions are set as follows:

Oven Temperature: 50

Detector Temperature: fiD 385

Injection temperature: On column injection, 380

Carrier gas: Nitrogen

3.5 Gantt chart

No	Project Activities	Week No													
		1	2	3	4	5	6	7	BREAK	8	9	10	11	12	13	14
1	Laboratory works															
2	Submission of Progress Report 1															
3	Submission of Progress Report 2															
4	Poster Exhibition															
5	Submission of Dissertation (Softcopy)															
6	Oral Presentation															
7	Submission of Project Dissertation (Hard Bound)															

Milestone
Work in Progress

CHAPTER 4
RESULTS AND DISCUSSION

4.1. X-Ray Diffraction (XRD) Graphs

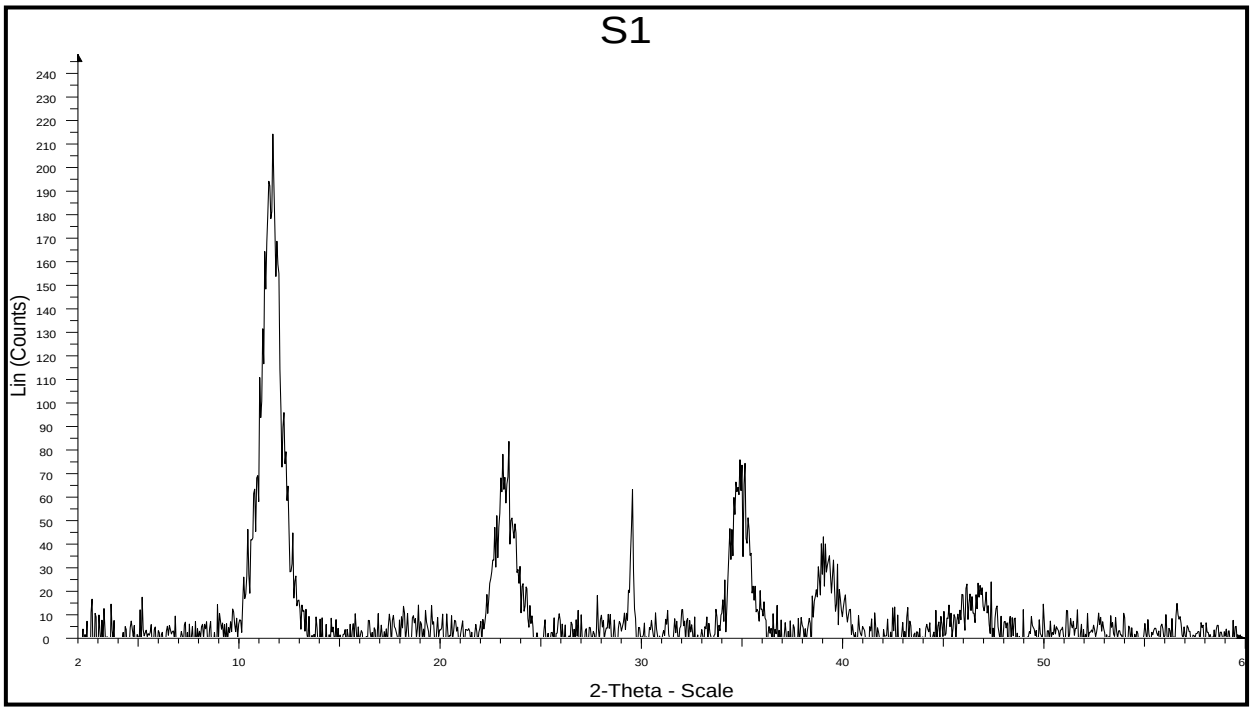


Figure 15: The hydrotalcite Mg-Al catalyst dried at 373K for molar ratios 3.0.

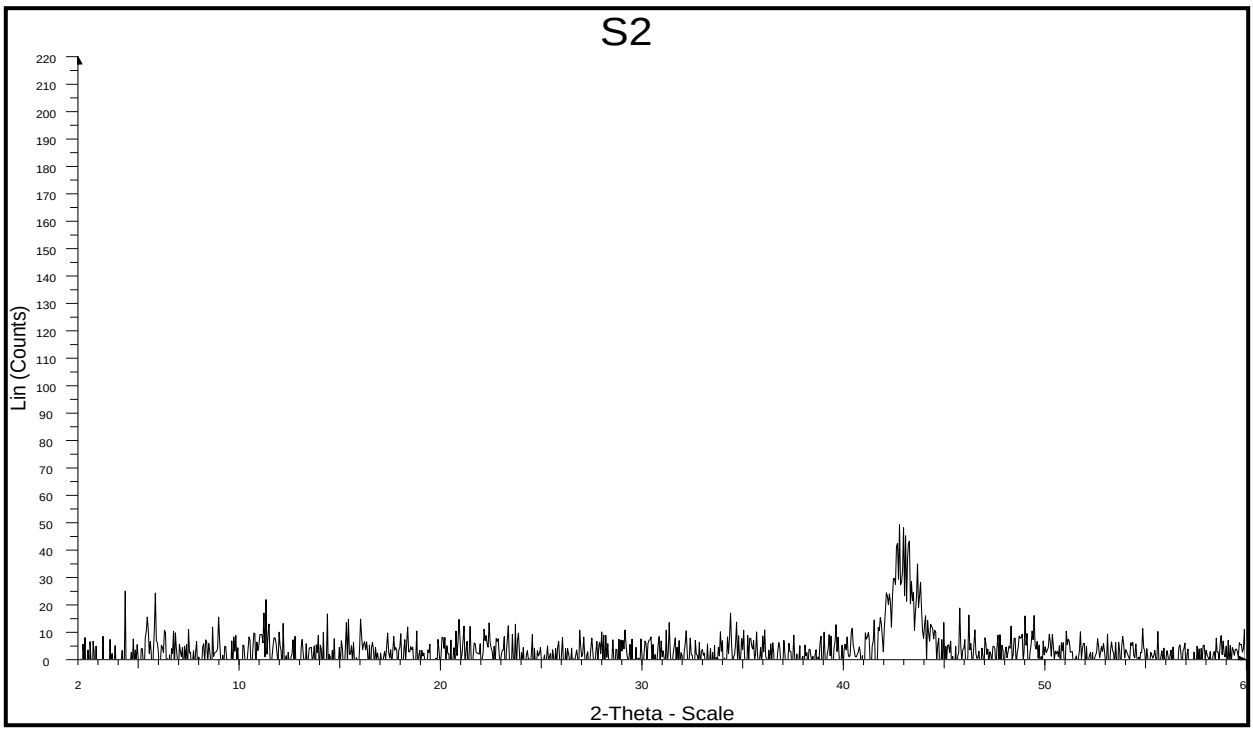


Figure 16: The hydrotalcite Mg-Al catalyst with calcining at 773K for molar ratio 3.0.

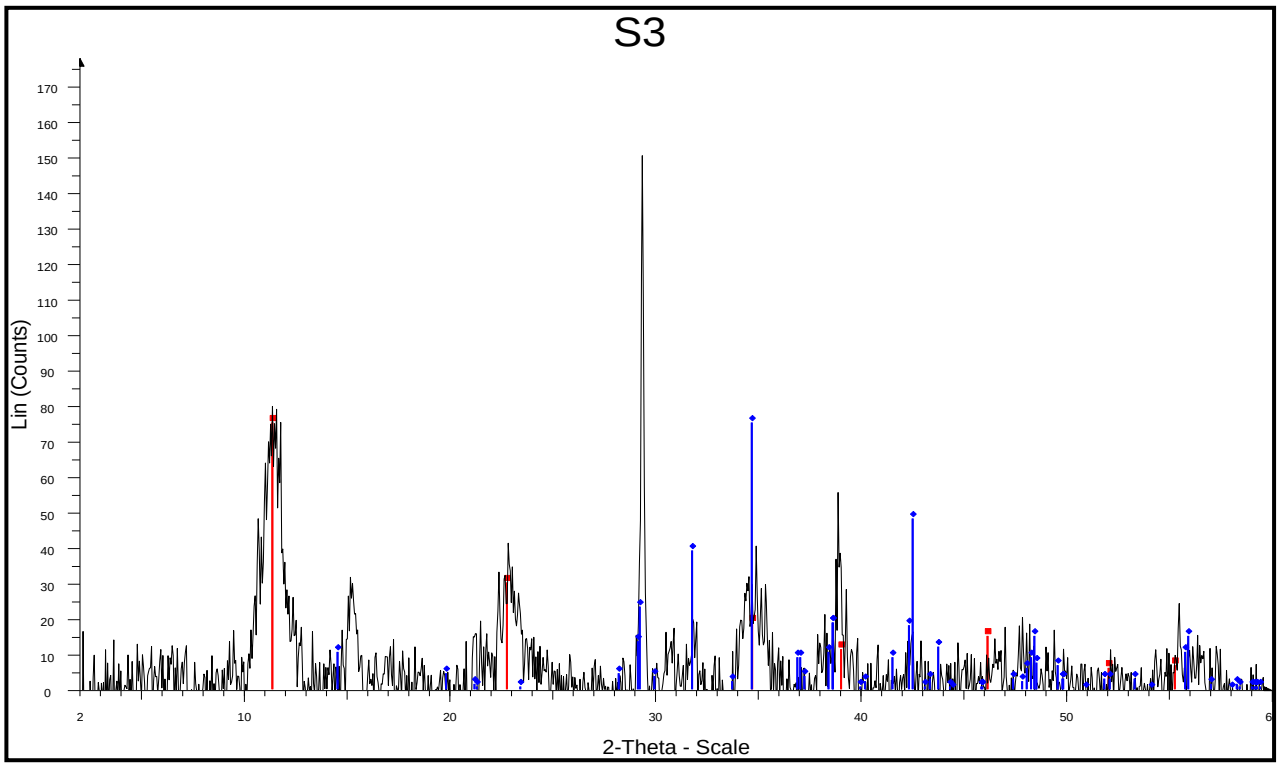


Figure 17: The hydrotalcite Mg-Al catalyst dried at 373K for molar ratio 4.0.

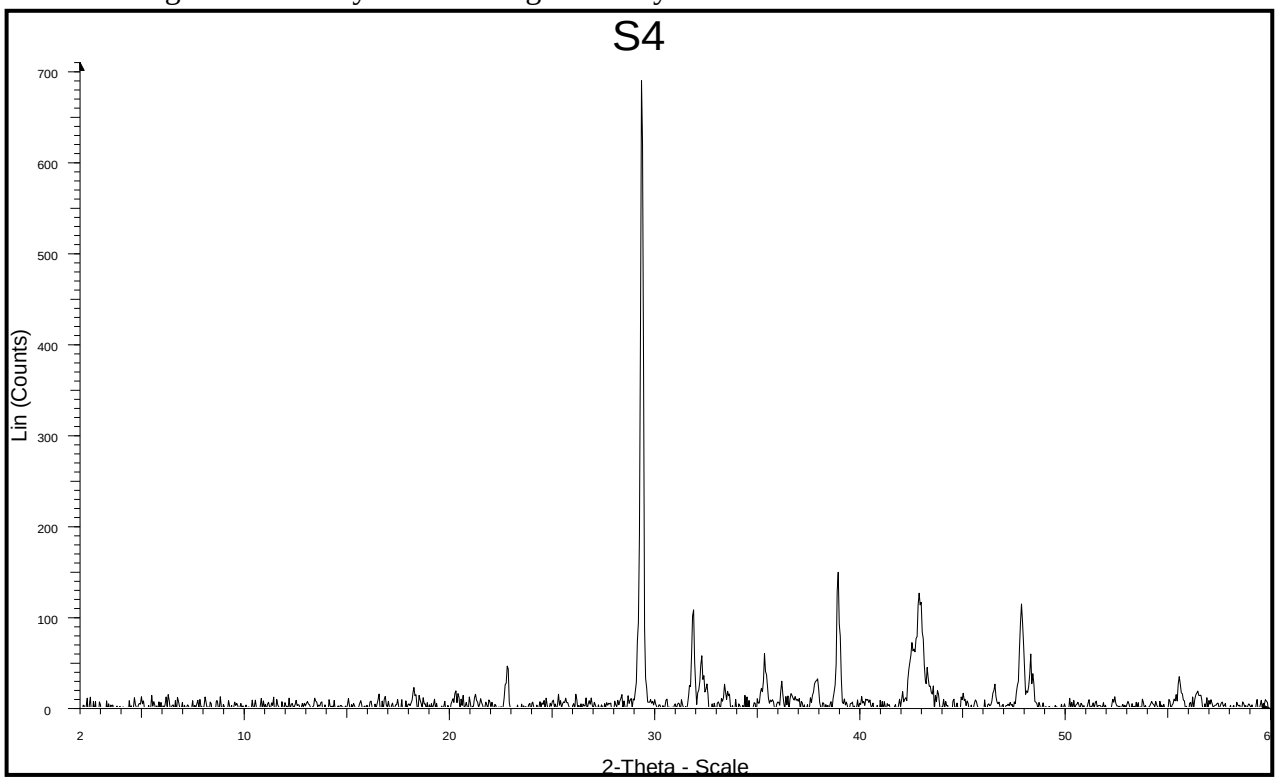


Figure 18: The hydrotalcite Mg-Al catalyst with calcining at 773 K for molar ratio 4.0.

4.1.1 Catalyst characterization on XRD

First the author prepared the hydrotalcite catalyst without calcining it and tests it with X-Ray Diffraction (XRD). Then the author calcined and tests it again to see the difference before and after calcining.

The ratio used is 3.0 Mg-Al since from literature the basicity is the highest at a ratio of 2.5 – 3.0 Mg-Al ratio. The author also did for 4.0 Mg-Al ratio. The highest the basicity the better the transesterification reaction. So, that it can generate higher conversion and yield of biodiesel.

For 3.0 mol ratio of catalyst, the XRD patterns of the 100˚C dried samples showed sharp and symmetric peaks which gave clear indication that the samples were well crystallized and and there were four peaks and planes were characteristic of clay mineral (hydrotalcite) having a layered structure. The peaks at 11.25 and 23 were assigned to the reflections, respectively and could be used to calculate the basal spacing between the layers. The peak was assigned to the unit cell dimension, a, where a =$2d_{110}$ .During calcinations, the decomposition of hydrotalcite resulted in formation of mixed Mg-Al oxides phases.By 673 K,all the hydrotalcite reflections were gone,with the exception of a broadened and shifted peak which might have evolved from the hydrotalcite .The only other peaks present at 673K were the major reflections of MgO which were broadened due to poor crystallization or small particle size,or both which confirmed the result of Mackenzie et al. For all the calcined samples,the characteristics reflections observed cleary at 2 θ 43 corresponded to MgO like phase or magnesia-alumina phase,while the peaks of Al_2O_3 phase were very small,indicatibg Al^{3+} cations were dispersed in the structure of MgO without the formation of spinnel species[4].

