BIODIESEL PRODUCTION VIA HOMOGENEOUS LEWIS ACID CATALYZED TRANSESTERIFICATION

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BIODIESEL PRODUCTION VIA HOMOGENEOUS LEWIS ACID CATALYZED TRANSESTERIFICATION

DIYANTI BINTI ABD RAHMAN

**A thesis submitted in fulfillment of the
requirements for the award of the degree of
Bachelor of Chemical Engineering**

**Faculty of Chemical and Natural Resources Engineering
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APRIL, 2010

“I declare that this thesis entitled “Biodiesel Production via Homogeneous Lewis Acid Catalyzed Transesterification” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree”

Signature : ………………………………………….....
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Date : 30th APRIL 2010

To my beloved parents, sisters & best friends..

Thank you for your support, guidance and confidence in me..

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ABSTRACT

The transesterification of triglyceride mostly found in vegetable oils with methanol using homogeneous lewis acid is one of promising method to convert triglyceride into fatty acid methyl ester which is an alternative to replace fossil fuel as energy source mostly in transportation industry. This study aimed to determine the conversion of fatty acid methyl ester and also to determine the optimum conditions for the production of methyl ester via transesterification process using aluminium chloride as the catalyst and methanol as solvent. By using conventional catalyst such as NaOH and KOH, it formed soap via saponification process and produce huge amount of wastewater in order to separate the reactant and product. Scopes for this research including the effect of molar ratio methanol to oil, effect of reaction temperature and effect of catalyst concentration. After experiments have been done, the most optimum conditions for sunflower oil transesterification can be achived at reaction temperature is 100°C, molar ratio 12:1 methanol to oil and 5 g of aluminium chloride. The highest conversion from these conditions is 91% conversion of fatty acid methyl ester.

ABSTRAK

Pengtransesteran trigliserida banyak ditemui di minyak sayuran dengan metanol menggunakan asid homogen Lewis yang merupakan salah satu cara untuk menukar trigliserida menjadi metil ester asid lemak yang merupakan alternatif untuk menggantikan bahan bakar fosil sebagai sumber tenaga terutama dalam industri pengangkutan. Penelitian ini bertujuan untuk menentukan penukaran metil ester asid lemak dan juga untuk menentukan keadaan optimum untuk pengeluaran metil ester melalui proses pengtransesteran menggunakan aluminium klorida sebagai mangkin dan metanol sebagai pelarut. Dengan menggunakan mangkin konvensional seperti NaOH dan KOH, ianya menyebabkan pembentukan sabun melalui proses saponifikasi dan menghasilkan sejumlah besar sisa air dalam usaha untuk memisahkan reaktan dan produk. Skop penelitian ini termasuk pengaruh nisbah molar metanol minyak, pengaruh suhu dan pengaruh reaksi konsentrasi mangkin. Setelah percubaan telah dilakukan, keadaan yang paling optimum untuk pengtransesteran minyak bunga matahari dapat dicapai pada suhu reaksi 100 ° C, nisbah molar metanol 12:1 untuk minyak dan 5 g aluminium klorida. Penukaran tertinggi dari keadaan ini adalah penukaran 91% metil ester asid lemak.

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T	-	Temperature
°C	-	Degree Celcius
ml	-	Mililiter
kJ	-	KiloJoule
min	-	Minute
K	-	Kelvin
w/w	-	Weight per weight
kg	-	Kilogram
g	-	Gram
%	-	Percentage
rpm		Revolutions per minute
M		Molar (mol/dm^3)
FFA	-	Free Fatty Acid

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CHAPTER 1

INTRODUCTION

The whole world is slowly accepting the fact that the main source for fuel and energy are rapidly depleted. The major energy supplier for the whole world is petroleum derived fuel that has wide range of industry application. Oil geologists, oil company executives and most scientists know the fact that an oil crisis is nearly upon us. World peak oil production is about to happen whether in a few years or within the decade, world oil production will decline. Peak oil is the point in time when the maximum rate of global petroleum extraction is reached, after which the rate of production enters terminal decline. Eventually, some of the world's oil producing regions has already experienced steep declines. It happened in the US in 1971. It happened in the North Sea in 1999. It happened in Mexico in 2006.

Generally, biodiesel is a non-toxic, biodegradable and greenhouse gas neutral. Modern diesel engine technology has advanced to the point where the advantages of biofuel usage are becoming much greater than the disadvantages such as less noise, smoke or vibrations and they are more fuel-efficient than older model engines. Besides, diesel engines have the added advantage of greater acceleration when compared to gasoline engines on the same model of vehicle.

Basically, diesel fuel is one of the petroleum based fuels. It has variety of application especially in transportation and development of country. Moreover, diesel is widely used for agriculture purpose and equipment like tractors and trucks and also other application that involve the uses of machinery equipment. Unluckily, the price of diesel fuel is not really constant and until today, the price of diesel issue for every consumer because the increasing of diesel fuel gives a huge impact. Eventually, researches came up with some fresh new ideas to develop an alternative to replace the current energy source. A lot of effort has been carried out such as methanol, ethanol, hydro power, solar energy and geothermal energy as energy sources while for transportation vehicle system, liquefied petroleum gas (LPG), liquefied natural gas (LNG), reformulated gasoline, reformulated diesel fuel have been considered as an alternative way for replacing diesel fuel.

Human caused global warming is one of the greatest and the most urgent challenges facing humanity and life on earth today. The main culprit is the enormous amount of the potent greenhouse gas carbon dioxide (CO_2) released into the atmosphere by burning of fossil fuels (petroleum, coal, natural gas). Burning fossil fuels releases more than 6 billion tons of CO_2 per year, twice as much as the biosphere can absorb. The excess of CO_2 is clogging the atmosphere, with the result that less solar heat is reflected away, more heat reaches the earth's surface, and global temperatures rise. In term of environment benefit, biodiesel contains no sulfur or aromatics, and use of biodiesel in a conventional diesel engine results in substantial reduction of unburned hydrocarbons, carbon monoxide and particulate matter. U.S. Department of Energy study showed that the production and use of biodiesel, compared to petroleum diesel, resulted in a 78.5% reduction in carbon dioxide emissions.

1.1 Background of study

The most feasible alternative that can replace our source of fuel lately is by using the extracted oil from plant origin such as from vegetable oil or animal fats and react it with amount of alcohol through transesterification process. This feasible method produces biodiesel. Basically, biodiesel defined as fuel made from natural, renewable sources, such as new and used vegetable oils and animal fats, for use in a diesel engine or the process that involves reacting vegetable oils or animal fats catalytically with a short-chain aliphatic alcohols.

There are main several advantages for using the biodiesel which are renewable, cheaper than petrodiesel, not acquire an engine modification, not harmful to environment, can make vehicle perform better, reduce the environment effect of waste product, high energy efficiency, and the most important is biodiesel can be produced locally. Biodiesel is surely a viable fuel alternative. Moreover, it is also a sustainable fuel. Using biodiesel not only helps maintain our environment, it also helps in keeping the people around us healthy. The production of biodiesel all over the world is now being looked upon favorably. In Europe, many biodiesel stations have been set up already. There is also a move to convert or make cars compatible with biodiesel fuel in the near future.

Today, there are multiple operating options available for making biodiesel. Many of these technologies can be combined under various conditions and feedstock in an infinite number of ways. The technology choice is a function of desired capacity, feedstock type and quality, alcohol recovery, and catalyst recovery. One of the technologies is by using ultrasound technologies**.** The ultrasonic mixing improves mass transfer and reaction kinetics leading to faster transesterification and higher yield. It saves excess of methanol and catalyst. Excess methanol and catalyst are significant cost factors in biodiesel production. The ultrasonic reactors add cavitational shear to the mixing process. This gives much smaller methanol droplets resulting in improved methanol and catalyst utilization. Therefore, less methanol and catalyst are required. In addition to that, the cavitation influences the reaction kinetics, leading to faster and more complete transesterification.

Besides, there are absorbents on the market that selectively absorb hydrophyllic materials such as glycerol and mono- and di-glycerides. This treatment, followed by an appropriate filter, has been shown to be effective in lowering glycerides and total glycerol levels. The fats and oil industry literature has other bleaching technologies that may also be explored for biodiesel producers. The European specification for sulfur content is much tighter than the U.S. requirement. As a result, a number of producers in Europe are resorting to the use of vacuum distillation for the removal of sulfur compounds from the biodiesel product. By 2006, all U.S. biodiesel must meet new sulfur standards of 15 ppm or less. Filtering is an essential part of all biodiesel production. While feedstocks entering the plant should be filtered to at least 100 μm, biodiesel leaving the plant should be filtered to at least

5 μm to ensure there is no contaminants are carried with the fuel that could damage the engine.

Manufacturing biodiesel from vegetable oils such as sunflower oil, palm oil jatropha or animal fats, involves the transesterification of fatty acids with methanol or ethanol to give the corresponding methyl esters or ethyl esters. Glycerin is an inevitable byproduct of this reaction. Vegetable oils as animal fats are triglycerides composed of three chains of fatty acids bound by a glycerin molecule. Chemically, triglycerides are called esters. Esters are acids, like fatty acids combined with an alcohol. In the conversion process, triglyceride esters are turned into alkyl esters using a catalyst and an alcohol reagent such as methanol which yields methyl esters biodiesel. The methanol replaces the glycerin while the glycerine which is the heavier phase, will sink to the bottom. On the other side, biodiesel the lighter phase floats on top and can be separated, by centrifugal separator. This conversion process is called transesterification process. Figure 1.1 below shows the reaction of triglyceride with methanol.

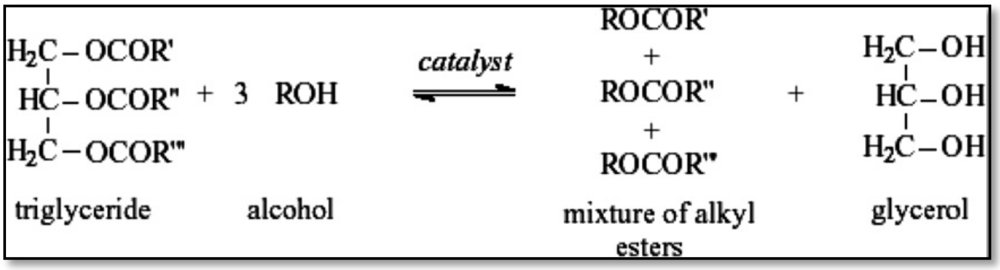


Figure 1.1: Transesterification of triglycerides

Transesterification means taking a triglyceride molecule or a complex fatty acid, neutralizing the free fatty acids, removing the glycerin, and creating an alcohol ester. The reaction is shown in Figure 1.1. Theoretically, transesterification reaction is an equilibrium reaction. In this reaction, however, more amount of methanol was used to shift the reaction equilibrium to the right side and produce more methyl esters as the proposed product.

Conventionally, the strong basic or acidic solutions such as NaOH, KOH and H_2SO_4 are used as a catalyst and food-grade vegetable oils as raw material according to Soriano *et al*. (2009). These homogeneous catalysts are quite sensitive to free fatty acids (FFA) and water in the oil feedstocks and alcohols. While the base-catalyzed transesterification of vegetable oil or animal fat is the most adopted technology for biodiesel commercial production, the process makes the biodiesel of higher manufacturing cost compared to petroleum-based diesel fuel. The process is sensitive to the quality of the feedstock requiring vegetable oil or animal fat with very low amount of free fatty acid (FFA).

1.2 Problem Statement

The main purpose to continue this study is because of the headlines of the current issue involve the renewable resources, petroleum based fuel and global warming. Renewable energy plays an important role in the supply of energy. When renewable energy sources are used, the demand for fossil fuels is reduced. Generally, the production and use of renewable fuels has grown more quickly in recent years due to higher prices for oil and natural gas, and a number of State and Federal Government incentives, including the Energy Policy Acts of 2002 and 2005. The use of renewable fuels is expected to continue to grow over the next 30 years, although people still rely on non-renewable fuels to meet most of our energy needs.

Chemically, transesterification is taking a triglyceride molecule or a complex fatty acid, neutralizing the free fatty acid, removing the glycerin and creating and alcohol ester. The advantage in using transesterification process is reducing the viscosity of vegetable oil. In the industry, common conventional catalyst used such as NaOH and KOH formed extensive soap formation as its react with high amounts of FFA via a saponification reaction. Soap renders biodiesel purification and catalyst removal even more challenging due to the formation of a stable emulsion generating a significant amount of waste water. The presence of high amounts of FFA in the feedstock therefore eventually leads to decreased biodiesel conversion and yield. In fact, studies have demonstrated that the amount of FFA in the feedstock for biodiesel production should not be higher than 0.5% in order to afford a product that passes the ASTM biodiesel standard.

Hence, the most appropriate catalyst is homogeneous Lewis acid which is aluminium chloride ($AlCl_3$). $AlCl_3$ catalyzed the transesterification of vegetable oil far more effectively rather than $ZnCl_2$ since $AlCl_3$ is a strong Lewis acid. It was also demonstrated that $AlCl_3$ could catalyze the esterification of stearic acid suggesting that it is a potential alternative catalyst for biodiesel preparation using cheaper vegetable oil containing high amount of FFA.

1.3 Objectives

The aims of this study are:

i. To determine the conversion of oil using transesterification process catalyzed by homogeneous Lewis acid.
ii. To determine the optimum operating conditions for the reaction.

1.4 Scope of the research

The scopes have been identified for this study in order to achieve the objective of this research:

i. To study the effect of methanol to oil molar ratio.
ii. To study the effect of catalyst concentration.
iii. To study the effect of reaction temperature.

1.5 Significance of the research

The significance of the research is reducing the usage of gasoline by boosting the efficiency of green technology such as biodiesel since it is non-toxic, renewable, biodegradable and also environmental friendly fuel. Besides, the byproduct of this process which is glycerol is mainly used in food, pharmaceutical and cosmetic industries. Moreover, methyl esters have a positive energy balance, that is, the total consumed energy in the production process is lower than the energy that they can provide as fuels. By using homogeneous Lewis acid, large amount of water can be saved. This is because in the conventional method by using sodium or potassium hydroxide, a large amount of waste water was produced to separate and clean the catalyst and the products. Therefore, by using aluminium chloride ($AlCl_3$), there is no such problem will occur and the cost for treat the wastewater can be saved and environment is not an issue.

CHAPTER 2

LITERITURE REVIEW

2.1 Introduction

Diesel fuel is the common term for the motor vehicle fuel used in the compression ignition engines named for their inventor, the German engineer Rudolf Diesel, who has patented his original design in 1892. While diesel engines are capable of burning a wide variety of fuels, diesel fuel refined from crude oil is the most widely used nowadays. Diesel fuel is important to the whole world's economy, quality of life, and industry application. Basically, consumer started to accept the fact that the diesel fuel prices are soaring and someday it will come to an end. As the result, there are a lot of other alternative fuel and also energy sources that have been carried out such as ethanol, natural gas, solar power, wind power, hydrogen and also hydroelectric power.

One of the best alternatives is biodiesel. Chemically, biodiesel can be defined as fatty acid methyl esters, which is derived from triglycerides by transesterification with methanol. The National Biodiesel Board (NBB) which is the national trade association representing the biodiesel industry in the United States, defines biodiesel as a product that typically produced by a reaction of a vegetable oil or animal fat with an alcohol such as methanol or ethanol in the presence of a catalyst to yield mono-alkyl esters and glycerin as a by-product. Biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend. In addition it can be used in compression-ignition (diesel) engines with little or no modifications. Besides, it is simple to use, biodegradable, nontoxic, and essentially free of sulfur and aromatics.

Technically, biodiesel refers to the pure fuel before blending with diesel fuel. Biodiesel blends are denoted as, "BXX" with "XX" representing the percentage of biodiesel contained in the blend (ie: B20 is 20% biodiesel, 80% petroleum diesel). Fuel-grade biodiesel must be produced to strict industry specifications (ASTM D6751) in order to insure proper performance which ASTM D6751 is a Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels. Biodiesel is the only alternative fuel to have fully completed the health effects testing requirements of the 1990 Clean Air Act Amendments. Biodiesel that meets ASTM D6751 and is legally registered with the Environmental Protection Agency is a legal motor fuel for sale and distribution. Raw vegetable oil cannot meet biodiesel fuel specifications, it is not registered with the EPA, and it is not a legal motor fuel. Table 2.1 show the specification for pure (100%) biodiesel prior to use or blending with diesel fuel.

Table 2.1: ASTM D6751 Biodiesel Specification (2008)

Property	ASTM Method	Limits	Units
Flash point	D93	93 minimum	Degrees °C
Water & Sediment	D 2709	0.05 maximum	% vol.
Kinetic Viscosity, 40°C	D 445	1.9-6.0	mm^2/sec
Sulfated Ash	D 874	0.02 maximum	% mass
Sulfur			
S 15 Grade	D 5453	0.0015 max. (15)	% mass (ppm)
S 500 Grade	D 5453	0.05 max. (500)	% mass (ppm)
Copper Strip Corrosion	D 30	130 maximum	
Cetane	D 613	47 minimum	

Cloud Point	D 250	Report	Degrees °C
Carbon Residue 100% sample	D 4530*	0.05 maximum	% mass
Acid Number	D 664	0.50 maximum	mg KOH/g
Free Glycerin	D 6584	0.020 maximum	% mass
Total Glycerin	D 6584	0.240 maximum	% mass
Phosphorus Content	D 4951	0.001 maximum	% mass
Distillation, 90°C	D 1160	360 maximum	degrees °C

2.2 Raw material

Basically, there a two raw material that widely used for biodiesel production which are vegetable oil and animal fats. Usually vegetable oil is the common material that being used.

2.2.1 Animal fats

Theoretically, animal fatty acid esters are usually very cheap but have negative physical properties such as high pour point, high viscosity, high flash point and hard processing. Tashtoush *et al*. (2004) has studied the evaluation and optimization of the conversion for waste animal fat (WAF) into ethyl and methyl ester called biodiesel. The physical and chemical characteristics of these esters were much closer to those of diesel fuel than those of fresh vegetable oil or fat, which makes them a good substitute for diesel fuel. Experiments have been performed to determine the optimum conditions for this conversion process using a three factor factorial design for producing biodiesel. At the end of the research, it can be conclude that WAF is a good raw material for biodiesel production, but 20–25% of this fat is glycerin, which makes them thick and sticky. This glycerin is substituted in a chemical process called transesterification to make the WAFs thinner or to reduce their viscosity.

2.2.2 Vegetable oil

The possibility of using vegetable oils as fuel has been recognized since the beginning of diesel engines. Generally, vegetable oil is being used instead of animal fats.

2.2.2.1 Virgin oil

Virgin oil feedstock such as soybean and rapeseed are the most common material that has been used. Furthermore, soybean oil itself accounting for about ninety percent of all fuel stocks in United States. It also can be obtained from field pennycress and Jatropha other crops such as mustard, flax, sunflower, palm oil, coconut and hemp. Sunflower oil is being tested in quite a few places worldwide for its biodiesel capability while the chemical properties of the oil lend themselves well for biodiesel manufacture. Antolin *et al.* (2002) has proved that sunflower oil does not have one fixed quality, but different qualities depending on weather conditions and agricultural practices, and that intraspecific variation in biodiesel quality can be larger than interspecific differences in his simulation experiment of variability of sunflower oil in biodiesel production.

The simulations using a validated model showed that, sunflower oil from high-oleic hybrids is suitable for biodiesel production, regardless of growing conditions and sunflower oil from traditional hybrids is suitable for biodiesel production under the standards of Argentina and US, while only certain hybrids grown in warm regions such as Northern Argentina, Southern US, China, India, and Pakistan are suitable for biodiesel production according to the European standard. Based on Table 2.2 below, it shows the fatty acid composition of vegetable oil samples that usually used in this study of biodiesel while for Table 2.3 below, it shows the physical properties and also the compositions of the sunflower oil that has been used as the raw material in this experiment.

Table 2.2: Fatty acid composition of vegetable oil samples

Sample	16:0	16:1	18:0	18:1	18:2	18:3	Others
Sunflowerseed	6.4	0.1	2.9	17.7	72.9	0	0
Palm	42.6	0.3	4.4	40.5	10.1	0.2	1.1
Rapeseed	3.5	0	0.9	64.1	22.3	8.3	0
Soybean	13.9	0.3	2.1	23.2	56.2	4.3	0
Peanut kernel	11.4	0	2.4	48.3	32.0	0.9	4.0
Walnut kernel	7.2	0.2	2.6	18.5	56.0	16.2	0
Hazelnut kernel	4.9	0.2	2.6	83.6	8.5	0.2	0
Olive kernel	5.0	0.3	1.6	74.7	17.6	0	0.8
Coconut	7.8	0.1	3.0	4.4	0.8	0	65.7
Almond kernel	6.5	0.5	1.4	70.7	20.0	0	0.9

Table 2.3: Physical properties and composition of sunflower oil

Physical state and appearance	Liquid
Molecular weight	887 g/L
Colour	Light yellow
Composition	• Palmitic acid : 4 – 9 % • Stearic acid : 1 – 7 % • Oleic acid : 14 – 40 % • Linoleic acid : 48 – 74 %
Density	917 kg/m^3
Smoke point (refined)	232°C

Smoke point (unrefined)	227°C

2.2.2.2 Waste vegetable oil

Many advocates suggest that waste vegetable oil is the best source of oil to produce biodiesel, but since the available supply is drastically less than the amount of petroleum-based fuel that is burned for transportation and home heating in the world. Besides, there are a lot of disadvantages are using waste vegetable oil which will thickening the fuel, cause gumming in engine, acid in waste vegetable oil will damage the fuel system and if has been used in along time, it may become hydrogenated and the acidity will increase.