For 4.0 mol ratio of catalyst, the XRD patterns of the 100 C dried samples showed sharp and symmetric peaks which gave clear indication that the samples were well crystallized and the samples were well crystallized and there were four peaks and planes were characteristic of clay mineral (hydrotalcite) having a layered structure. The peaks at 11.5 and 22.9 were assigned to the reflections, respectively and could be used to calculate the basal spacing between the layers..During calcinations, the decomposition of hydrotalcite resulted in formation of mixed Mg-Al oxides phases.By 673 K,all the hydrotalcite reflections were gone,with the exception of a broadened and shifted peak which might have evolved from the hydrotalcite .The only other peaks present at 673K were the major reflections of MgO which were broadened due to poor crystallization or small particle size,or both which confirmed the result of Mackenzie et al. For all the calcined samples,the characteristics reflections observed cleary at 2 θ 43 corresponded to MgO like phase or magnesia-alumina phase,while the peaks of Al_2O_3 phase were very small,indicatibg Al^{3+} cations were dispersed in the structure of MgO without the formation of spinnel species[4].

Among the various existing methods for the preparation of hydrotalcite like compounds coprecipitation has many advantages. It allows the preparation of HTIcs with a high level of purity and high crystallinity .X-Ray diffraction confirmed that we prepared a single crystallined phase whose patterns were characteristics of the hexagonal lattice of hydrotalcite like compounds. However, this methods results often in strong agglomeration of primary particles in aggregates with a very large distribution of size. These aggregates are formed by strong edge-surface platelet interaction in a so-called “sand raze morphology”. This type of morphology is induced by the conditions generally used. Such morphology. Such morphology leads to very leads to very low specific surface areas and nearly non porosity. Moreover, once the aggregates are formed they are very stable and resistant to de-cohesion even under powerful ultrasonic treatments. Particle sizes larger than 6 m were measured by laser granulometry [34].

4.1.2 Relationship between Mg-Al Ratios

With the increase in the Al/Mg molar ratio, both Al-O and Mg-O distances gradually became large and reached maximum at the ratio of 7:12. However, once the Al-O-Al triple was formed by continuously increasing the ratio, the case was dramatically different and the hydrotalcite structure phase dissolved. In consideration of the difference of the bond energy between Al-O and Mg-O, the structures formed at Al/Mg molar ratios of 6:13 and 7:12 were much more stable among all the constructed ones. In fact, if these results are extended to single layer hydrotalcite, high symmetry structures with ratios of 1:2 and 1:3 will be easily obtained in experiment.

4.2 Scanning Electron Microscope (SEM)

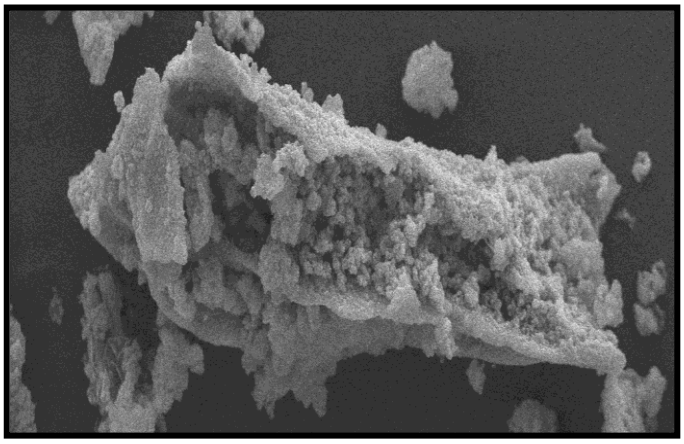


Figure 19: SEM 1000X catalyst 3.0 before calcined

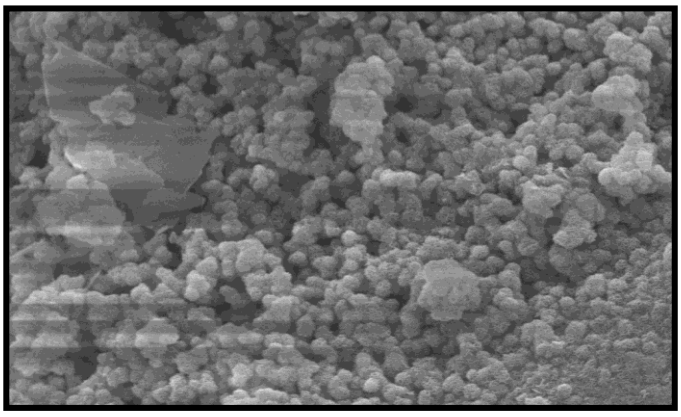


Figure 20: SEM 5000X catalyst 3.0 before calcined

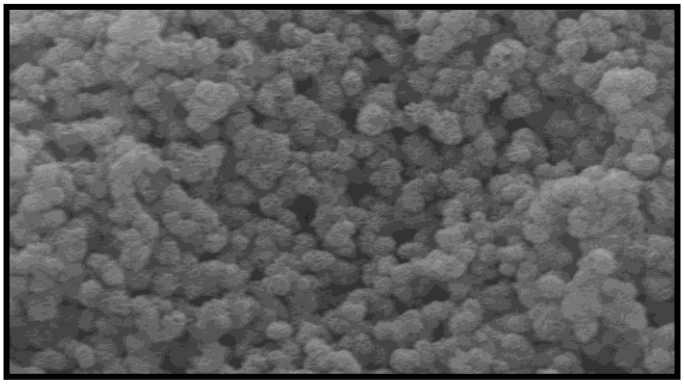


Figure 21: SEM 10000X catalyst 3.0 before calcined

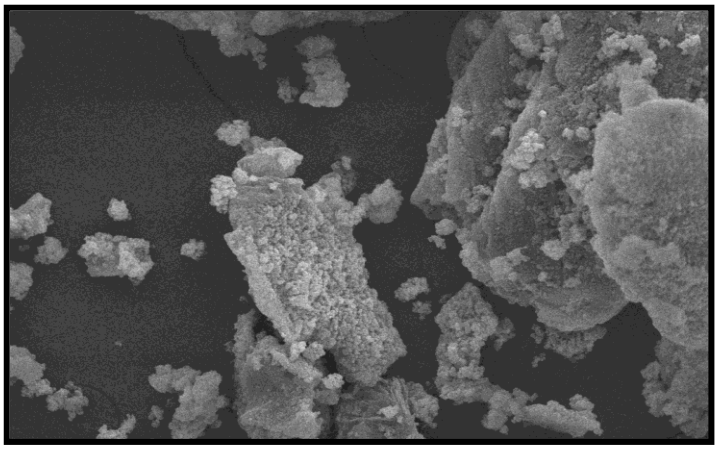


Figure 22: SEM 1000X catalyst 3.0 after calcined

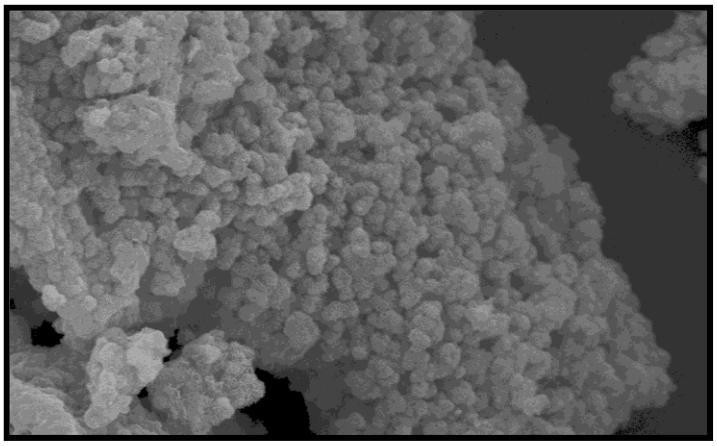


Figure 23: SEM 5000X catalyst 3.0 after calcined

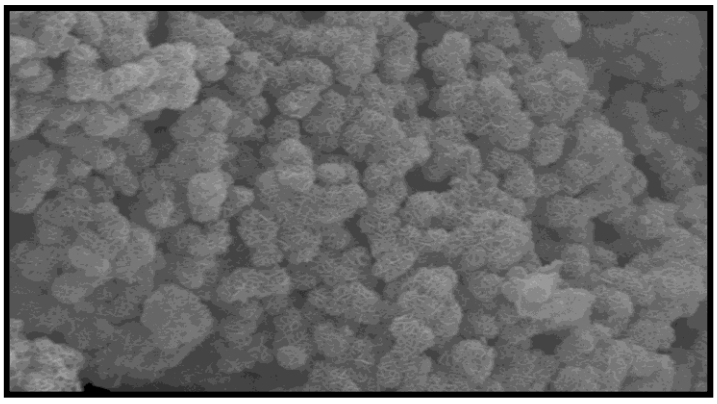


Figure 24: SEM 10000X catalyst 3.0 after calcined

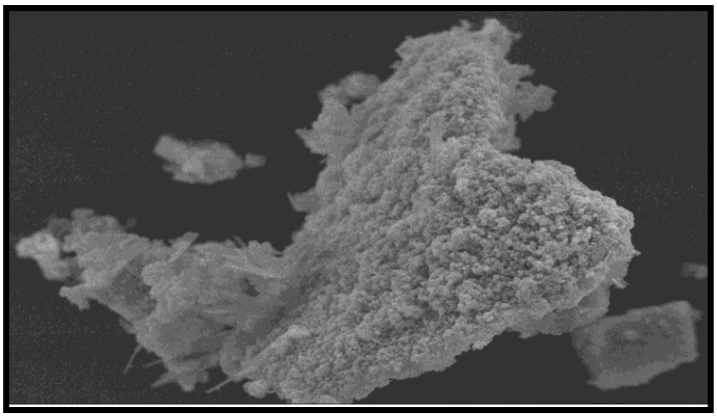


Figure 25: SEM 1000X catalyst 4.0 before calcined

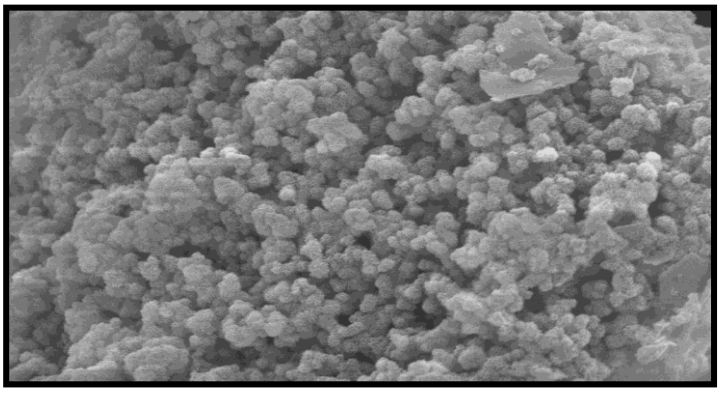


Figure 26: SEM 500X catalyst 4.0 before calcined

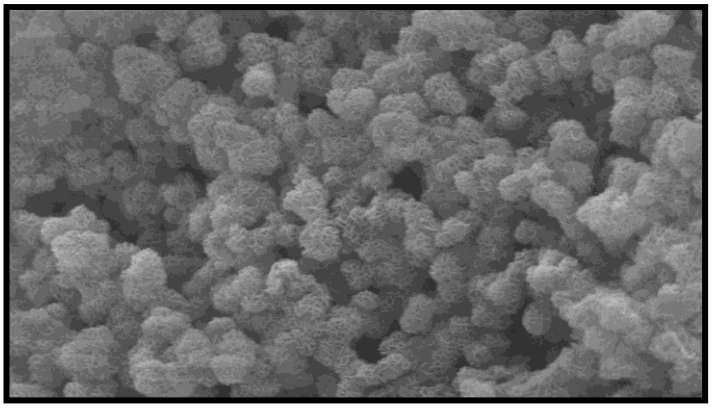


Figure 27: SEM 10000X catalyst 4.0 before calcined

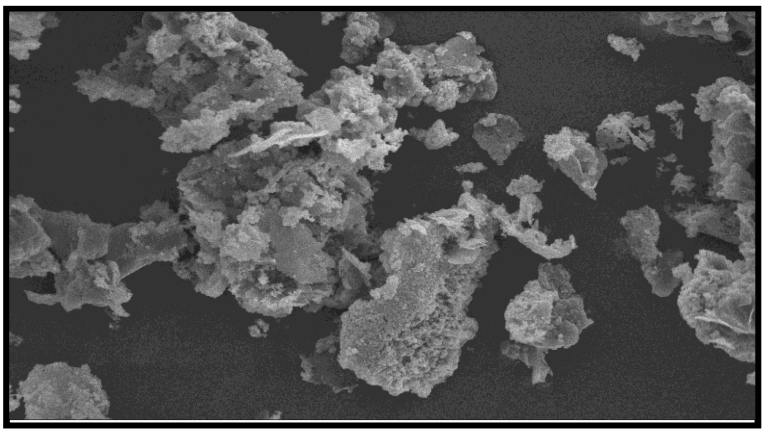


Figure 28: SEM 1000X catalyst 4.0 after calcined

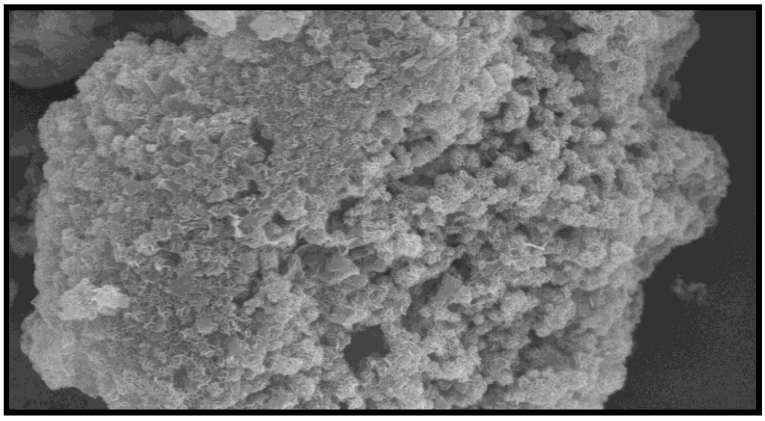


Figure 29: SEM 5000X catalyst 4.0 after calcined

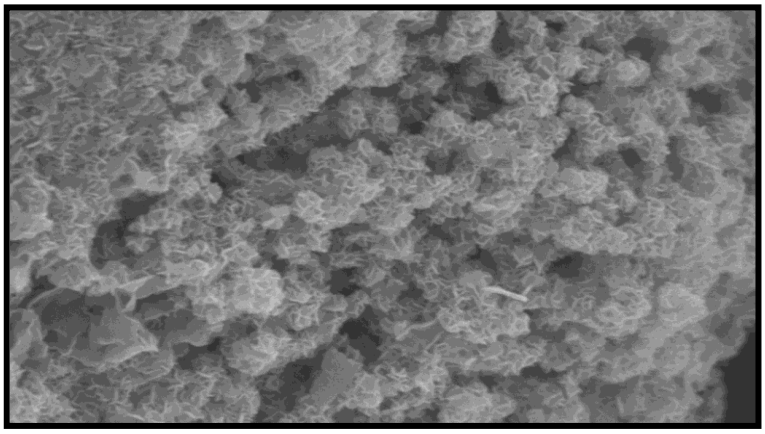


Figure 30: SEM 10000X catalyst 4.0 after calcined.