2.2.2.3 Waste cooking oil

In this context, waste cooking oil is a promising alternative for producing biodiesel because it is a cheaper raw material that also avoids the cost of waste product disposal and treatment. Besides, it reduces the need to use land for biodiesel producing crops. Waste cooking oils are currently collected from large-scale food processing and service facilities. In fact, the quantities of waste cooking oils available for biodiesel production in Europe are relatively high. The amount of waste cooking oil collected for recycling in the Europe is estimated to be approximately 0.7–1.0 million tonnes per year. Traditionally, these waste oils were used as an additive to animal feed. However, many harmful compounds are produced during the frying of vegetable oils. Awareness of this problem results in banned the use of waste cooking oils in the composition of animal feed in 2002. Most of the toxic compounds in the waste cooking oil are oxidation products from fatty acids, especially from polyunsaturated fatty acids.

Biodiesel production for waste cooking oil has been previously studied. Kulkarni and Dalai (2006) published an excellent review of biodiesel production processes from waste cooking oils. The soap formation using alkaline catalyst is an undesirable side reaction, because it partially consumes the catalyst, decreases the biodiesel yield and complicates the separation and purification steps. For this reason, the methanolysis of waste cooking oils using an acid catalyst like sulphuric, hydrochloric or sulfonic acid has also been reported since soap formation can be avoided by using this type of catalyst. Furthermore, the above acids catalyze the free fatty acid esterification to produce fatty acid methyl esters, increasing the biodiesel yield. Nevertheless, the acid-catalyzed transesterification is much slower than the basic catalyzed reaction and also needs more extreme temperature and pressure conditions. Table 2.4 shows the common raw material that usually being used in biodiesel manufacturing.

Table 2.4: Raw material used in biodiesel production

Raw materials	Findings	References
1. Waste animal fats	• Temperature had no detectable effect on the ultimate conversion ratio and viscosity for both ester products. • However, higher temperatures decreases the time required to reach maximum conversion, which will be at the expense of the cost of energy. • Besides animal fats, is good raw material for biodiesel production, but 20–25% of this fat is glycerin, which makes them thick and sticky. • Animal fat reacts very sensitive if too much catalyst is used. Soap will formed and cause whole mixture turns into some kind of thick glob, which results in production loss.	Tashtoush *et al.* (2004)
2. Virgin oil	• Optimisation of the most important variables such as temperature	Antolin *et al.* (2002)

	conditions, reactants pro- portion and methods of purification, with the purpose of obtaining a high quality biodiesel that fulfils the European pre legislation with the maximum process yield. • Finally, sunflower methyl esters were characterised to test their properties as fuels in diesel engines, such as viscosity, flash point, cold filter plugging point and acid value. Results showed that biodiesel obtained under the optimum conditions is an excellent substitute for fossil fuels. • Sunflower methyl esters, whose characteristics as fuel in diesel engines are within the specifications of the current Eu-ropean pre-legislation, has been obtained, duly fulfilling the main demanded parameters. These char-acteristics are density, viscosity, flash point and sulphur content, which also present good values of calorific power and cetane index.	
3. Waste cooking oil	• The conversion of free fatty acids of WCO into FAME in the two-step method was 97.22% at the reaction time of 4 h, mole ratio of methanol to TG of 10:1, compared in the acid method with 90%, 10 h, and 20:1, respectively, showing much higher	Yong *et al.* (2006)

	catalyzed activity of ferric sulfate. - This new two-step process showed advantages of no acidic wastewater, high efficiency, low equipment cost, and easy recovery of catalyst compared with the limitations of acidic effluent, no reusable catalyst and high cost of equipment in the traditional acid process.	

2.3 Process

Since the existence of biodiesel in small scale production, dilution, micro-emulsification, pyrolysis and transesterification are the four techniques applied. Each of them has its own advantages and also disadvantages.

2.3.1 Dilution

One of the methods that have been considered in production of biodiesel is dilution. Generally, dilution method not involved other chemical method. Usually, only 25 parts of vegetable oil are diluted with 75 parts of diesel fuel. But the problem with this method is it is not efficient at all.

2.3.2 Micro-emulsification

In the biodiesel manufacture process, that consists in the transesterification of oils or fats with short chain alcohols, sodium or potassium hydroxide are used as catalysts. However the presence of potassium or sodium in the end product results in the formation of insoluble soap and consequently deposit formation in the vehicles filters. The use of microemulsion as sample preparation for biodiesel analysis, to the best of our knowledge, has not been described yet. However the microemulsion formation with vegetable oils has been investigated by some authors. Jesus *et al.* (2007) proposed a water-in-oil microemulsion with vegetable oils as medium for electrochemical measurement and as background electrolyte in reverse microemulsion electrokinetic capillary chromatography.

2.3.3 Pyrolysis

Pyrolysis is the process of thermal decomposition to produce gases, liquids, and char. These pyrolysis products can all be used as fuels, with or without prior upgrading, or they can be utilized as feedstocks for chemical or material industries. The types of materials which are candidates for pyrolysis processing include coal, plant biomass, animal and human waste, food scraps, paper, cardboard, plastics, and rubber.

Onay *et al.* (2003) has done pyrolysis experiment of rapeseed that has been carried out in a free fall reactor. The maximum pyrolysis conversion of 87.8% was obtained at a pyrolysis temperature of 700°C. The maximum bio-oil yield of 75% was obtained at a final pyrolysis temperature of 600°C and the particle size range of +0.224 to 0.6 mm. As the result, the bio-oil contains higher proportion of oxygen than that of diesel fuel, and thus they are quite reactive and not as stable as diesel fuel and their characteristics change rapidly during condensation and under storage condition. Their utilization as fuels or sources of chemical feed stock requires some form of upgrading to improve storage stability and heating value.

2.3.4 Transesterification

One popular process for producing biodiesel from the fats/oils is transesterification of triglyceride by methanol to make methyl esters of the straight chain fatty acid. The purpose of the transesterification process is to lower the viscosity of the oil. Krishnamoorthy *et al.* (2006) has found that the transesterification seems to be the best choice, as the physical characteristics of fatty acid esters (biodiesel) are very close to those of diesel fuel and the process is relatively simple. Furthermore, the methyl or ethyl esters of fatty acids can be burned directly in unmodified diesel engines, with very low deposit formation. Although short-term tests using neat vegetable oil showed promising results, longer tests led to injector coking, more engine deposits, ring sticking, and thickening of the engine lubricant. These experiences led to the use of modified vegetable oil as a fuel. Although there are many ways and procedures to convert vegetable oil into a diesel-like fuel, transesterification process was found to be the most viable oil modification process.

According to Kansedo *et al.* (2009), the transesterification process variables were reaction temperature, x_1 (50–190ºC), reaction period, x_2 (60–300 min), methanol/oil ratio, x_3 (4–12 molmol^{-1}) and amount of catalyst, x_4 (1–5 wt%). It was found that the yield of palm oil fatty acid methyl esters (FAME) could reach up to 79.6% using the following reaction conditions: reaction temperature of 190ºC, reaction period at 180min, ratio of methanol/oil at 8:1 molmol^{-1} and amount of catalystat 3%. Based on the experimental result obtained, it can be concluded that montmorillonite could be used as an effective catalyst for the conversion of palm oil to FAME. However, future research on this catalyst is still required to investigate wider range of the parameters, and also new possible parameters which can be included in the reaction process such as the mixing intensity, reaction pressure and so forth to properly commercialize this technology.

A simple procedure has been found by Granados *et al.* (2009) that significantly promotes the transesterification reaction rate catalyzed by CaO and moreover prevents the catalyst poisoning by ambient CO_2 and H_2O. The presence of a small amount of biodiesel in the initial methanol triglyceride mixture (3 wt % referred to oil) results in a significant increase of the rate of triglyceride methanolysis carried out in a batch reactor. The biodiesel must be previously mixed with the activated CaO, forming a paste. Finally, the formation of such a paste also results in a remarkable protection of the activated CaO against the poisoning by ambient CO_2 and H_2O that may occur during handling of the activated solid.

2.4 Catalyst

Catalyst is a substance that usually used in small amounts relative to the reactants, that modifies and increases the rate of a reaction without being consumed in the process. Generally, catalysts can be divided into two main types which are heterogeneous and homogeneous. Table 2.5 and Table 2.6 shows the summary of catalyst that have been used by researchers.

Table 2.5: Homogeneous catalyst used in the biodiesel production.

Homogeneous catalyst	Findings	References
Aluminium chloride ($AlCl_3$)	• Acid-catalyzed transesterification is more suitable for waste or unrefined oil. • Effectively catalyzed the process since it is strong acid and also a potential catalyst using cheap vegetable oil and high FFA. • The optimum conditions with $AlCl_3$ that achieved 98% conversion were 24:1 molar ratio at 110ºC and 18 h reaction time with tetrahydrofuran as co-solvent. • The presence of tetrahydrofuran minimized the mass transfer problem normally encountered in heterogeneous systems. • Nucleophilic reactions catalysed by $AlCl_3$	Soriano *et al.* (2009)

	are recommended to be carried out in organic solvents under anhydrous conditions.	Dermibas *et al.* (2005)
Zinc chloride ($ZnCl_2$)	• $ZnCl_2$ was far less effective as a catalyst, which was attributed to its lesser acidity. • Nevertheless, statistical analysis showed that the conversion with the use of $ZnCl_2$ differs only with reaction time but not with molar ratio. • With the use of $ZnCl_2$, the maximum conversion achieved was only 48%, obtainable with molar ratio of 60 which is too high and a reaction time of 24 h.	Soriano *et al.* (2009)
Zinc aluminate	• The transesterification reaction of rapeseed oil by methanol was studied using a zinc aluminate catalyst in order to develop an alternative to the currently used homogeneous processes. • Optimization of the reaction parameters for achieving high yields and obtaining high quality products was performed. • Indeed the influence on the activity, stability and selectivity of the temperature, the reactants ratio, and the presence of water in the reactants, was studied. • However, this catalyst was quite sensitive to water and the limitation of water content in oils is 0.15 (wt%).	Pugnet *et al.* (2010) Bournay and Hillion, (2003).
Zinc and iron	• Transesterifying unrefined and used oils. • This catalyst is active in both esterification	Sreeprasanth *et al.*

	and transesterification. • However, the catalyst is also active in the hydrolysis of FAME to FFA, thus the overall yield of biodiesel is decreased.	(2006)
Sodium hydroxide (NaOH), Potassium hydroxide (KOH)	• This process produce faster reaction rate and the main factor affecting the methyl ester yield is the catalyst content. • High amounts of FFA resulted in extensive soap formation as FFA reacts with these catalyst, via a saponification reaction. • Soap renders biodiesel purification and catalyst removal even more challenging due to the formation of a stable emulsion generating a significant amount of waste water. • The presence of high amounts of FFA in the feedstock therefore eventually leads to decreased biodiesel conversion and yield. In fact, studies have demonstrated that the amount of FFA in the feedstock for biodiesel production should not be higher than 0.5% in order to afford a product that passes the ASTM biodiesel standard.	Wang *et al.* (2007) Soriano *et al.* (2008)

Table 2.6: Heterogeneous catalyst used in the biodiesel production.

Heterogeneous Catalyst	Findings	References
Supported CaO	• Ca3La1 has a stronger base strength, a higher amount of basicity, higher specific surface area and also FAME yield.	Yan *et al.* (2007)

	- Crude soybean oil, crude palm oil and waste cooking oil without any pretreatment were converted to FAME directly using Ca3La1 catalyst. The average yield of these oils was about 96% at 3 hours. - Directly catalyzed reaction of crude oil into biodiesel when water content < 2 (wt%) and FFA content < 3.5 (wt%). - However, further increase of FFA and water content in oil could inhibit transesterification.	
Alumina-supported potassium iodide	- In this work, the transesterification of soybean oil with methanol has been studied in a heterogeneous system, using alumina loaded with potassium iodide as a solid base catalyst. - The catalyst with 35wt.% KI loading on Al_2O_3 and calcined at 773K for 3 h was found to be the optimum catalyst, which gave the highest basicity and the best catalytic activity. - When the reaction was carried out at reflux of methanol, with a molar ratio of methanol to oil of 15:1, a reaction time 8 h, and a catalyst amount 2.5%, the highest conversion of soybean oil reached 96%.	Xie *et al.* (2006)
$ZnO-La_2O_3$	- A strong interaction between Zn and La species was observed with enhanced catalyst activities. - Lanthanum promoted zinc oxide distribution, and increased the surface acid and base sites. The catalyst with 3:1 ratio of zinc to lanthanum was found to	Yan *et al.* (2007)

	simultaneously catalyze the oil transesterification and fatty acid esterification reactions, while minimizing oil and biodiesel hydrolysis. • A reaction temperature window of 170–220ºC was found for the biodiesel formation. A high yield (96%) of fatty acid methyl esters (FAME) was obtained within 3 h even using unrefined or waste oils.	

2.5 Solvent

Practically, any of the organic molecules of the alcohol family can be used as a fuel. The alcohols that can be used for motor fuels are methanol (CH_3OH), ethanol (C_2H_5OH), propanol (C_3H_7OH), butanol (C_4H_9OH). However, only two of these alcohols (methanol and ethanol) are technically and economically suitable as fuels for internal combustion engines. Methanol, also known as 'wood alcohol', is commonly used in biodiesel production for its reactivity. Generally, it is easier to find than ethanol. Sustainable methods of methanol production are currently not economically viable. The use of methanol as a motor fuel received attention during the oil crises of the 1970s due to its availability and low cost. Problems occurred early in the development of gasoline–methanol blends. As a result of its low price some gasoline marketers over blended. Many tests have shown promising results using 85–100% by volume methanol as a transportation fuel in automobiles, trucks and buses. Methanol is currently manufactured worldwide by conversion or derived from syngas, natural gas, refinery off-gas, coal or petroleum.

According to Cao *et al.* (2004), transesterification of soybean oil in supercritical methanol has been carried out in the absence of catalyst. A co-solvent was added to the reaction mixture in order to decrease the operating temperature, pressure and molar ratio of alcohol to vegetable oil. With propane as co-solvent in the reaction system, there was a significant decrease in the severity of the conditions required for supercritical reaction, which makes the production of biodiesel using supercritical methanol viable as an industrial process. A high yield of methyl esters (biodiesel) was observed and the production process is environmentally friendly.

While based on Guo *et al.* (2008) the transesterification of sunflower seed oil was carried out in supercritical ethanol without using any catalyst. Vapor pressures for the mixtures of biodiesel methylcyclohexane were measured by comparative ebulliometry with inclined ebulliometers. The vapor pressure versus composition can be obtained from the correlation on the experimental results. The flash points of the mixtures covering the entire composition range of methylcyclohexane in biodiesel were tested by closed cup test. As the result, the predicted values of flash point using regular solution theory appear to be in much better agreement with the experimental data.

CHAPTER 3

METHODOLOGY

3.1 Introduction

In order to produce biodiesel, there are five common steps that have to be considered which are equipment selection, raw material preparation, catalyst preparation, experimental procedure and analytical method. In the experimental procedure, the single step catalyzed process will be carried out using aluminium chloride ($AlCl_3$) as a homogenous Lewis acid catalyst. In this experiment, there are three parameters that can be studied which are effect of methanol to oil molar, catalyst concentration and the reaction temperature. While for analytical method, gas chromatography (GC) has been used in determining the amount of fatty acid methyl ester (biodiesel) that successfully produced in this experiment.

3.2 Equipment selection

The reaction was carried out in a batch reactor that attached with a condenser, thermometer, heating mantle, oil bath and other equipment that required. Table 3.1 and Table 3.2 show the chemicals and equipments that have been used in this research studies.

Table 3.1: Chemicals used in this experiment

Chemicals	Uses
• Sunflower oil	Main raw material
• Methanol	Solvent and reactant
• Aluminium chloride ($AlCl_3$)	Catalyst

Table 3.2: Equipments used in this experiment

Equipment	Function
• Oil bath	To heat mixture up to high temperature (200°C)
• Overhead Stirrer Moto	To stir mixture for oil bath
• Heating mantle	To heat mixture below 100°C
• Three neck flask	To place the mixture
• Magnetic Stirrer Bar	To stir mixture for heating mantle
• Thermometer	To measure temperature
• Condenser	To condense methanol
• Pipette	To take samples for each time interval
• Retort stand	To support condenser

3.2.1 Batch reactor

Based on Lopez *et al.* (2009), the presence of a small amount of biodiesel in the initial methanol-triglyceride mixture (3 wt % referred to oil) results in a significant increase of the rate of triglyceride methanolysis carried out in a batch reactor. Batch reactors may be preferred for small-scale production of high priced products, particularly if many sequential operations are carried out to obtain high product yields. Batch reactors may also be justified when multiple, low volume products are produced in the same equipment or when continuous flow is difficult, as it is with highly viscous or sticky solids-laden liquids. Because residence time can be more uniform in batch reactors, better yields and higher selectivity may be obtained than with continuous reactors. Figure 3.1 below show the schematic diagram of batch reactor that usually used in industry for biodiesel production.

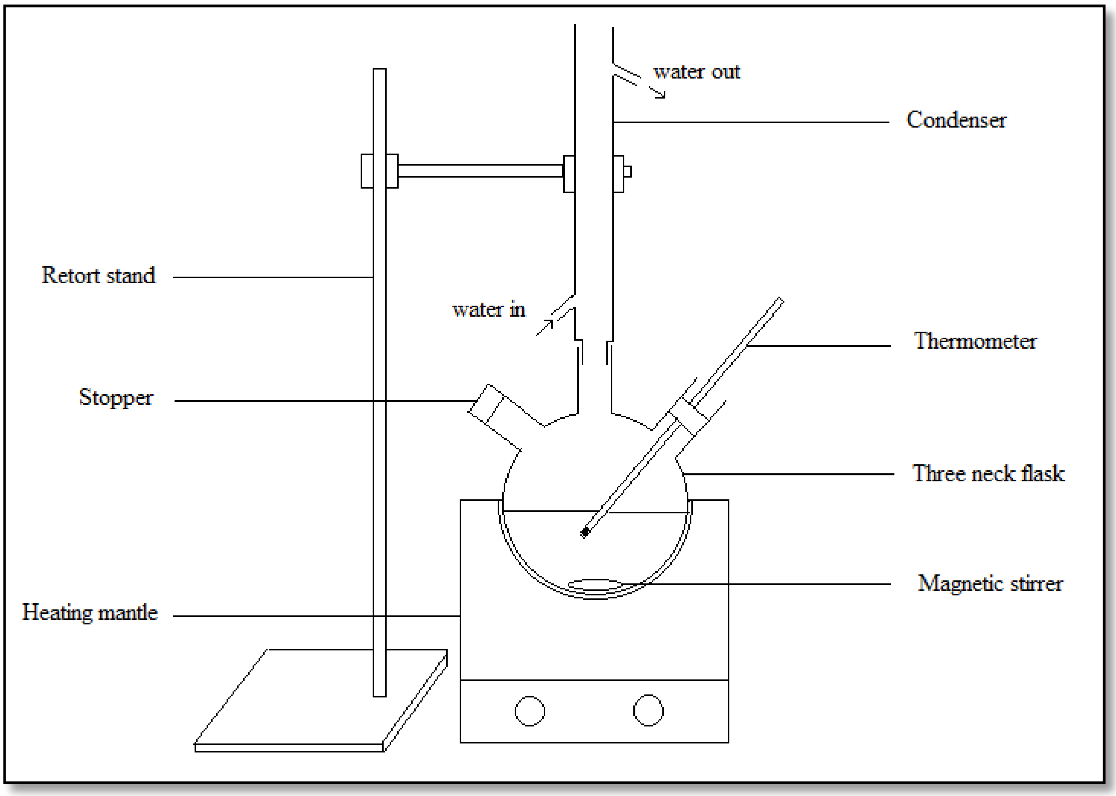


Figure 3.1: Schematic diagram of batch reactor used in this research

3.2.1.1 Condenser

The three-neck flask has been attached with a condenser since the condenser can condense the methanol during the reaction to maintain the amount of methanol used.

3.2.1.2 Thermometer

The thermometer is used to set the temperature but the disadvantage for using this equipment is the temperature needed to be controlled.