In order to determine the morphology and particle size distribution of Mg-Al hydrotalcite,we selected the hydrotalcite sample observe with SEM. It could be observed clearly from SEM image of uncalcined hydrotalcite that the sample formed well developed, thin flat crystals with various edges indicating the layered structure. The flat crystals with particle sizes in range of 3- 120 μm were observed by SEM and probably consisted of Mg-Al hydrotalcite crystals.Moreover,there were also many bar like particles and curved sheet..Also, there was some tendency for platelets to aggregate in the bar and platy sheet manner. As originally suggested by De Roy et al.the plate-plate overlapping of crystallites gave rise to interfaces that could accommodate extrinsic surface water, as well as other adsorbates[33].After calcined with temperature 773˚C,the particles combined and stick together.

4.3 Transesterification reaction

Transesterification of triglyceride with methanol, in the presence of catalyst yield esters of fatty acids and glycerin, monoglyceride and diglyceride are the intermediates.

$$\text{Triglyceride} + CH_3OH \leftrightarrow \text{Diglyceride} + R_1COOCH_3$$

$$\text{Diglyceride} + CH_3OH \leftrightarrow \text{Monoglyceride} + R_2COOCH_3$$

$$\text{Monoglyceride} + CH_3OH \leftrightarrow \text{Glycerin} + R_3COOCH_3$$

Overall reaction:

$$\text{Triglyceride} + 3CH_3OH \leftrightarrow 3RCOOCH_3 + \text{Glycerin}$$

The molar ratio of methanol to oil was one of the most important variables that affect ester formation because the conversion and the viscosity of produced ester depended on it. The stoichiometric molar ratio of methanol to oil is 2.0.But when mass transfer is limited due to problems of mixing, the mass transfer rate seems to be much slower than the reaction rate, and so the conversion can be elevated by introducing excess amount of the reactant methanol to shift the equilibrium to the right hand side. Higher molar ratios result in greater ester conversions in a shorter time. In addition, the conversion increased sharply with a reaction time, then reached a plateau value representative of a nearly equilibrium conversion after 4 h reaction. A nearly maximum conversion of 90.8% was obtained after 4h reaction time [4].

For data analysis, the samples have been taken out from the reaction for every an hour interval. The top part is biodiesel and the bottom part is the glycerol. Only the top part will be analyzed by using GC.

4.3.1Data Gathering

4.3.1.1 Data from GC analysis for catalyst loading 0.25 g/g with molar ratio of catalyst 3.0

Catalyst loading: 0.25 g/g of oil
Methanol/oil molar ratio: 3
Correction factor for total glycerol: 14.47368

Sample2 (1 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	30048	37529.95	543196.7	5904.312	0.822654
MG	38948	12463.36	12463.36	40.20439	0.005602
DG	334981	214387.8	214387.8	345.23	0.048101
TG	860624	827059.7	827059.7	887.4031	0.123643
				7177.149	1

Sample4 (2 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	47666	59534.83	861688.4	9366.178	0.9882
MG	26434	8458.88	8458.88	27.28671	0.002879
DG	82043	52507.52	52507.52	84.55317	0.008921
TG	-	-	-	-	-
				9478.018	1

Sample6 (3 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	76854	95990.65	1389338	15101.5	0.996367
MG	15955	5105.6	5105.6	16.46968	0.001087
DG	37454	23970.56	23970.56	38.59994	0.002547
TG	-	-	-	-	-
				15156.57	1

Sample8 (4 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	62518	78084.98	1130177	12284.54	0.992579
MG	31398	10047.36	10047.36	32.41084	0.002619
DG	57671	36909.44	36909.44	59.43549	0.004802
TG	-	-	-	-	-
				12376.38	1

Sample10 (6 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	131724	164523.3	2381258	25883.24	0.966922
MG	27878	8920.96	8920.96	28.77729	0.001075
DG	803751	514400.6	514400.6	828.3424	0.030944
TG	27476	26404.44	26404.44	28.33094	0.001058
				26768.69	1

Table 4: Data from GC analysis for catalyst loading 0.25 g/g with molar ratio of catalyst 3.0

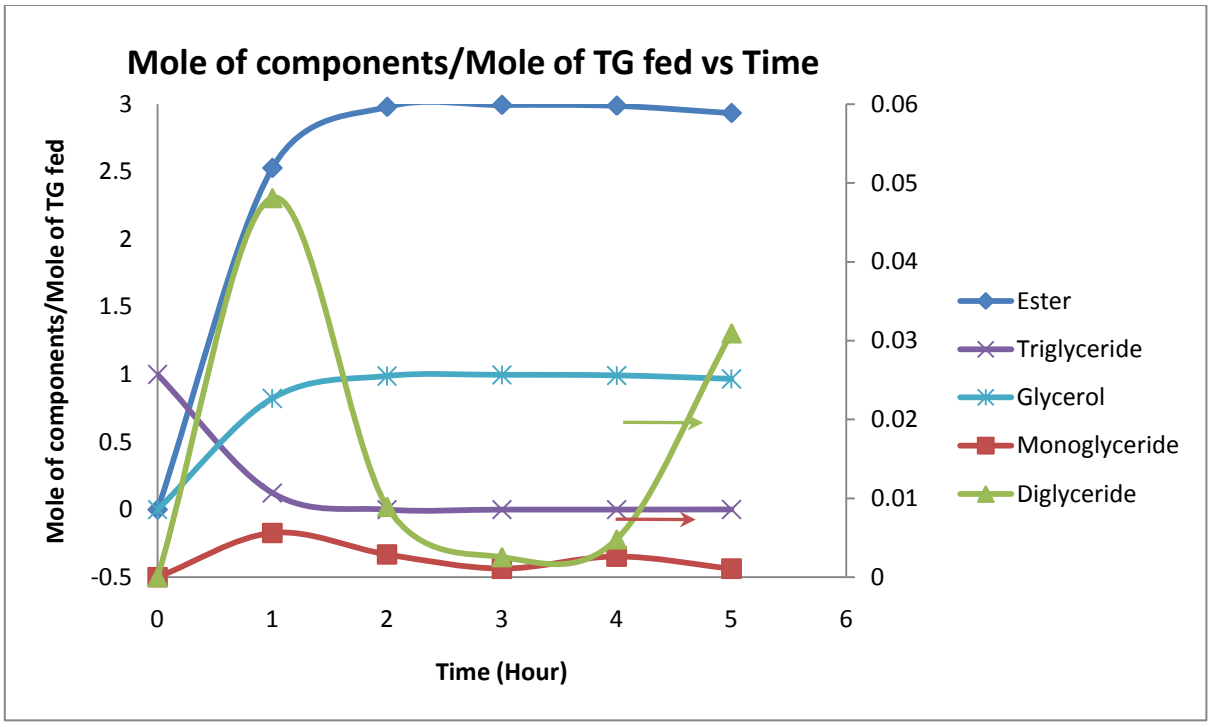


Figure 31: Graph on mole of components/Mole of TG fed vs Time

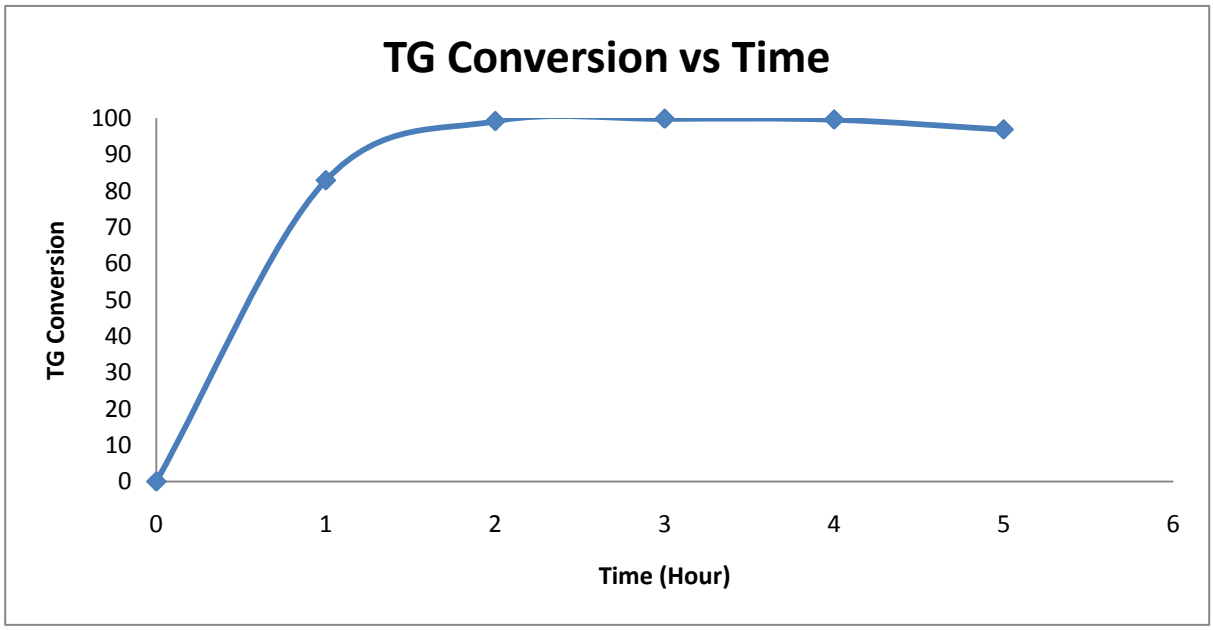


Figure 32: Graph on TG Conversion vs Time

Parameter A: Temperature: 60 , Catalyst loading 1.67 % for catalyst ratio 3.

Figure 31 shows graph on mole of components/Mole of TG fed vs Time for parameter temperature 60 , catalyst loading 0.25 g (1.67 % from 15ml of castor oil)for molar ratio of catalyst 3.0. From the graph, after 1 hour reaction, ester will produce at 2330g.The author then compared the result with different catalyst loading at 0.3 g (2% from 15 ml castor oil) for the same catalyst ratio 3.0.The author found that higher catalyst loading will result in greater production of ester. The author also compared the result between different in molar ratio of catalyst. Higher molar ratio with same catalyst loading (1.67% from 15 ml of castor oil) with produce more ester.Mg-Al hydrotalcites is an active multifunction catalyst that promote to the production of biodiesel. The reaction temperature is maintained at 60 .The temperature for the reaction is limited by methanol boiling point. At 65 .At 65 methanol will vaporize and the reaction will be in 3 phase.

Triglyceride will decrease proportionally to the time. Ester production is more than glycerin as ester in the main product in the reaction. Ester will be produced after 1 hour reaction.

From the TG conversion vs time graph, ester will be produced after 1 hour reaction and reach equilibrium after 2 hour reaction. Transesterification reaction is a reversible reaction. Equilibrium reaction is a state of balance in which two opposing reversible chemical reactions proceed at constant equal rates with no net change in the system.

4.3.1.2 Data from GC analysis for catalyst loading 0.25 g/g with molar ratio of catalyst 4.0

Catalyst loading: 0.25g
Methanol/oil molar ratio: 4

Correction factor for total glycerol: 14.47368

Sample12 (1 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	336461	420239.8	6082418	66113.24	0.998668
MG	59151	18928.32	18928.32	61.0591	0.000922
DG	26288	16824.32	16824.32	27.0923	0.000409
TG	-	-	-	-	-
				66201.39	1

Sample14 (2 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	32053	40034.2	579442.3	6298.286	0.987487
MG	54337	17387.84	17387.84	56.08981	0.008794
DG	23012	14727.68	14727.68	23.71607	0.003718
TG	-	-	-	-	-
				6378.092	1

Sample16 (3 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	33503	41845.25	605654.9	6583.205	0.979757
MG	65737	21035.84	21035.84	67.85755	0.010099
DG	66139	42328.96	42328.96	68.16258	0.010144
TG	-	-	-	-	-
				6719.225	1

Sample18 (4 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	527849	659283.4	9542260	103720.2	0.999561
MG	31453	10064.96	10064.96	32.46761	0.000313
DG	12673	8110.72	8110.72	13.06074	0.000126
TG	-	-	-	-	-
				103765.7	1

Sample20 (5 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	38033	47503.22	687546.6	7473.332	0.974582
MG	27278	8728.96	8728.96	28.15794	0.003672
DG	45713	29256.32	29256.32	47.11163	0.006144
TG	116030	111504.8	111504.8	119.6403	0.015602
				7668.242	1

Table 5: Data from GC analysis for catalyst loading 0.25 g/g with molar ratio of catalyst 4.0