3.2.1.3 Heating mantle

In this experiment, the heating mantle was used for low temperature up to 75°C. This is because the boiling point of methanol is 65°C. That is why the temperature of heating mantle can’t be too high or else all of the methanol will vaporize. Heating mantle will heat the mixture in three-neck bottom flask and in the same time being stirred by magnetic stirrer bar. It is important to stir the mixture because the catalyst needs to be soluble in the mixture of methanol and oil.

3.2.1.4 Oil bath

Besides heating mantle, oil bath have been used instead of heating mantle. Oil bath was usually used for high temperature up to 200°C. The advantage for using oil bath is the temperature controller. Stirrer motor has been used to stir the mixture during the experiment. Figure 3.2 below shows an oil bath that usually used for biodiesel research.

Figure 3.2: Figure of oil batch used in this research

3.2.2 Gas chromatography

Gas chromatography can serve as tool for process troubleshooting during biodiesel production to ensure trouble free operation of the fuel in diesel engines. Monitoring the level of free glycerin and any unrelated monoglyceride, diglyceride or triglyceride will indicate the efficiency and progress of the chemical reaction during the process of making biodiesel. To measure the quality that needed by consumer, there number of different laboratory techniques to evaluate different parameters. Gas chromatography is often used as the analytical method of choice for free and total glycerin since it is simple, sensitive and reliable, requiring only a small amount of sample preparation.

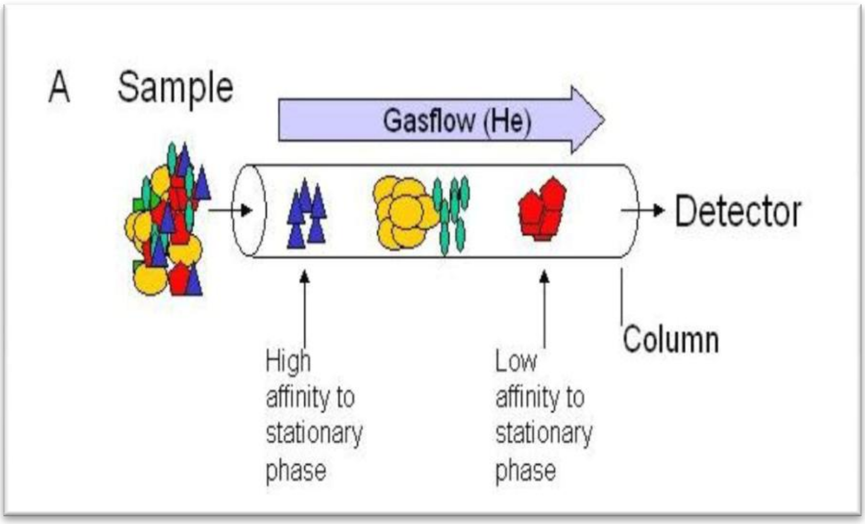


Figure 3.3: Scheme of gas chromatography.

Figure 3.3 shows how the gas chromatography works. First of all, sample is vaporized and directed to the GC-column where separation of the applied mixture takes place. Compounds with high affinity to the stationary phase of the column are retarded by interaction with the stationary phase. Components with a low affinity to the stationary phase rush through the column were pushed by the gas flow and were eluted from the column first.

3.3 Raw material preparation

The raw material that will be used in this experiment is the sunflower oil that already been extracted. The whole experiment is about to produce biodiesel, so in the experimental procedure, the extraction of sunflower oil are not necessary. So that is why the extracted sunflower oil will be purchased. Besides that, methanol also had been used as a solvent in this research.

3.4 Catalyst preparation

The type of catalyst that has been used in this experiment is homogeneous Lewis acid catalyst. In term of efficiency, the aluminium chloride ($AlCl_3$) had been chosen. It is known that $AlCl_3$ can perform efficiently in existence of water. Since most of the vegetable oil contains abundance of water percentage, so the $AlCl_3$ as the catalyst will be the best choice but in this experiment only $AlCl_3.6H_2O$ (aluminium chloride hydrous) is available. So the most effective way is to burn the $AlCl_3.6H_2O$ to become $AlCl_3$. $AlCl_3.6H_2O$ has been dried in an oven for one and a half hour at 100°C since water will vaporize at 100°C.

3.5 Experimental procedure

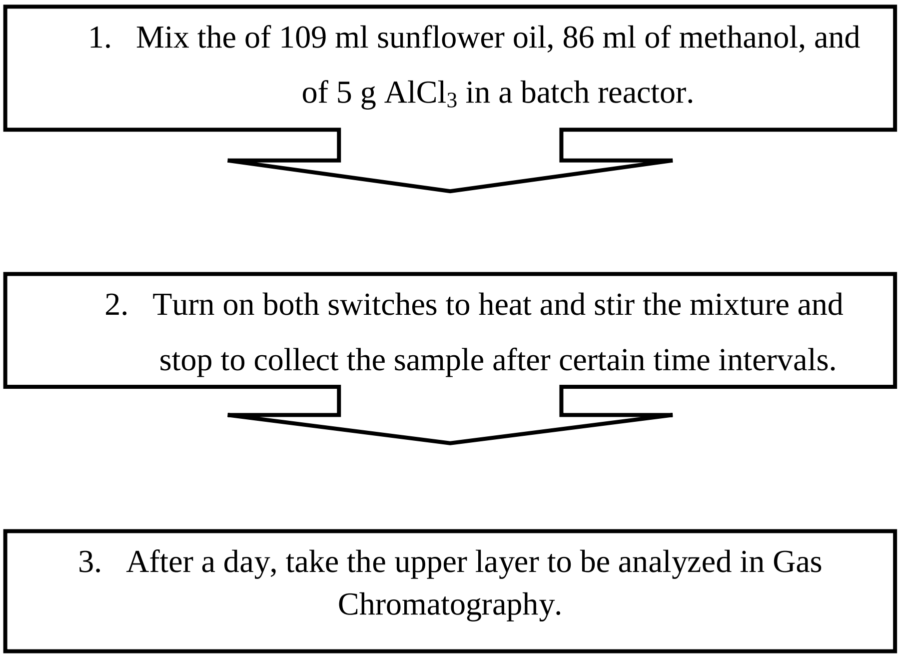
The experimental procedure for production of biodiesel through this experiment involves several steps which are transesterification and settling process. All of these steps need to be followed in order to make a successful experiment.

3.5.1 Transesterification

In this experiment, the molar ratio of methanol to sunflower oil was fixed at 6:1. The transesterification process was carried out in a batch reactor where 109 ml of sunflower oil, 86 ml of methanol, and 5 g of $AlCl_3$ are used. During the reaction, 1 mL of reaction mixture is collected every 10 minutes until first one hour using pump pipette. Then, another 1 mL of mixture was taken for every one hour. After 6 hours, the sample collection can be stopped.

3.5.2 Settling

After finish the transesterification process, the product obtained needs to be settled. In this experiment, the product has been settled for a day only before being injected to Gas Chromatography. The final product was in two layers which the upper layer that mainly containing fatty acid methyl esters was characterized by a GC equipped with a capillary column and the second layer was glycerol. Figure 3.4 below shows the steps involved for this experiment procedure.



1. Mix the of 109 ml sunflower oil, 86 ml of methanol, and of 5 g $AlCl_3$ in a batch reactor.
2. Turn on both switches to heat and stir the mixture and stop to collect the sample after certain time intervals.
3. After a day, take the upper layer to be analyzed in Gas Chromatography.

Figure 3.4: Flow Diagram for the experiment procedure

3.6 The Experimental Procedure for Sample with Different Variable Manipulated

In this homogeneous catalyzed process, the effect of three parameters has been studied. These parameters are catalyst concentration, methanol to oil molar ratio and the reaction temperature. For the catalyst concentration, the experiment will be carried out for 5g, 7g and 9g of $AlCl_3$ while for methanol to oil molar ratio 6:1; 9:1; 12:1; 24:1 and for the reaction temperature are 70°C, 85°C and 110°C.

The experiment is investigated step by step. The optimal value for each parameter was determined while for other parameters must keep constants. After the value is obtained, then the next parameter can be determined. In this study, it has three sets of experiment. For the 1st experiment, the main objective is to study the effect of molar ratio methanol to oil. So, only the molar ratio methanol to oil that has different value while the other two parameters will be constant as shown in Table 3.3 below:

Table 3.3: Operating conditions for the study of the effect of molar ratio methanol to oil

Experiment	Temperature (°C)	Catalyst concentration (g)	Molar ratio
1	70	5	6 : 1
2	70	5	9 : 1
3	70	5	12 : 1
4	70	5	24 : 1

For 2nd experiment, the main objective is to study the effect of temperature. So only the temperature value that will be different while for molar ratio value is taken from the optimal value from the 1st experiment which is 12:1 as shown in Table 3.4 below:

Table 3.4: Operating conditions for the study of the effect of reaction temperature

Experiment	Temperature (°C)	Catalyst concentration (g)	Molar ratio
3	70	5	12 : 1
5	85	5	12 : 1
6	100	5	12 : 1

For 3rd experiment, the main objective is to study the effect of catalyst concentration. Therefore, only the catalyst concentration value that has been varied while for molar ratio value will be taken as 12:1 and the reaction temperature is 100°C as shown in Table 3.5 below:

Table 3.5: Operating conditions for the study of the effect of catalyst concentration

Experiment	Temperature (°C)	Catalyst Concentration (g)	Molar ratio
6	100	5	12 : 1
7	100	7	12 : 1
8	100	9	12 : 1

3.7 Analytical method

Generally, there are various analytical methods that can analyze the biodiesel produce by transesterification process using homogeneous Lewis acid as catalyst.

3.7.1 Procedure for Stock Standard

50mg of glycerol are weighed out the appropriate amount of standard required in a 10ml volumetric flask for a concentration of 50mg/ml. Then, it was diluted in 10ml volumetric flask with n-Heptane; reagent grade. Table 3.6 below shows the amount of chemicals involved to produce stock standard.

Table 3.6: Stock standards

Component	Concentration (mg/ml)	Volumetric flask (ml)	Mass of sample (mg)
Glycerol	25	25	625
Methyl palmitate	25	25	625
Methyl linoleate	25	25	625
Methyl oleate	25	25	625

3.7.2 Procedure for Working Standard

Appropriate volumes of stock solution of glycerol are pipetted into a 10ml volumetric flask along with appropriate volume of methyl palmitate, methyl oleate and methyl linoleate. Then it is diluted to the mark with n-Heptane. After that it is cap and mix in the vials. Table 3.7 below shows the preparation of working standards.