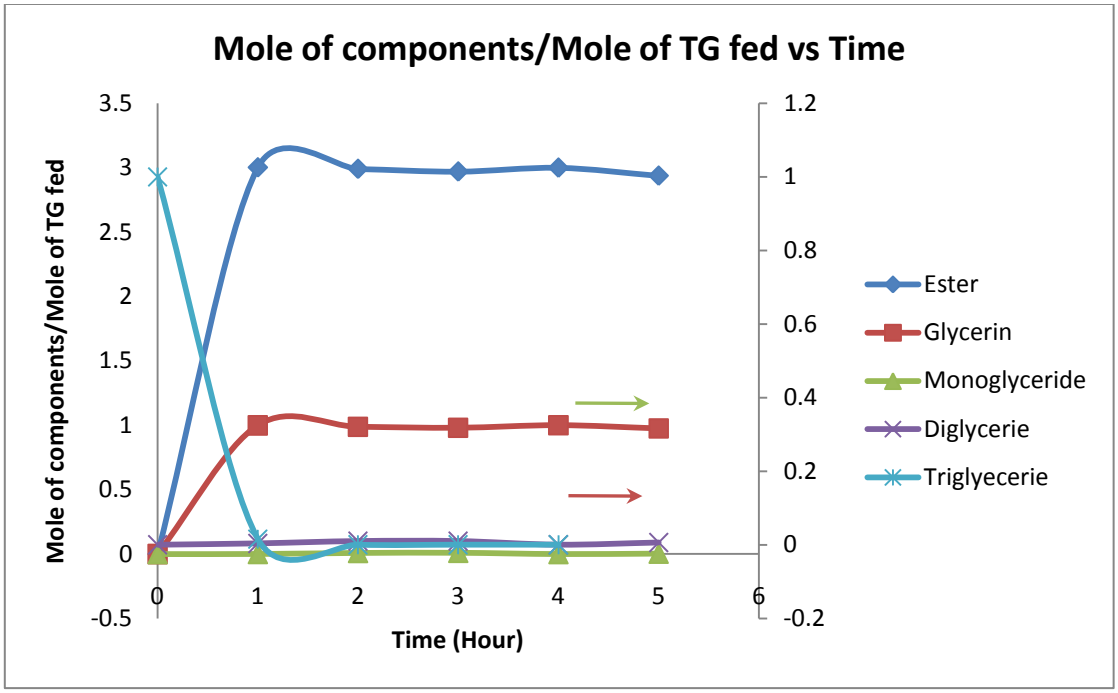


Figure 33: Graph on mole of components/Mole of TG fed vs Time

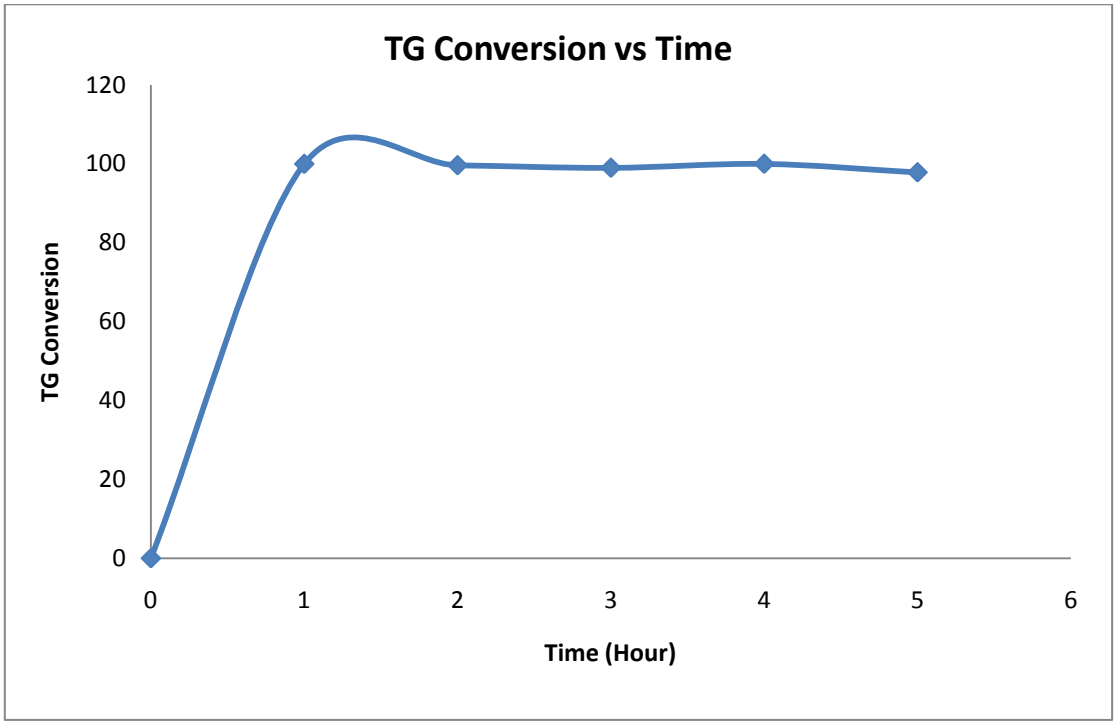


Figure 34: Graph on TG Conversion vs Time

Parameter B: Temperature: 60 , Catalyst loading 1.67% for catalyst ratio 4

Figure 33 shows graph on mole of components/Mole of TG fed vs Time for parameter temperature 60 , catalyst loading 0.25 g for molar ratio of catalyst 4.0. From the graph, after 1 hour reaction, ester will produce at 2796g.As compared to molar ratio of catalyst 3.0 while others parameter remain constant, more ester have been produced. The different is 466 g.This shows higher molar ratio of catalyst will produce more ester. The author also compared with different catalyst loading.0.3g catalyst loading will give slightly higher production compared to 0.25 g catalyst loading. The temperature for the reaction is maintained at 60 Boiling point of methanol is at 65 At 65 methanol will vaporized.

Ester will be produced after 1 hour reaction. Triglyceride will decrease proportionally to the time. Ester production is more than glycerin as ester in the main product in the reaction

From the TG conversion vs time graph on figure 34, ester will be produced after 1 hour reaction and reach equilibrium after 2 hour reaction. Transesterification reaction is a reversible reaction. At equilibrium, rate of reaction is constant.

4.3.1.3 Data from GC analysis for catalyst loading 0.3 g/g with molar ratio of catalyst 3.0

Catalyst loading: 0.3 g
Methanol/oil molar ratio: 3

Correction factor for total glycerol: 14.47368

Sample22 (1 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	38548	48146.45	696856.5	7574.528	0.997286
MG	1067	341.44	341.44	1.101419	0.000145
DG	18929	12114.56	12114.56	19.50815	0.002569
TG	-	-	-	-	-
				7595.137	1

Sample24 (2hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	100306	125282.2	1813295	19709.73	0.998587
MG	3857	1234.24	1234.24	3.981419	0.000202
DG	23206	14851.84	14851.84	23.91601	0.001212
TG	-	-	-	-	-
				19737.62	1

Sample26 (3 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	43357	54152.89	783791.9	8519.477	0.996737
MG	25627	8200.64	8200.64	26.45368	0.003095
DG	1396	893.44	893.44	1.438712	0.000168
TG	-	-	-	-	-
				8547.369	1

Sample28 (4 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	44352	55395.65	801779.1	8714.99	0.990817
MG	2783	890.56	890.56	2.872774	0.000327
DG	75590	48377.6	48377.6	77.90274	0.008857
TG	-	-	-	-	-
				8795.766	1

Table 6: Data from GC analysis for catalyst loading 0.3 g/g with molar ratio of catalyst 3.0

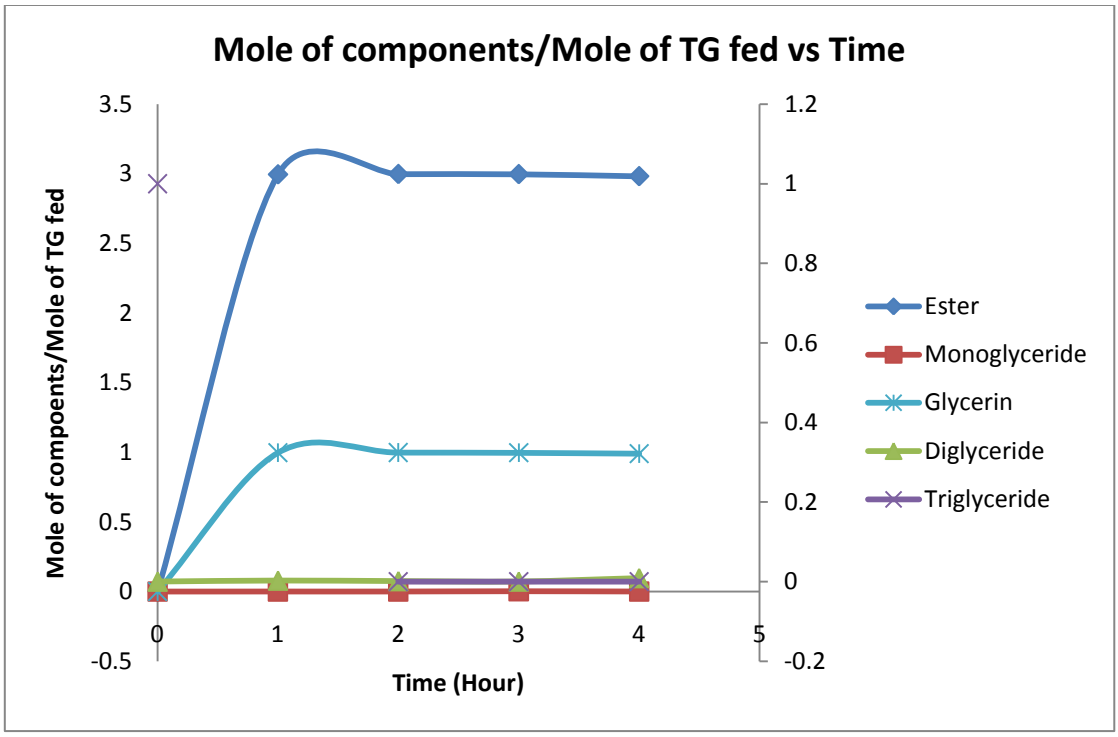


Figure 35: Graph on mole of components/Mole of TG fed vs Time

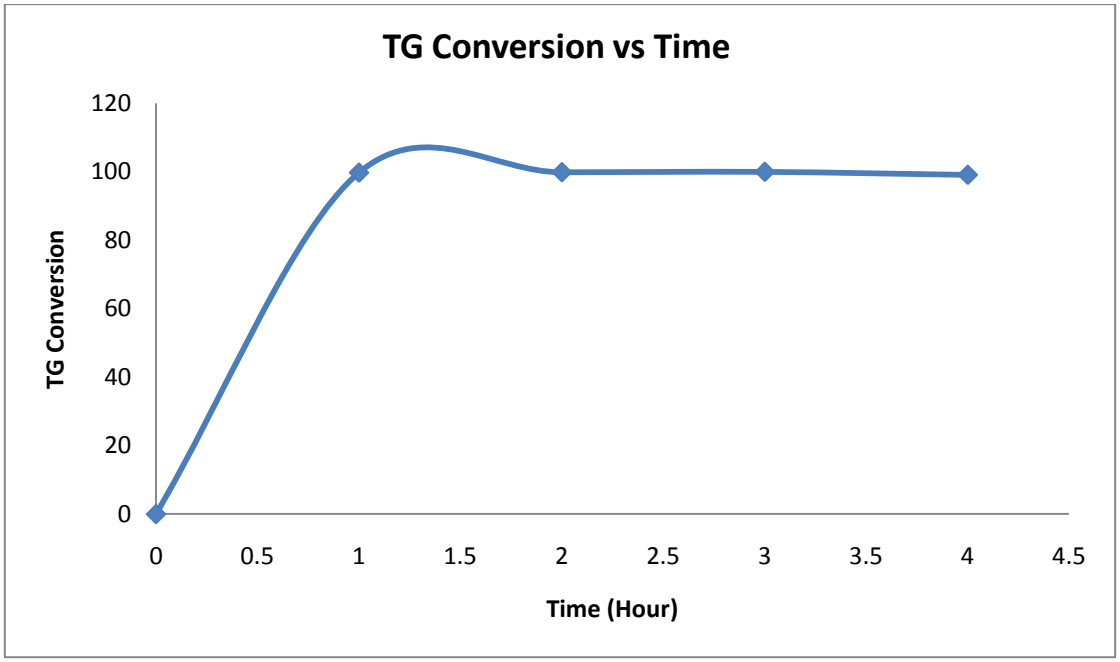


Figure 36: Graph on TG Conversion vs Time

Parameter C: Temperature: 60 , Catalyst loading 2 % for catalyst ratio 3.0.

Figure 35 shows graph on mole of components/Mole of TG fed vs Time for parameter temperature 60 , catalyst loading 0.3 g for molar ratio of catalyst 3.0. From the graph, after 1 hour reaction, ester will produce at 2796g.As compared to figure 31 for same parameter but different catalyst loading, more ester have been produced for 0.3g.

More catalyst loading will produce more ester. This has been proving by using 2 different catalysts loading for 0.25 g and 0.3g.Ester production is more than glycerin as ester in the main product in the reaction

From the TG conversion vs time graph, ester will be produced after 1 hour reaction and reach equilibrium after 2 hour reaction. Transesterification reaction is a reversible reaction. At equilibrium, rate of reaction is constant.