Table 3.7: Working standards

Component	S1	S2	S3	S4	S5
Glycerol	500	1000	1500	2000	2500
Methyl palmitate	5000	1000	1500	2000	2500
Methyl linoleate	500	1000	1500	2000	2500
Methyl oleate	500	1000	1500	2000	2500

3.7.3 Calibration curve

A calibration curve would be in area under each peak vs. concentration for each homogeneous group. The calibration curve is obtained from the working solution before. Each mixture of varying concentration of standard S1, S2, S3, S4 and S5 is used to plot the calibration curve to calculate the concentrations of each homogeneous group. From the calibration curve with an original know mass of sample we can calculate the quantity of that compound and its relative proportions in the sample. Figure 3.5, 3.6 and 3.7 below is the calibration curve of methyl palmitate, methyl linoleate and methyl oleate respectively.

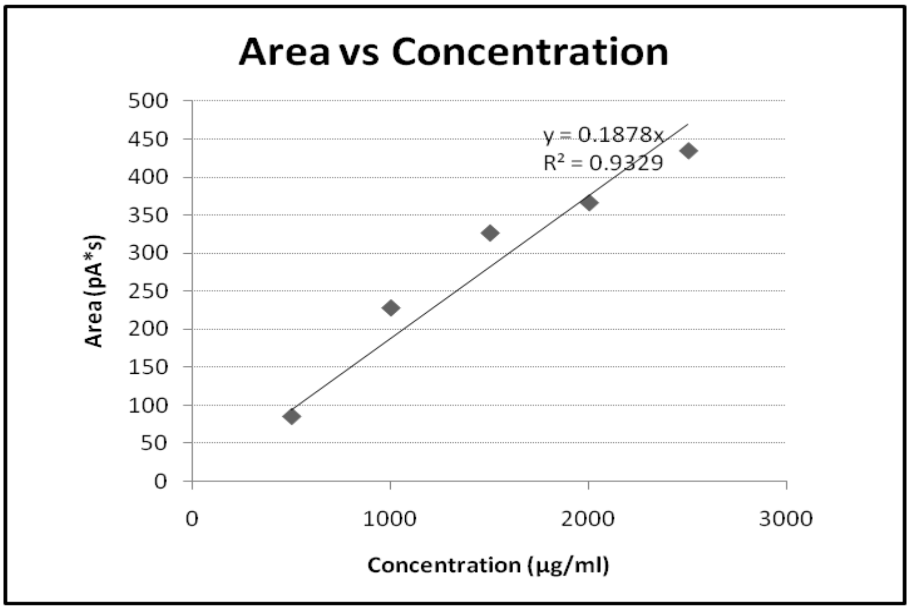


Figure 3.5: Calibration curve for methyl palmitate

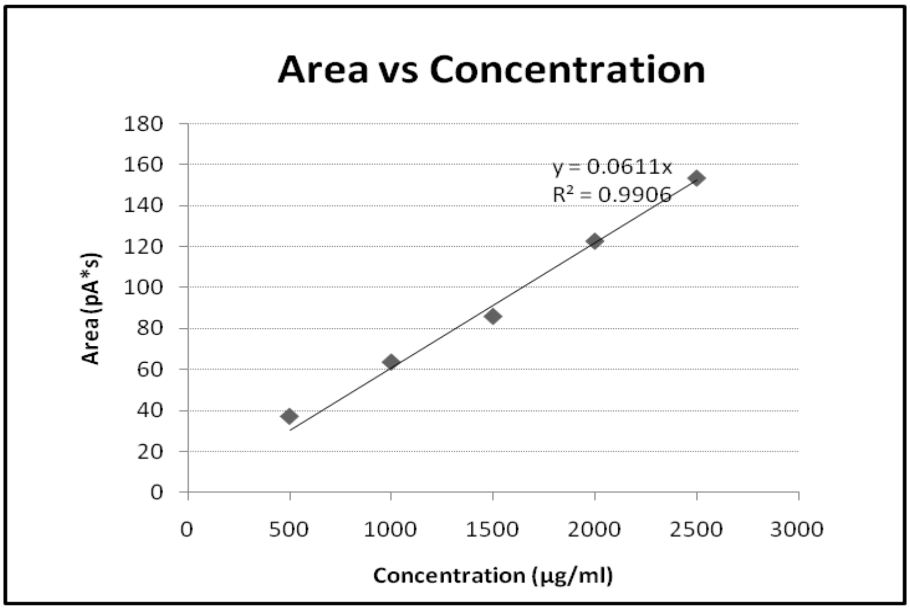


Figure 3.6: Calibration curve for methyl linoleate

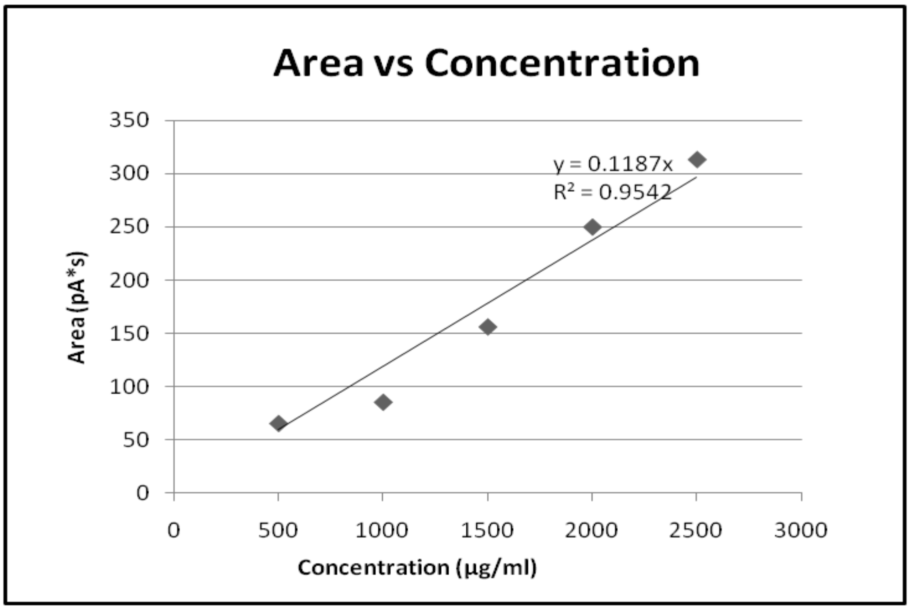


Figure 3.7: Calibration curve for methyl oleate

3.7.4 Procedure for Samples

50-70mg of the sample was weighed into a 10ml volumetric flask and the mass is recorded. The samples then are diluted with n-Heptane to the mark and it is cap and mix

3.7.5 Analysis with gas chromatography

The sample of this experiment has been analyzed by gas chromatography because of its efficiency in separating compound into their separate components. The sample of each parameter injected into this equipment and at the end of the process, the component of the product obtained is in form of chromatogram which contains peaks. Each of peaks represents the area of our component. Finally, the conversion calculated using the calibration curve as references. Table 3.8 below shows the condition of column for biodiesel that has been used in this study.

Table 3.8: Condition for biodiesel column

Type of column	Hp-innowax
Length	30 m
Internal Diameter, ID	0.250 mm
Film	0.25 µm
Oven setpoint	50°C
Maximum oven configuration	250°C

CHAPTER 4

RESULT AND DISCUSSION

In this study, three types of parameter have been studied which were effect of molar ratio methanol to oil, effect of reaction temperature and effect of catalyst concentration. The effects of these parameters are varied to achieve the maximum conversion of oil.

4.1 Effect of molar ratio

The first parameter was molar ratio of methanol to sunflower oil. Four experiments have been done by varied the amount of methanol to oil and the conversion have been determined while the other two parameters was fixed during this experiment. The operating conditions for the effect of molar ratio were temperature equal to 70°C and catalyst loading was 5 g.

Figure 4.1 shows the effect of molar ratio methanol to oil is 6:1 with temperature 70ºC and catalyst loading is 5 g. As the result, the maximum conversion from these conditions was 3% conversion of methyl ester. The amount of methanol used was too low, resulting in limitation of mass transfer which cause the mass transfer rate is much slower than reaction rate.

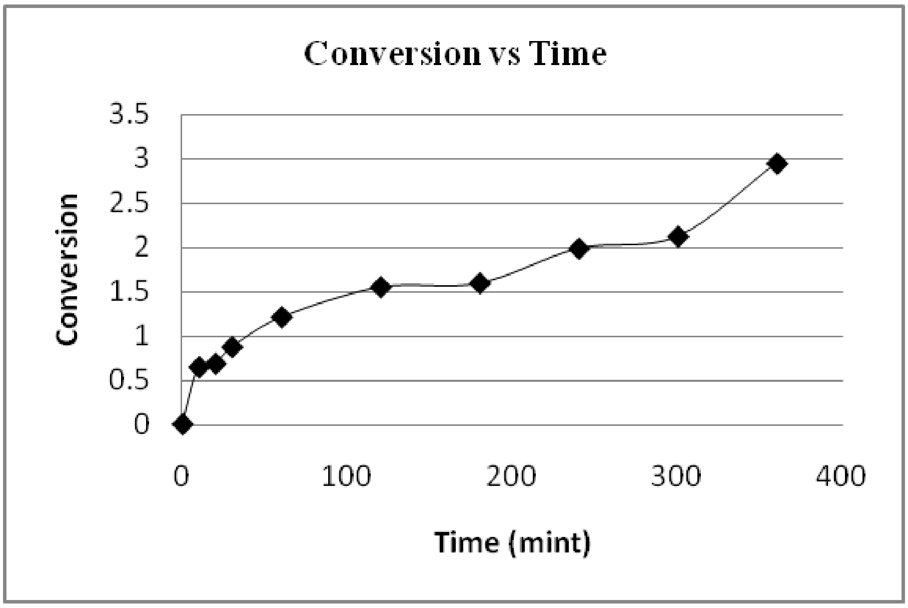


Figure 4.1: Conversion profile for the operating conditions of the effect of molar ratio 6:1, temperature 70°C and 5 g of catalyst loading.

Figure 4.2 shows the effect of molar ratio methanol to oil is 9:1 with temperature 70ºC and catalyst loading was 5 g. As the result, the maximum conversion from these conditions is 26% conversion of oil. The conversion was much higher compared to the first experiment since the amount of methanol was higher.