4.3.1.4 Data from GC analysis for catalyst loading 0.3 g/g with molar ratio of catalyst 4.0

Catalyst loading: 0.3g
Methanol/oil molar ratio: 4
Correction factor for total glycerol: 14.58333

Sample12 (1 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	56320	70343.68	1025845	11150.49	0.992156
MG	3764	1204.48	18928.32	61.0591	0.005433
DG	8616	5514.24	16824.32	27.0923	0.002411
TG	-	-	-	-	-
				11238.64	1

Sample14 (2 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	108939	136064.8	1984278	21568.24	0.996313
MG	39773	12727.36	17387.84	56.08981	0.002591
DG	1199	767.36	14727.68	23.71607	0.001096
TG	-	-	-	-	-
				21648.05	1

Sample16 (3 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	43011	53720.74	783427.4	8515.516	0.984278
MG	6614	2116.48	21035.84	67.85755	0.007843
DG	8936	5719.04	42328.96	68.16258	0.007879
TG	-	-	-	-	-
				8651.536	1

Sample18 (4 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	47533	59368.72	865793.8	9410.802	0.995185
MG	7876	2520.32	10064.96	32.46761	0.003433
DG	4983	3189.12	8110.72	13.06074	0.001381
TG	-	-	-	-	-
				9456.33	1

Sample20 (5 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	112966	141094.5	2057629	22365.53	0.996646
MG	20501	6560.32	8728.96	28.15794	0.001255
DG	28720	18380.8	29256.32	47.11163	0.002099
TG	-	-	-	-	-
				22440.8	1

Table 7: Data from GC analysis for catalyst loading 0.3 g/g with molar ratio of catalyst 4.0

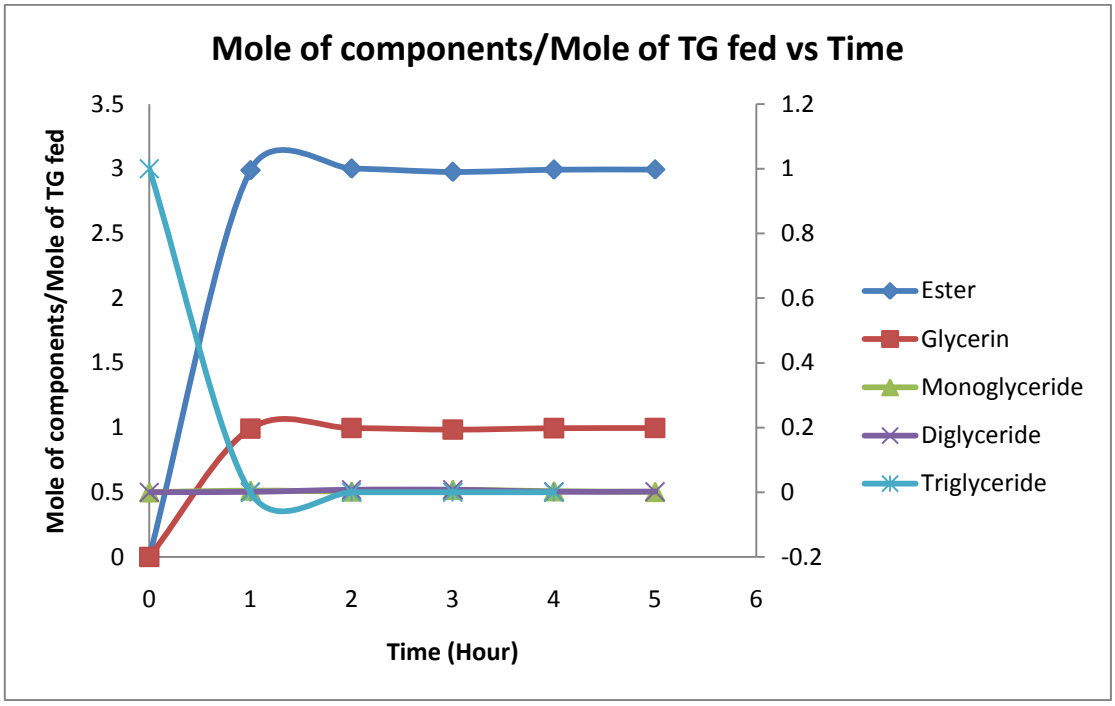


Figure 37: Graph on mole of components/Mole of TG fed vs Time

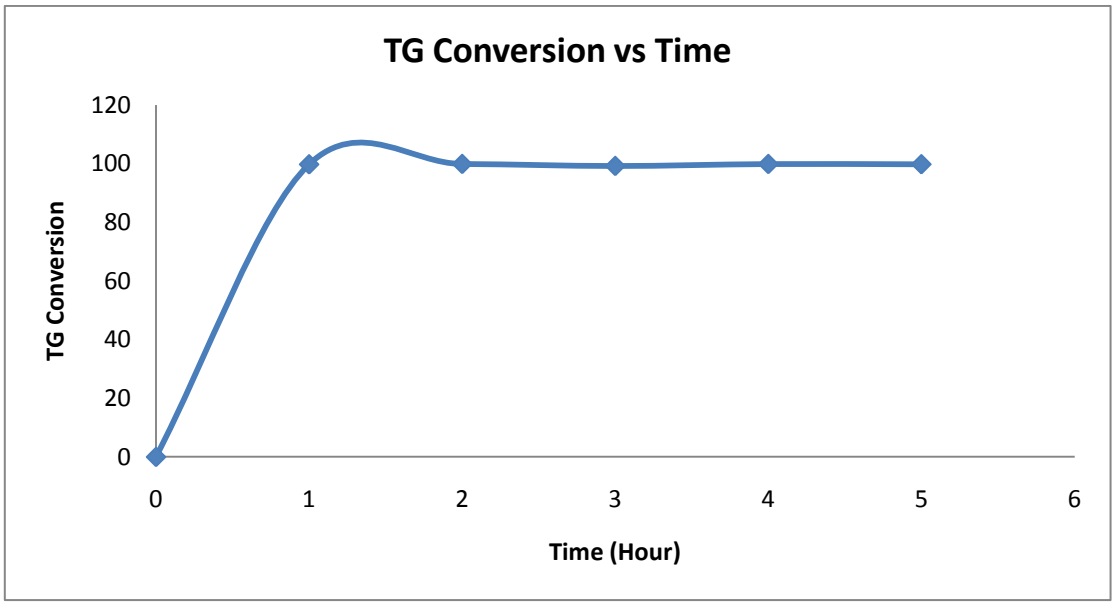


Figure 38: Graph on TG Conversion vs Time

Parameter D: Temperature: 60 , Catalyst loading 2% g for catalyst ratio 3.0

Figure 37 shows graph on mole of components/Mole of TG fed vs Time for parameter temperature 60 , catalyst loading 0.3 g for molar ratio of catalyst 4.0. From the graph, after 1 hour reaction, ester will produce at 2796g.

As compared to figure 33, no different in the amount of ester produced for the same parameter except for different catalyst loading. Catalyst loading for 0.25 g and 0.3 g molar ratio of catalyst 4.0 produced same amount of catalyst.

Ester will be produced after 1 hour reaction. Triglyceride will decrease proportionally to the time. Ester production is more than glycerin as ester in the main product in the reaction

The reaction temperature is maintained at 60 .The temperature for the reaction is limited by methanol boiling point. At 65 .At 65 methanol will vaporize and the reaction will be in 3 phase

From the TG conversion vs time graph on figure 38, ester will be produced after 1 hour reaction and reach equilibrium after 2 hour reaction. Transesterification reaction is a reversible reaction. For all parameters, it can be conclude that the reaction reach equilibrium after 2 hours of reaction.

4.3.2 Effect of time

The author carried out the experiment for 6 hours. As we can see from the graph, biodiesel is produced after 2 hours of reaction. The longer the reaction time, triglyceride will change to diglyceride and monoglyceride. This means that there is a reaction between the castor oil and methanol with the presence of the catalyst.

4.3.3 Effect of catalyst loading

The effect of catalyst can be seen that as the author increases the amount of catalyst from 2-5% ,there is not much significant difference in the amount of monoglyceride and diglyceride .The only change can be seen is only in the free fatty acid amount.

When increasing the amount of catalyst, the slurry (mixture of catalyst and reactants) becomes too viscous giving rise to a problem of mixing and a demand of higher power consumption for adequate stirring. On the other hand, when the catalyst amount is not sufficient, maximum conversion cannot be reached [4].

Mixing is very important for the transesterification if castor oil, because castor oil and methanol solution are immiscible. Generally, a more vigorous stirring speed causes better contact among the reactants and solid catalyst, resulting in the increase of reaction rate.

4.3.4 Effect of reaction temperature

The effect of reaction temperature on the ester conversion was studied with the catalyst at 60˚C temperature. From the literature, lower temperature resulted in a drop of the ester conversion because only a small amount of molecules was able to get over the required energy barrier. The optimum temperature for the preparation of the ester was found to be 65˚C, which was near the boiling point of anhydrous methanol. The conversion fell to about 80.0% in the temperature range 70 – 75˚C, probably because the molar rate of methanol to oil decreased when methanol reactant volatilized into gas phase above 65˚C, the boiling point of pure methanol [4].

CHAPTER 5
CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Transesterification of castor oil with methanol was studied in the presence of hydrotalcite-derived Mg-Al catalyst to produce methyl ester or biodiesel and glycerin. In the transesterification of castor oil, castor oil is totally consumed because of excess methanol. After the reaction was complete, the reaction products are separated into two layers, the ethyl esters formed the upper layer and the by-product glycerin formed the lower layer.

It is also observed that optimum reaction time for transesterification reaction is 2 hours .After 2 hours,the reaction become equilibrium. Catalyst loading does not have much effect on the production of biodiesel.

5.2 Recommendations

The following recommendations are made:

1. Molar ratio of methanol to castor oil should be varies to see the effect in the transesterification reaction.
2. The effect of temperature to the transesterification process should be studied.
3. Calcinations time and temperature need to be changed to see the effect to the transesterification reaction.
4. High Performance Liquid Chromatography (HPLC) can be used to analyze the conversion of triglycerides, diglycerides and monoglycerides and overall ethyl ester concentration.
5. Another multifunction catalyst can be used for transesterification process.

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Appendix

A. Calculations for catalyst preparation

Molar ratio of methanol to castor oil

Basis = 6:1

Molecular weight of castor oil = 927 g/mol

$$(\frac{gram}{MW})_{alcohol} \text{ x } (\frac{MW}{gram})_{oil} = 6$$

Assume 15 g of castor oil use in the transesterification reaction.

$$(\frac{(v)}{32.04g/mol})_{alcohol} \text{ x } (\frac{927g/mol}{15g})_{oil} = 6$$

$V_{methanol}$ = 10.36 ml by using 15g of castor oil

Concentration of catalyst that needs to be used (must be 1-2% from volume of oil)

Weight of hydrotalcite Mg-Al: 0.2g Percentage: $(\frac{0.2}{15g})$ x 100 = 1.33 %

Weight of hydrotalcite Mg-Al: 0.25g Percentage: $(\frac{0.25}{15})$ x100= 1.67 %

Weight of hydrotalcite Mg-Al: 0.3g Percentage: $(\frac{0.3}{15})$ x 100 = 2 %

Catalyst loading which will be used

A = $Mg(NO_3)_2.6H_2O$, Ma =284 g/gmole

B = $Al(NO_3)_3.9H_2O$, Mb = 417 g/gmole

C = $Na_2(CO_3)10H_2O$, Mc=286 g/gmole

Equations that are used

(i) $2[Mg(NO_3)_2.6H_2O] + Na_2(CO_3)10H_2O \rightarrow Mg_2(OH_2)_2.CO_3 + 2NaNO_3 + H_2O$

(ii) $Al(NO_3)_3.9H_2O + Na_2(CO_3)10H_2O \rightarrow Al(OH)CO_3 + 2NaNO_3 + H_2O$

The amount of $Mg(NO_3)_2.6H_2O$ & $Al(NO_3)_3.9H_2O$ needed

(a) Molar ratio of 3.0

$m_A + m_B = 50g$

$$(\frac{\text{Mole of A}}{\text{Mole of B}}) = 3.0 = (\frac{mA/MA}{mB/MB}) = (\frac{mA/284g/mol}{mB/417g/mol})$$

$m_A = 1.0216\ m_B$

$m_A + m_B = 50g$

$2.04\ m_B + m_B = 50g$

m_B = **16.43 g**while m_A = **33.56g**

To get the amount of Na2CO3.10H2O needed: Based on equation (i) and (ii):

(a) Mg:Na = 2:1

$$(\frac{NA}{NC}) = 2$$

$$\left(\frac{mA/MA}{mC1/MC}\right) = 2$$

$$\left(\frac{mA/284g/mol}{mB/286g/mol}\right) = 2$$

$m_A = 1.986\ m_{C1}$

$m_{C1} = 0.5035\ m_A$

(b) Al:Na = 1:1

$$\left(\frac{NB}{NC}\right) = 1$$

$$\left(\frac{mB/MB}{mC2/MC}\right) = 2$$

$$\left(\frac{mB/417g/mol}{mC2/286g/mol}\right) = 1$$

$m_{C2} = 0.686\ m_B$

$m_C = m_{C1} + m_{C2}$

$= 0.5035\ m_A + 0.685 m_B$

Molar ratio 3.0 $\rightarrow$ $M_C = 0.5035\ (33.56) + 0.685\ (16.43g)$

$= 28.152$ g

By using excess amount of 10% = (1.1) (28.152 g)

= **30.96g.**

B.Calculations for transesterification reaction

Catalyst loading: 0.25 g/g of oil
Methanol/oil molar ratio: 3
Correction factor for total glycerol: 14.47368

Sample2 (1 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	30048	37529.95	543196.7	5904.312	0.822654
MG	38948	12463.36	12463.36	40.20439	0.005602
DG	334981	214387.8	214387.8	345.23	0.048101
TG	860624	827059.7	827059.7	887.4031	0.123643
				7177.149	1

Sample4 (2 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	47666	59534.83	861688.4	9366.178	0.9882
MG	26434	8458.88	8458.88	27.28671	0.002879
DG	82043	52507.52	52507.52	84.55317	0.008921
TG	-	-	-	-	-
				9478.018	1

Sample6 (3 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	76854	95990.65	1389338	15101.5	0.996367
MG	15955	5105.6	5105.6	16.46968	0.001087
DG	37454	23970.56	23970.56	38.59994	0.002547
TG	-	-	-	-	-
				15156.57	1

Sample8 (4 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	62518	78084.98	1130177	12284.54	0.992579
MG	31398	10047.36	10047.36	32.41084	0.002619
DG	57671	36909.44	36909.44	59.43549	0.004802
TG	-	-	-	-	-
				12376.38	1

Sample10 (6 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	131724	164523.3	2381258	25883.24	0.966922
MG	27878	8920.96	8920.96	28.77729	0.001075
DG	803751	514400.6	514400.6	828.3424	0.030944
TG	27476	26404.44	26404.44	28.33094	0.001058
				26768.69	1

						Total				conversion, %
		x3	x2 - x3	x1 - x2	1 - x1	1	x2	x1	x1+x2+x3	x1*100
	Time, hr	G	MG	DG	TG				E	
	0	0	0	0	1	1	0	0	0	0
S2	1	0.822654	0.005602	0.048101	0.123643	1	0.828256	0.876357	2.527267	82.82559
S4	2	0.9882	0.002879	0.008921	-	1	0.991079	1	2.979279	99.1079
S6	3	0.996367	0.001087	0.002547	-	1	0.997453	1	2.99382	99.74533
S8	4	0.992579	0.002619	0.004802	-	1	0.995198	1	2.987777	99.51977
S10	5	0.966922	0.001075	0.030944	0.001058	1	0.967997	0.998942	2.933861	96.79972