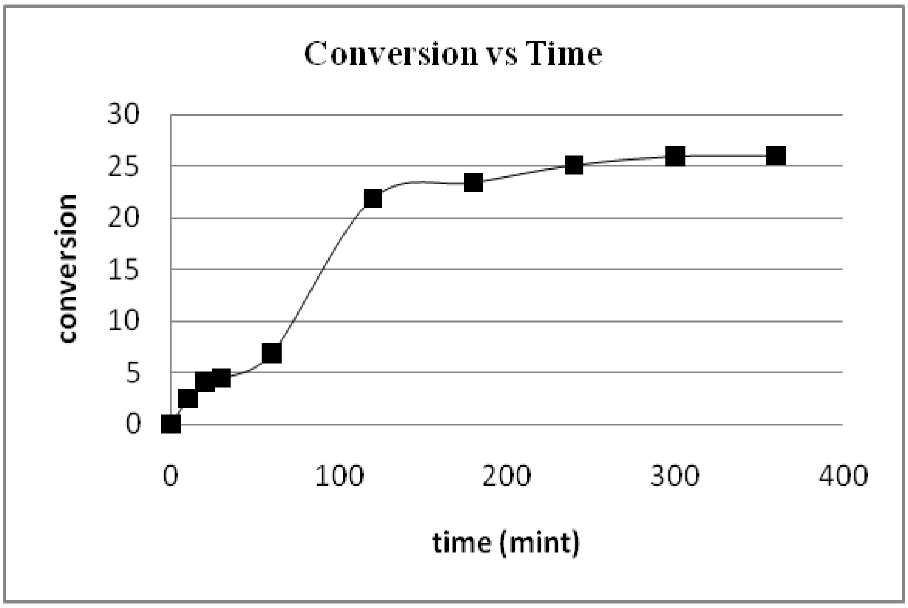


Figure 4.2: Conversion profile for the operating conditions of the effect of molar ratio 9:1, temperature 70°C and 5 g of catalyst loading.

Figure 4.3 shows the effect of molar ratio methanol to oil was 12:1 with temperature 70ºC and catalyst concentration is 5 g. As the result, the maximum conversion from these conditions is 62% conversion of oil. At time 250 minutes, the conversion seems to increase due to the activation of catalyst and amount of methanol used. Since transesterification process was a reversible process, hence the production yield could be elevated by introducing excess amount of methanol to shift the equilibrium to the right hand side.

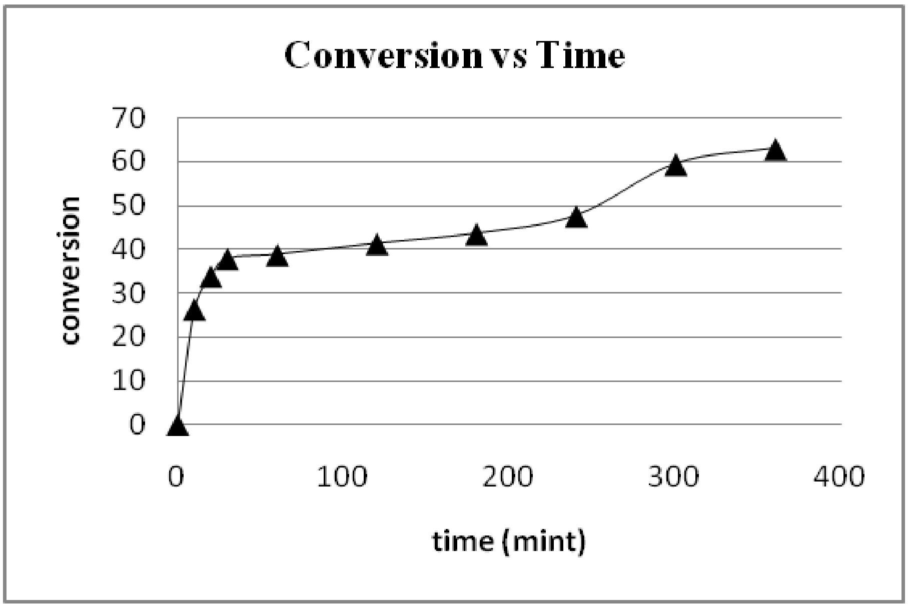


Figure 4.3: Conversion profile for the operating conditions of the effect of molar ratio 12:1, temperature 70°C and 5 g of catalyst loading.

Figure 4.4 shows the effect of molar ratio methanol to oil is 24:1 with temperature 70ºC and catalyst loading is 5 g. As the result, the maximum conversion from these conditions is 11% conversion of methyl ester. Although this process needed high amount of methanol, however an excess of methanol in large quantities slowed down the separation of the two phases produced. Besides, presence of high excess of methanol could have deactivated the catalyst used.

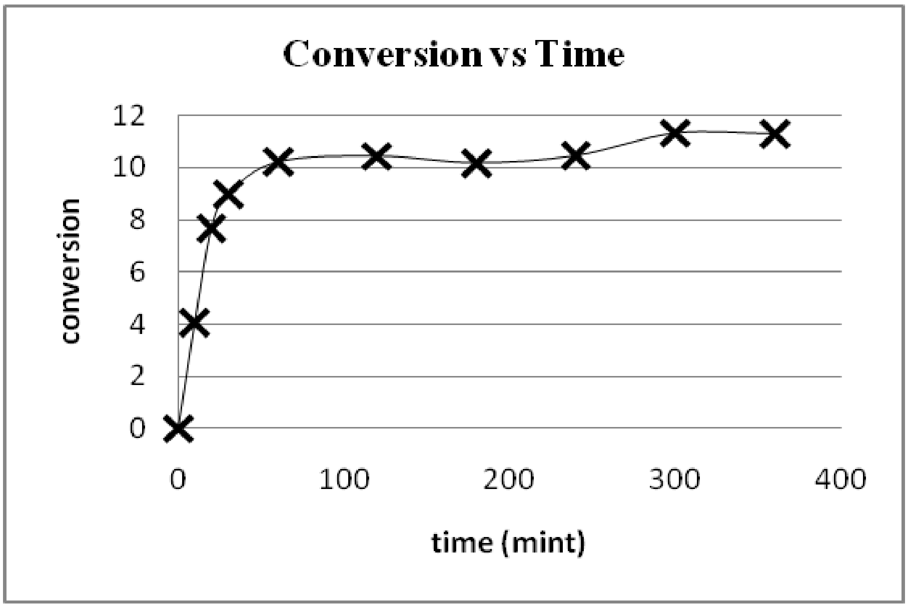


Figure 4.4: Conversion profile for the operating conditions of the effect of molar ratio 24:1, temperature 70°C and 5 g catalyst loading.

Comparison for each molar ratio is shown in Figure 4.5 and the optimum conditions for effect of molar ratio are 12:1 molar ratio methanol to oil with reaction temperature 70°C and 5 g of catalyst loading.

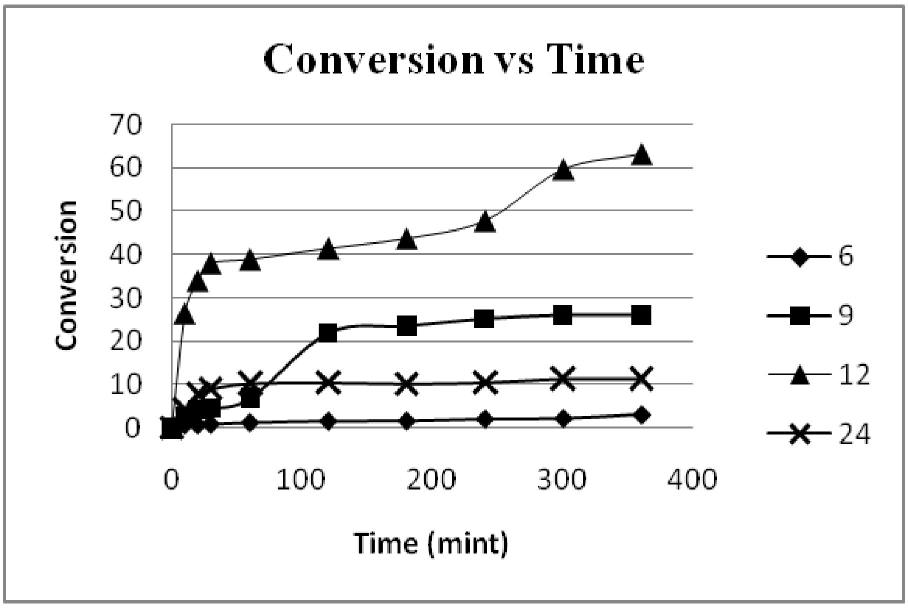


Figure 4.5: Conversion profile of effect of molar ratio to conversion of oil for operating conditions using temperature 70°C and 5 g of catalyst loading.

4.2 Effect of reaction temperature

The second parameter was reaction temperature. Three experiments have been done by varying the reaction temperature and the conversion have been determined while the other two parameters were fixed during this experiment and the molar ratio optimum condition was taken as 12. The operating conditions for effect of reaction temperature were 12:1 molar ratio methanol to oil and 5 g of catalyst loading.

Figure 4.6 shows the effect of reaction temperature 85ºC, with molar ratio methanol to oil was 12:1 and catalyst loading was 5 g. As the result, the maximum conversion from these conditions was 81% conversion of oil. Conversion from this experiment was higher than using temperature 70ºC. It was observed that increasing the reaction temperature, had a favorable influence on methyl ester conversion.

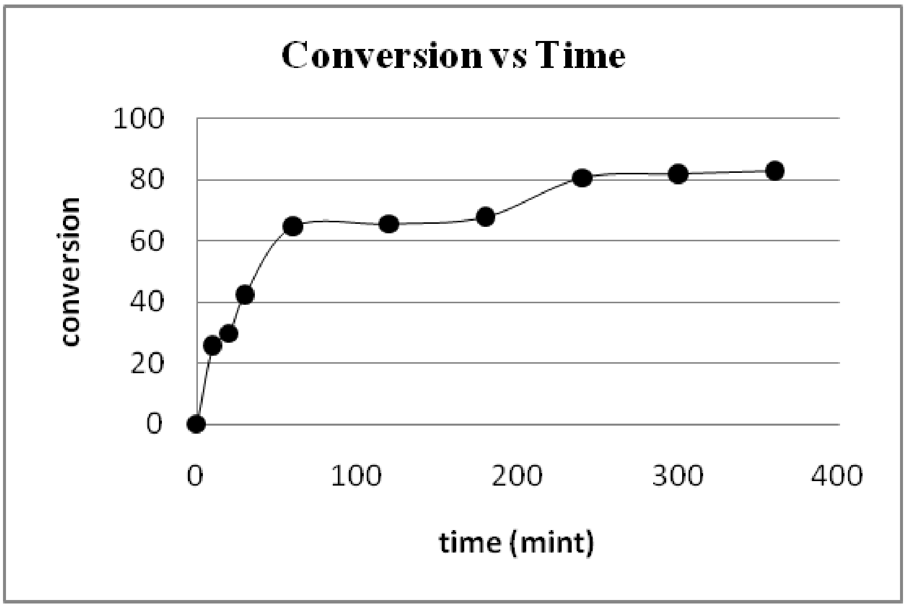


Figure 4.6: Conversion profile for the operating conditions of the effect of reaction temperature 85°C, molar ratio 12:1 and 5 g catalyst loading.