Catalyst loading: 0.25g
Methanol/oil molar ratio: 4

Correction factor for total glycerol: 14.47368

Sample12 (1 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	336461	420239.8	6082418	66113.24	0.998668
MG	59151	18928.32	18928.32	61.0591	0.000922
DG	26288	16824.32	16824.32	27.0923	0.000409
TG					
				66201.39	1

Sample14 (2 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	32053	40034.2	579442.3	6298.286	0.987487
MG	54337	17387.84	17387.84	56.08981	0.008794
DG	23012	14727.68	14727.68	23.71607	0.003718
TG					
				6378.092	1

Sample16 (3 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	33503	41845.25	605654.9	6583.205	0.979757
MG	65737	21035.84	21035.84	67.85755	0.010099
DG	66139	42328.96	42328.96	68.16258	0.010144
TG					
				6719.225	1

Sample18 (4 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	527849	659283.4	9542260	103720.2	0.999561
MG	31453	10064.96	10064.96	32.46761	0.000313
DG	12673	8110.72	8110.72	13.06074	0.000126
TG					
				103765.7	1

Sample20 (5 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	38033	47503.22	687546.6	7473.332	0.974582
MG	27278	8728.96	8728.96	28.15794	0.003672
DG	45713	29256.32	29256.32	47.11163	0.006144
TG	116030	111504.8	111504.8	119.6403	0.015602
				7668.242	1

		x3	x2 - x3	x1 - x2	1 - x1	1	x2	x1	x1+x2+x3	x1*100
	Time, hr	G	MG	DG	TG				E	
	0	0	0	0	1	1	0	0	0	0
S2	1	0.998668	0.000922	0.003718	0.015602	1.018911	0.999591	1.003309	3.001568	99.95908
S4	2	0.987487	0.008794	0.010144	-	1.006426	0.996282	1.006426	2.990195	99.62816
S6	3	0.979757	0.010099	0.010144	-	1	0.989856	1	2.969612	98.98556
S8	4	0.999561	0.000313	0.000126	-	1	0.999874	1	2.999435	99.98741
S10	5	0.974582	0.003672	0.006144		0.984398	0.978254	0.984398	2.937234	97.82542

Catalyst loading: 0.3 g
Methanol/oil molar ratio: 3

Correction factor for total glycerol: 14.47368

Sample22 (1 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	38548	48146.45	696856.5	7574.528	0.997286
MG	1067	341.44	341.44	1.101419	0.000145
DG	18929	12114.56	12114.56	19.50815	0.002569
TG					
				7595.137	1

Sample24 (2hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	100306	125282.2	1813295	19709.73	0.998587
MG	3857	1234.24	1234.24	3.981419	0.000202
DG	23206	14851.84	14851.84	23.91601	0.001212
TG					
				19737.62	1

Sample26 (3 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	43357	54152.89	783791.9	8519.477	0.996737
MG	25627	8200.64	8200.64	26.45368	0.003095
DG	1396	893.44	893.44	1.438712	0.000168
TG					
				8547.369	1

Sample28 (4 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	44352	55395.65	801779.1	8714.99	0.990817
MG	2783	890.56	890.56	2.872774	0.000327
DG	75590	48377.6	48377.6	77.90274	0.008857
TG					
				8795.766	1

		x3	x2 - x3	x1 - x2	1 - x1	1	x2	x1	x1+x2+x3	x1*100
	Time, hr	G	MG	DG	TG				E	
	0	0	0	0	1	1	0	0	0	0
S2	1	0.997286	0.000145	0.002569		1	0.997431	1	2.994718	99.74315
S4	2	0.998587	0.000202	0.001212	-	1	0.998788	1	2.997375	99.87883
S6	3	0.996737	0.003095	0.000168	-	1	0.999832	1	2.996568	99.98317
S8	4	0.990817	0.000327	0.008857	-	1	0.991143	1	2.98196	99.11432

Catalyst loading: 0.3g
Methanol/oil molar ratio: 4

Correction factor for total glycerol: 14.58333

Sample12 (1 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	56320	70343.68	1025845	11150.49	0.992156
MG	3764	1204.48	18928.32	61.0591	0.005433
DG	8616	5514.24	16824.32	27.0923	0.002411
TG					
				11238.64	1

Sample14 (2 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	108939	136064.8	1984278	21568.24	0.996313
MG	39773	12727.36	17387.84	56.08981	0.002591
DG	1199	767.36	14727.68	23.71607	0.001096
TG					
				21648.05	1

Sample16 (3 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	43011	53720.74	783427.4	8515.516	0.984278
MG	6614	2116.48	21035.84	67.85755	0.007843
DG	8936	5719.04	42328.96	68.16258	0.007879
TG					
				8651.536	1

Sample18 (4 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	47533	59368.72	865793.8	9410.802	0.995185
MG	7876	2520.32	10064.96	32.46761	0.003433
DG	4983	3189.12	8110.72	13.06074	0.001381
TG					
				9456.33	1

Sample20 (5 hr)

	Area, ml	mass, g	mass, g	mol	mol fr
G	112966	141094.5	2057629	22365.53	0.996646
MG	20501	6560.32	8728.96	28.15794	0.001255
DG	28720	18380.8	29256.32	47.11163	0.002099
TG					
				22440.8	1

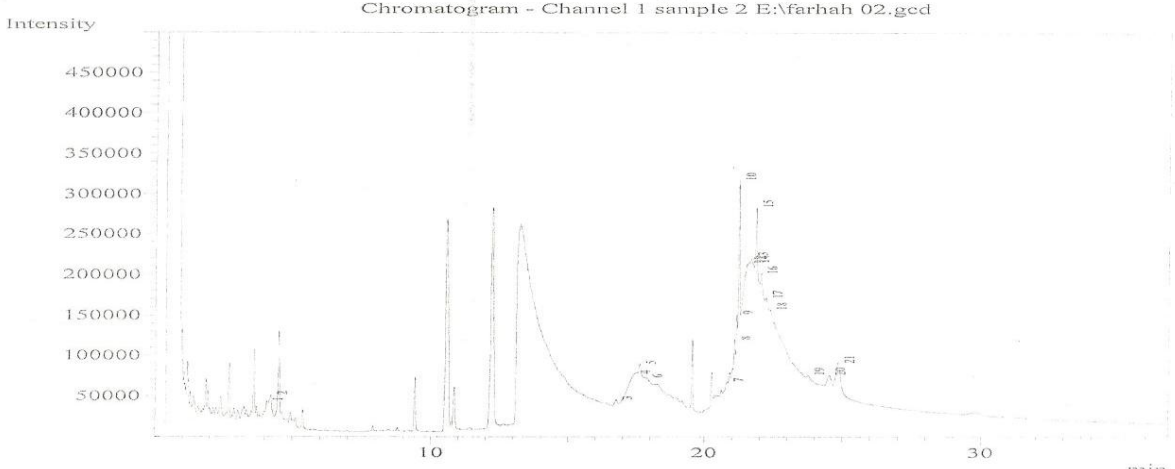
		x3	x2 - x3	x1 - x2	1 - x1	1	x2	x1	x1+x2+x3	x1*100
	Time, hr	G	MG	DG	TG				E	
	0	0	0	0	1	1	0	0	0	0
S2	1	0.992156	0.005433	0.001096	0	0.998685	0.997589	0.998685	2.988431	99.75894
S4	2	0.996313	0.002591	0.007879	-	1.006783	0.998904	1.006783	3.002001	99.89045
S6	3	0.984278	0.007843	0.007879	-	1	0.992121	1	2.976399	99.21213
S8	4	0.995185	0.003433	0.001381	-	1	0.998619	1	2.993804	99.86188
S10	5	0.996646	0.001255	0.002099		1	0.997901	1	2.994546	99.79006

Sample Information

Analysis Date & Time : 7/29/2010 5:23:21 AM

Sample Name : sample 2
Data Name : C:\GCsolution\Data\bioD 2008\mushtaq\farhah 02.gcd
Method Name : C:\GCsolution\Data\bioD 2008\total glyceride 2.gcm

Chromatogram - Channel 1 sample 2 E:\farhah 02.gcd



Peak Table - Channel 1

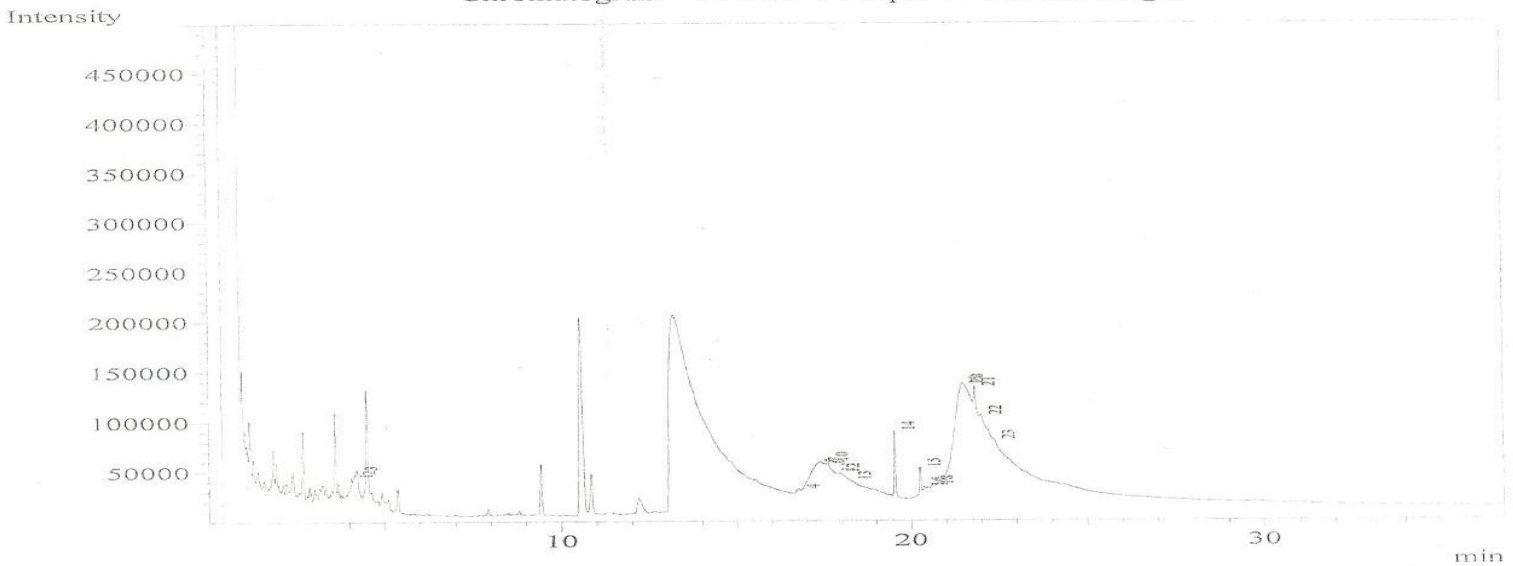
Peak#	Ret.Time	Area	Height	Conc.	Unit	Cmpd Name
1	4.069	30048	10888	0.000	ug	Glycerine
2	4.219	70121	13482	0.000		
3	16.763	38948	6277	0.000	ug	Mono-glyceride
4	17.398	559742	35393	0.000		
5	17.612	449196	46564	0.000	mg	
6	17.849	383497	28957	0.000		
7	20.819	334981	36220	0.000	ug	Di-glyceride
8	21.066	381819	88242	0.000		
9	21.146	423917	119893	0.000		
10	21.222	1157278	285372	0.000		
11	21.526	2425443	181402	0.000		
12	21.575	349876	182572	0.000		
13	21.667	959698	186562	0.000		
14	21.717	648764	182144	0.000		
15	21.840	2312240	250892	0.000		
16	22.027	1753635	168230	0.000		
17	22.208	1287991	137812	0.000		
18	22.371	5679031	122770	0.000		
19	23.751	860624	38789	0.000	ug	Tri-glyceride
20	24.520	602038	37384	0.000		
21	24.826	1001083	51842	0.000		
Total				0.000		

Sample Information

Analysis Date & Time : 7/29/2010 6:55:45 AM

Sample Name : sample 4
Data Name : C:\GCsolution\Data\bioD 2008\mushtaq\farhah 04.gcd
Method Name : C:\GCsolution\Data\bioD 2008\total glyceride 2.gcm

Chromatogram - Channel 1 sample 4 E:\farhah 04.gcd



Peak Table - Channel 1

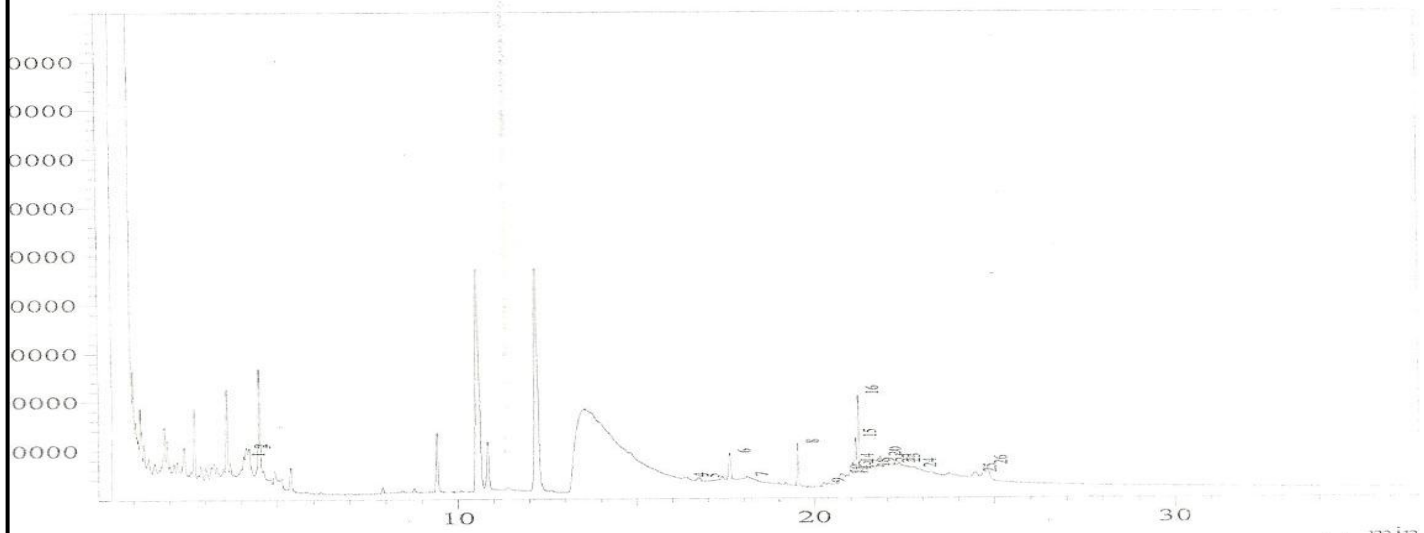
Peak#	Ret.Time	Area	Height	Conc.	Unit	Cmpd Name	mass %
1	4.068	30448	11045	0.000			
2	4.158	47666	11274	0.088	ug	Glycerine	3.86
3	4.217	41640	13948	0.000			
4	16.772	26434	3980	0.096	ug	Mono-glyceride	4.22
5	17.309	468788	28121	0.000		0.678	
6	17.355	52553	28846	0.000		0.695	
7	17.394	192099	29258	0.000		0.705	
8	17.486	34569	27203	0.000		0.655	
9	17.529	80839	26819	0.000		0.646	
10	17.610	308560	28893	0.000			
11	17.778	76036	18044	0.000			
12	17.917	307216	16566	0.000			
13	18.247	89420	7839	0.000			
14	19.524	179453	66034	0.000	ug	Tricaprin (IS)	
15	20.241	118296	30081	0.000			
16	20.355	50396	10249	0.000			
17	20.445	47327	9455	0.000			
18	20.600	82043	10803	2.093	ug	Di-glyceride	91.92%
19	21.467	2126333	108671	0.000		21.054	
20	21.514	1894798	109490	0.000		21.213	
21	21.836	1014691	105180	0.000		20.436	
22	22.019	1366689	75395	0.000			
23	22.366	1681430	49288	0.000			
Total				2.277			

P: 99.99

Date & Time : 7/29/2010 8:31:43 AM

Name : sample 6
ne : C:\GCsolution\Data\bioD 2008\mushtaq\farhah 06.gcd
Name : C:\GCsolution\Data\bioD 2008\total glyceride 2.gcm

Chromatogram - Channel 1 sample 6 E:\farhah 06.gcd



÷ mV

Peak Table - Channel 1

#	Ret.Time	Area	Height	Conc.	Unit	Cmpd Name
	4.067	30179	11414	0.000		
	4.133	76854	18082	0.240	ug	Glycerine
	4.215	44153	15161	0.000		
	16.366	15955	1845	0.087	ug	Mono-glyceride
	16.741	21533	3370	0.000		
	17.604	114099	26630	0.000		
	18.100	23384	2179	0.000		
	19.519	117436	43289	0.000	ug	Tricaprin (IS)
	20.241	16228	3535	0.000		
	20.751	67231	10135	0.000		
	20.809	24985	8709	0.000		
	20.889	37454	8420	1.673	ug	Di-glyceride
	20.980	50990	13014	0.000		
	21.054	72733	20177	0.000		
	21.134	141218	45137	0.000		
	21.208	314062	89319	0.000		
	21.351	109936	12572	0.000		
	21.498	61600	13277	0.000		
	21.651	166247	12839	0.000		
	21.829	147173	23128	0.000		
	22.014	160453	16206	0.000		
	22.210	158857	14208	0.000		
	22.354	140763	13883	0.000		
	22.801	235863	6966	0.000		
	24.467	36231	4413	0.000		
	24.772	139518	14113	0.000		
				2.000		

weight %
12 %
4.35 %
0.159
1.256
0.103
83.65 %
2.586
4.009
8.968
17.746
2.498

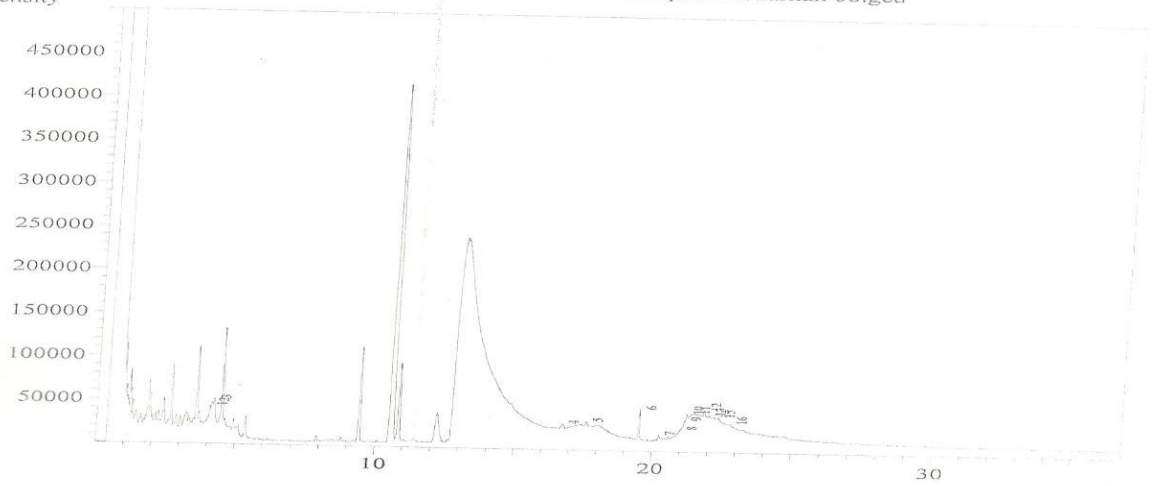
P: 99.998

Sample Information

Analysis Date & Time : 7/29/2010 10:05:16 AM

Sample Name : sample 8
Data Name : C:\GCsolution\Data\bioD 2008\mushtaq\farhah 08.gcd
Method Name : C:\GCsolution\Data\bioD 2008\total glyceride 2.gcm

Chromatogram - Channel 1 sample 8 E:\farhah 08.gcd



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Cmpd Name	Weight / min
1	4.066	33230	11959	0.000			
2	4.136	62518	14415	0.241	ug	Glycerine	7.95 /
3	4.214	45460	15533	0.000		0.2597	
4	16.739	31398	5004	0.245	ug	Mono-glyceride	8.08 /
5	17.604	39793	5828	0.000		0.285	
6	19.517	95140	34313	0.000	ug	Tricaprin (IS)	
7	20.233	21273	5603	0.000			
8	21.002	57671	8557	2.545	ug	Di-glyceride	83.94 /
9	21.139	121266	18784	0.000		5.587	
10	21.211	125321	25896	0.000		7.702	
11	21.430	733846	25429	0.000		7.563	
12	21.828	250372	27698	0.000			
13	22.010	191826	20984	0.000			
14	22.195	191673	18366	0.000			
15	22.350	298395	17475	0.000			
16	22.792	115163	8141	0.000			
Total				3.032			

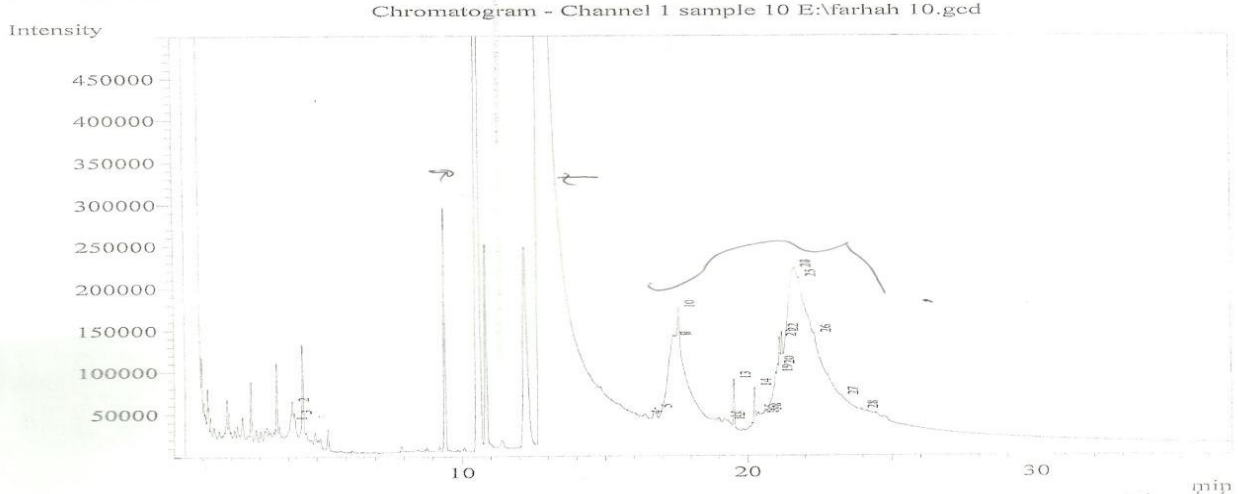
P : 99.99 /.

Sample Information

Analysis Date & Time : 7/29/2010 11:39:05 AM

Sample Name : sample 10
Data Name : C:\GCsolution\Data\bioD 2008\mushtaq\farhah 10.gcd
Method Name : C:\GCsolution\Data\bioD 2008\total glyceride 2.gcm

Chromatogram - Channel 1 sample 10 E:\farhah 10.gcd



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Cmpd Name
1	4.068	27802	11993	0.000		
2	4.128	131724	32450	0.329	ug	Glycerine
3	4.214	44412	15637	0.000		
4	16.396	27878	3640	0.128	ug	Mono-glyceride
5	16.753	85810	12917	0.000		
6	17.415	1455298	99528	0.000		
7	17.440	134986	99591	0.000		
8	17.461	182298	99495	0.000		
9	17.497	205945	99866	0.000		
10	17.608	2507245	132180	0.000		
11	19.178	27575	4756	0.000		
12	19.311	29850	3964	0.000		
13	19.518	149687	56267	0.000	ug	Tricaprin (IS)
14	20.235	197232	49865	0.000		
15	20.365	107758	18720	0.000		
16	20.451	50108	15720	0.000		
17	20.511	62198	16290	0.000		
18	20.589	97829	18645	0.000		
19	20.988	803751	62582	17.009	ug	Di-glyceride
20	21.065	305042	72223	0.000		
21	21.137	454278	104729	0.000		
22	21.213	510957	110632	0.000		
23	21.649	3371577	184731	0.000		
24	21.672	1451579	183933	0.000		
25	21.826	4166838	171945	0.000		
26	22.349	2939012	102847	0.000		
27	23.267	409156	22618	0.000		
28	23.939	27476	2515	0.607	ug	Tri-glyceride
Total				18.072		

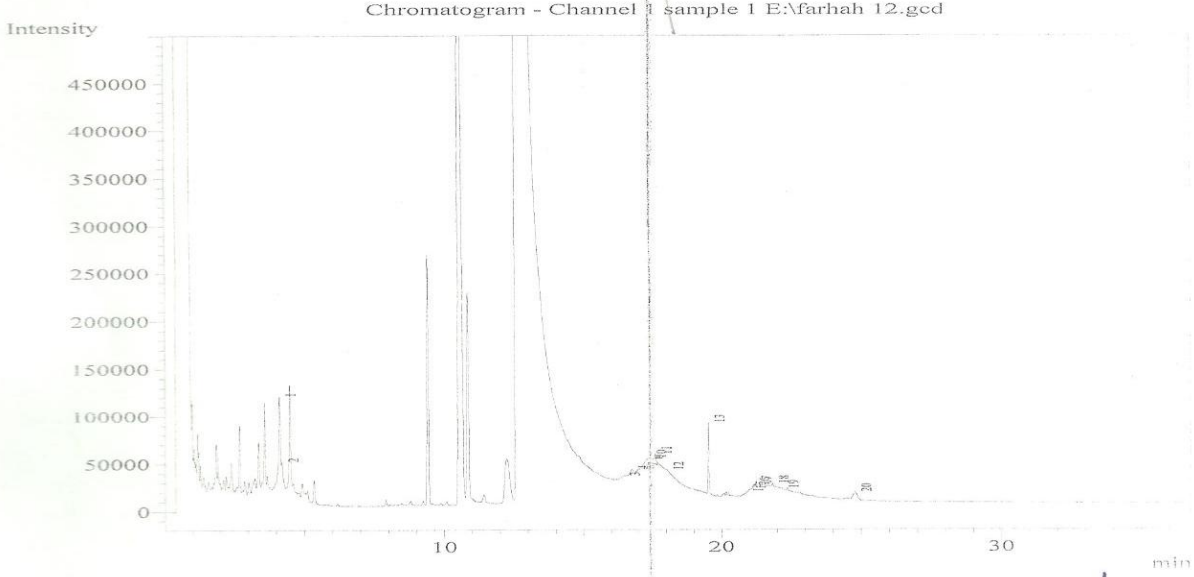
Weight /
1.82 /.
0.71 /.
94.12 /
3.35 /
p: 99.982

Sample Information

Analysis Date & Time : 7/30/2010 7:00:52 AM

Sample Name : sample 1
Data Name : C:\GCsolution\Data\bioD 2008\mushtaq\farhah 12.gcd
Method Name : C:\GCsolution\Data\bioD 2008\total glyceride 2.gcm

Chromatogram - Channel 1 sample 1 E:\farhah 12.gcd



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Cmpd Name
1	4.130	336461	86393	64.224	ug	Glycerine
2	4.218	35379	14235	0.000		
3	16.459	59151	4182	21.678	ug	Mono-glyceride
4	16.763	114242	12182	0.000		
5	16.965	85028	12391	0.000		
6	16.997	55618	13279	0.000		
7	17.125	85295	16803	0.000		
8	17.310	243451	24850	0.000		
9	17.353	100225	25629	0.000		
10	17.408	169070	26434	0.000		
11	17.603	657131	31242	0.000		
12	18.045	359298	16292	0.000		
13	19.524	202239	75186	0.000	ug	Tricaprin (IS)
14	20.907	26288	3577	111.011	ug	Di-glyceride
15	21.002	30916	5776	0.000		
16	21.141	36723	9072	0.000		
17	21.214	50391	10419	0.000		
18	21.832	268193	8253	0.000		
19	22.190	57320	1783	0.000		
20	24.786	78590	7692	0.000		
Total				196.913		

Mole con
Weight %
32.6 %
10.582
11.0 %
63.147
64.230
68.833
56.4 %
179.256
281.546
323.35

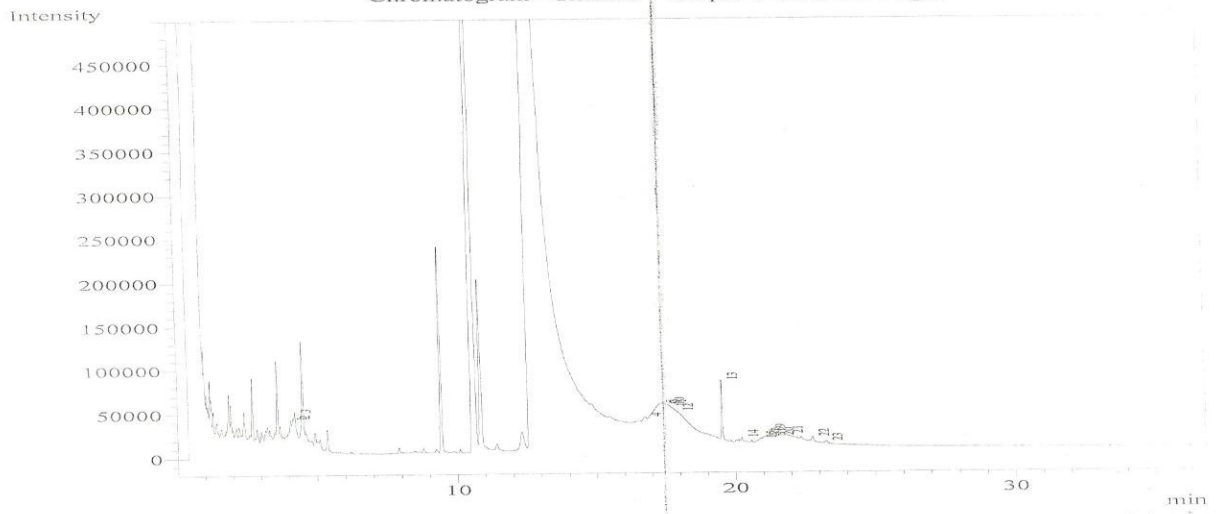
P : 99.80

Sample Information

Analysis Date & Time : 7/30/2010 8:33:09 AM

Sample Name : sample 3
Data Name : C:\GCsolution\Data\bioD 2008\mushtaq\farhah 14.gcd
Method Name : C:\GCsolution\Data\bioD 2008\total glyceride 2.gcm

Chromatogram - Channel 1 sample 3 E:\farhah 14.gcd



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Cmpd Name
1	4.067	32275	11508	0.000		
2	4.166	32053	9571	5.164	ug	Glycerine
3	4.216	46942	15012	0.000		
4	16.750	54337	6697	21.637	ug	Mono-glyceride
5	17.302	440761	24638	0.000		
6	17.395	187615	25534	0.000		
7	17.445	18012	25084	0.000		
8	17.469	65641	25048	0.000		
9	17.558	107451	24956	0.000		
10	17.599	158210	24757	0.000		
11	17.681	252600	23144	0.000		
12	17.890	482461	19611	0.000		
13	19.520	186103	67527	0.000	ug	Tricaprin (IS)
14	20.232	14761	4656	0.000		
15	20.891	23012	3271	109.068	ug	Di-glyceride
16	20.997	22234	4388	0.000		
17	21.064	20572	5200	0.000		
18	21.138	24056	6285	0.000		
19	21.210	44286	9437	0.000		
20	21.498	117845	4515	0.000		
21	21.828	29503	5216	0.000		
22	22.774	26927	5470	0.000		
23	23.255	16287	2775	0.000		
Total				135.868		

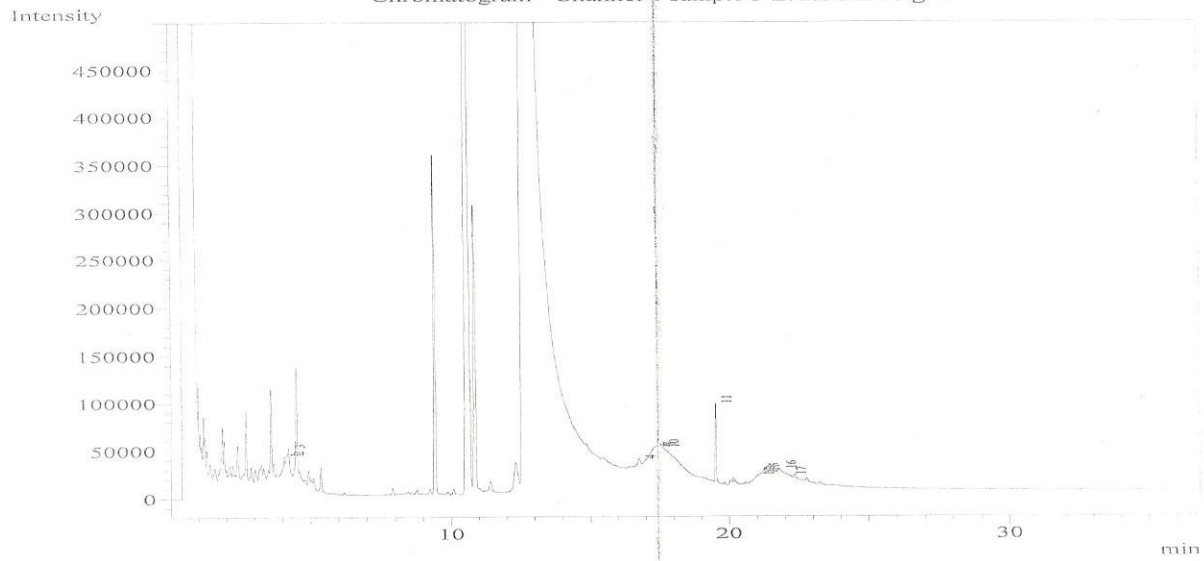
weight /.
3.8
8.0996
15.93 /.
79.602
82.497
80.27 /.
146 313
173 39
209 57
P: 99.86 /.

Sample Information

Analysis Date & Time : 7/30/2010 10:06:00 AM

Sample Name : sample 5
Data Name : C:\GCsolution\Data\bioD 2008\mushtaq\farhah 16.gcd
Method Name : C:\GCsolution\Data\bioD 2008\total glyceride 2.gcm

Chromatogram - Channel 1 sample 5 E:\farhah 16.gcd



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Cmpd Name	Weight %
1	4.066	34109	12048	0.000			
2	4.169	33503	10262	4.411	ug	Glycerine	2.313
3	4.215	50412	16017	0.000		6.884?	
4	16.756	65737	8511	22.352	ug	Mono-glyceride	11.72 %
5	17.283	379213	23318	0.000		61.238	
6	17.343	73545	24201	0.000		63.554	
7	17.390	63420	24957	0.000		65.542	
8	17.430	138747	25233	0.000			
9	17.520	134209	25341	0.000			
10	17.607	825291	24502	0.000			
11	19.518	218644	82558	0.000	ug	Tricaprin (IS)	
12	21.002	66139	6800	163.916	ug	Di-glyceride	85.96 %
13	21.063	37973	7860	0.000		189.468	
14	21.143	32099	8613	0.000		207.619	
15	21.210	52770	10419	0.000		251.153	
16	21.824	422203	10577	0.000			
17	22.163	54475	2849	0.000			
Total				190.679			

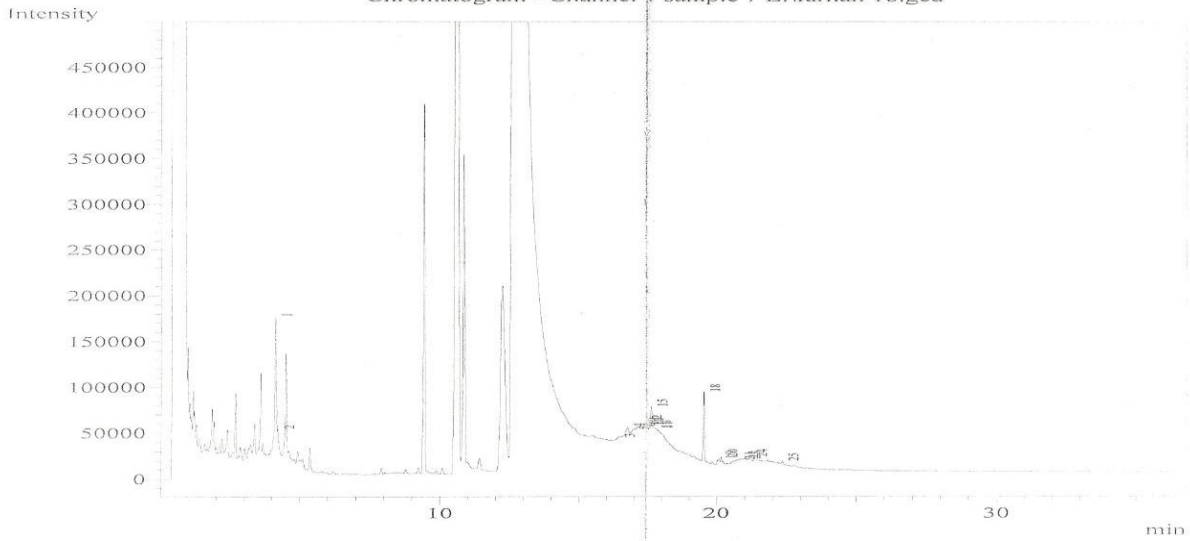
P: 99.8%

Sample Information

Analysis Date & Time : 7/30/2010 11:39:02 AM

Sample Name : sample 7
Data Name : C:\GCsolution\Data\bioD 2008\mushtaq\farhah 18.gcd
Method Name : C:\GCsolution\Data\bioD 2008\total glyceride 2.gcm

Chromatogram - Channel 1 sample 7 E:\farhah 18.gcd



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Cmpd Name	Weight %
1	4.126	527849	141492	99.935	ug	Glycerine	49.9 %
2	4.213	40638	16316	0.000		11.524	
3	16.431	31453	2908	10.182	ug	Mono-glyceride	5.089 %
4	16.748	108126	12353	0.000		43.252	
5	16.953	55996	8731	0.000		30.570	
6	17.015	37208	9402	0.000		32.919	
7	17.107	47582	10683	0.000			
8	17.138	26880	11027	0.000			
9	17.181	26047	11337	0.000			
10	17.234	31883	12017	0.000			
11	17.285	46948	12786	0.000			
12	17.399	117305	14172	0.000			
13	17.465	14202	11222	0.000			
14	17.485	13694	10844	0.000			
15	17.605	217147	31066	0.000			
16	17.746	24428	6808	0.000			
17	17.797	33771	5874	0.000			
18	19.518	205749	75802	0.000	ug	Tricaprin (IS)	
19	20.086	20904	6013	0.000			
20	20.155	23156	7732	0.000			
21	20.770	39962	3247	0.000			
22	20.888	12673	3424	90.036	ug	Di-glyceride	44.98 %
23	20.986	18737	3389	0.000		89.116	
24	21.206	13225	4318	0.000		113.54	
25	22.347	12392	3427	0.000			
Total				200.153			

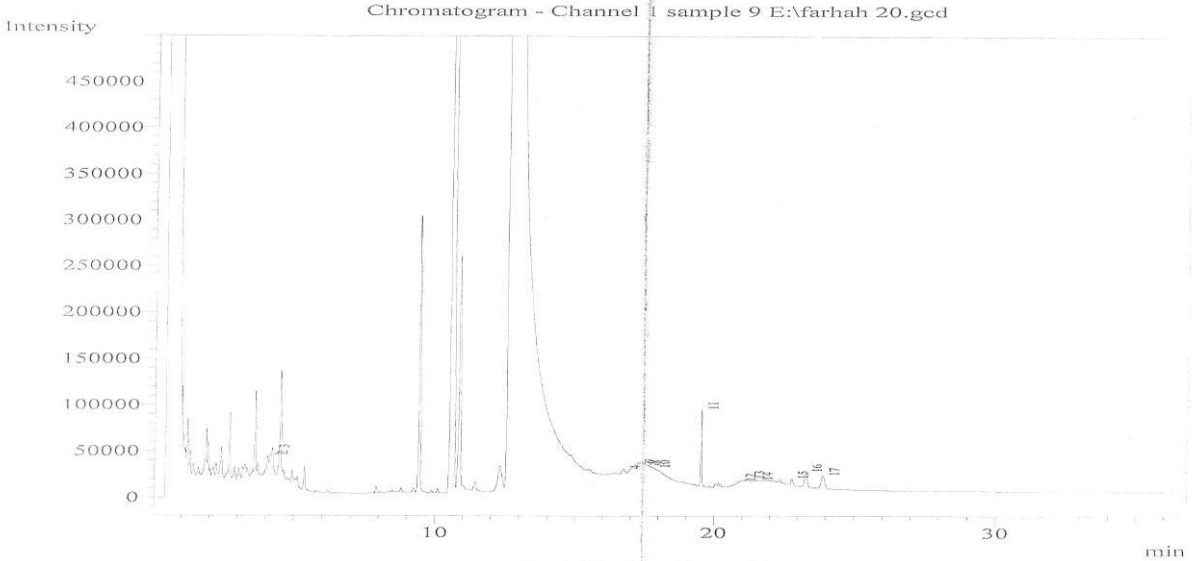
P: 99.8

Sample Information

Analysis Date & Time : 7/30/2010 1:12:07 PM

Sample Name : sample 9
Data Name : C:\GCsolution\Data\bioD 2008\mushtaq\farhah 20.gcd
Method Name : C:\GCsolution\Data\bioD 2008\total glyceride 2.gcm

Chromatogram - Channel 1 sample 9 E:\farhah 20.gcd



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Cmpd Name	Weight %
1	4.063	35122	12436	0.000			
2	4.163	38033	11057	5.144	ug	Glycerine	1.828
3	4.212	53974	16517	0.000		7.684	
4	16.745	27278	4511	7.736	ug	Mono-glyceride	2.75
5	17.154	82066	7764	0.000		13.315	
6	17.244	48140	9253	0.000		15.868	
7	17.279	33977	9661	0.000		16.568	
8	17.450	69161	8215	0.000			
9	17.611	84193	6388	0.000			
10	17.819	30665	2800	0.000			
11	19.517	221454	82513	0.000	ug	Tricaprin (IS)	
12	20.890	45713	4212	134.452	ug	Di-glyceride	47.79 %
13	21.205	27911	5597	0.000		178.663	
14	21.500	40696	2731	0.000		87.1768	
15	22.773	34086	6644	0.000			
16	23.268	101997	15880	0.000			
17	23.889	116030	13537	134.020	ug	Tri-glyceride	47.63 %
Total				281.353			

P : 99.72 .