While in Figure 4.7 shows the highest conversion of oil was obtained. Figure 4.7 shows the effect of reaction temperature 100ºC, with molar ratio methanol to oil was 12:1 and catalyst loading was 5 g. These conditions results in higher conversion compared to temperature 70ºC and 85ºC which is 90% conversion of oil. The higher temperature, the higher conversion was achieved and this was shown in Arrhenius equation, $k = A \times \exp^{(-E/RT)}$ which shows that the higher temperature results in higher rate constant. Hence, increased reaction rate caused increased in conversion of triglyceride.

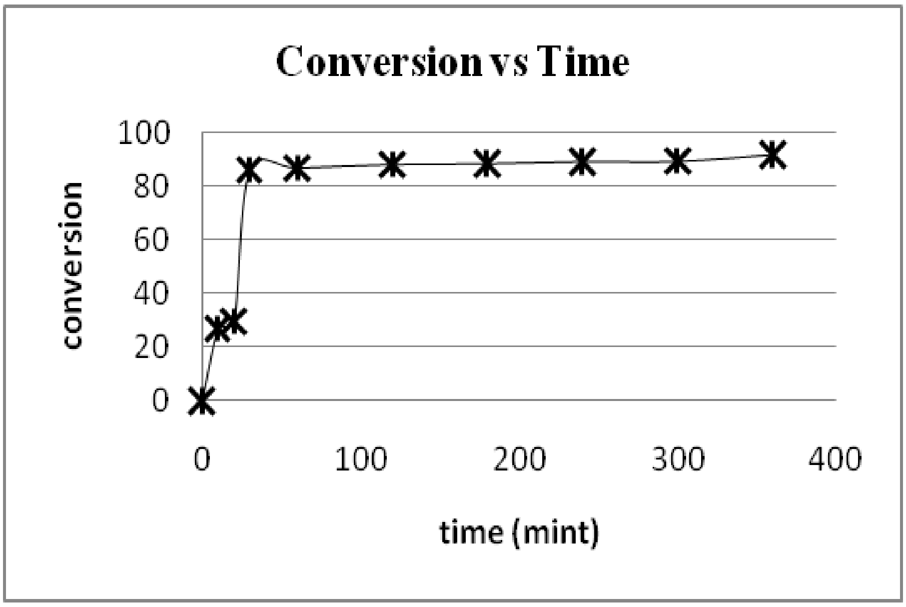


Figure 4.7: Conversion profile for the operating conditions of the effect of reaction temperature 100°C, molar ratio 12:1 and 5 g catalyst loading.

Comparison for each reaction temperature is shown in Figure 4.8 and the optimum conditions for effect of reaction temperature are 100ºC. However, too high temperature will burn the oil and affect the conversion yield. Since boiling point for methanol was around 65°C, higher reaction temperature caused methanol to vaporize which results in difficulties of methanol to shift the equilibrium to the right hand side since this process was a transesterification process.

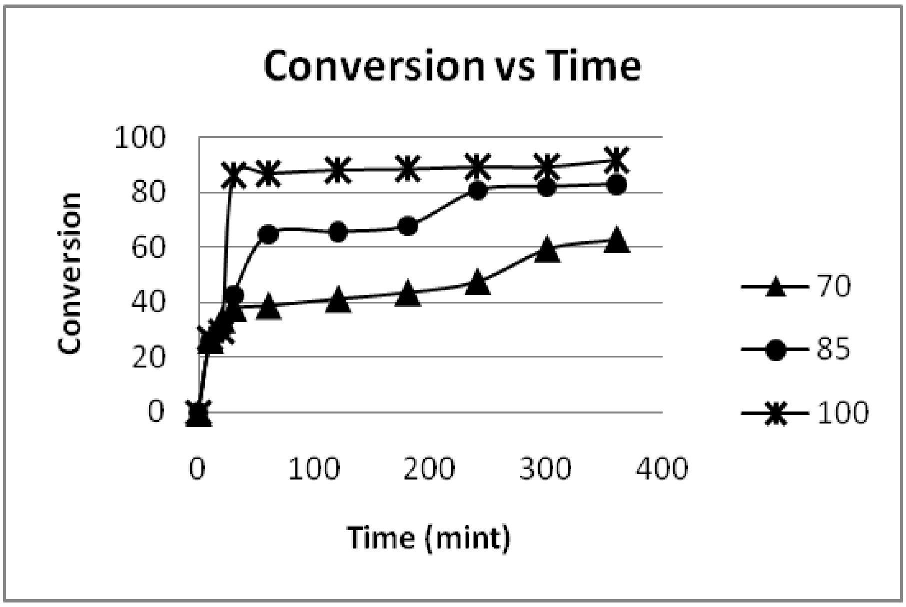


Figure 4.8: Conversion profile of effect of reaction temperature to conversion of oil for operating conditions using 12:1 molar ratio and 5 g of catalyst loading.

4.3 Effect of Catalyst Concentration

The third parameter was catalyst concentration. Three experiment have been done by varied the catalyst concentration and the conversion have been determined while the other two parameters was fixed and the optimum conditions was taken as molar ratio was 12 and reaction temperature was 100ºC. The operating conditions for catalyst concentration effect were molar ratio 12:1 and reaction temperature 100°C.

Figure 4.9 shows the effect of catalyst loading 3 g, with molar ratio methanol to oil is 12:1 and reaction temperature 100ºC. As the result, the maximum conversion from these conditions is 12% conversion of methyl ester. If compared the conversion with conversion that used 5 g of catalyst, this conversion was much lower. It was observed that if the loading catalyst was not enough, maximum production yield could not be reached.

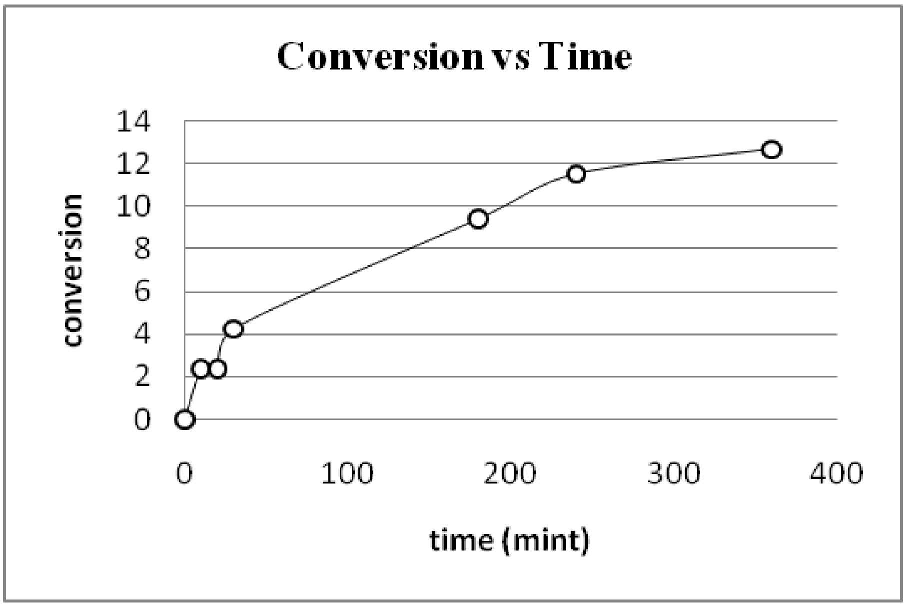


Figure 4.9: Conversion profile for the operating conditions of the effect of catalyst loading 3 g, molar ratio 12:1 and reaction temperature 100°C.

While based on Figure 4.10, by using catalyst loading 7 g, with molar ratio methanol to oil was 12:1 and reaction temperature 100ºC, the conversion produced still low which was 35% conversion. It was observed that further increase in the catalyst amount, possibly due to mixing problem involving reactants, products and catalyst. Furthermore, the slurry became too viscous if catalyst amount was too much giving rise to a problem of mixing and a demand of higher power consumption for adequate stirring.

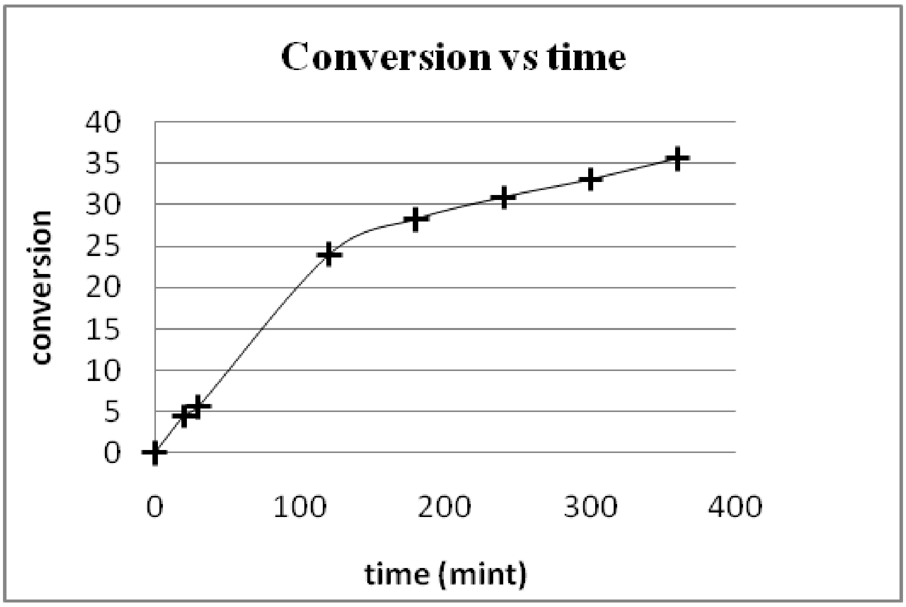


Figure 4.10: Conversion profile for the operating conditions of the effect of catalyst loading 7 g, molar ratio 12:1 and reaction temperature 100°C.

Comparison for each catalyst concentration is shown in Figure 4.11 and the optimum conditions for effect of catalyst concentration are 5 g with operating conditions using 12:1 molar ratio and 100°C of reaction temperature.

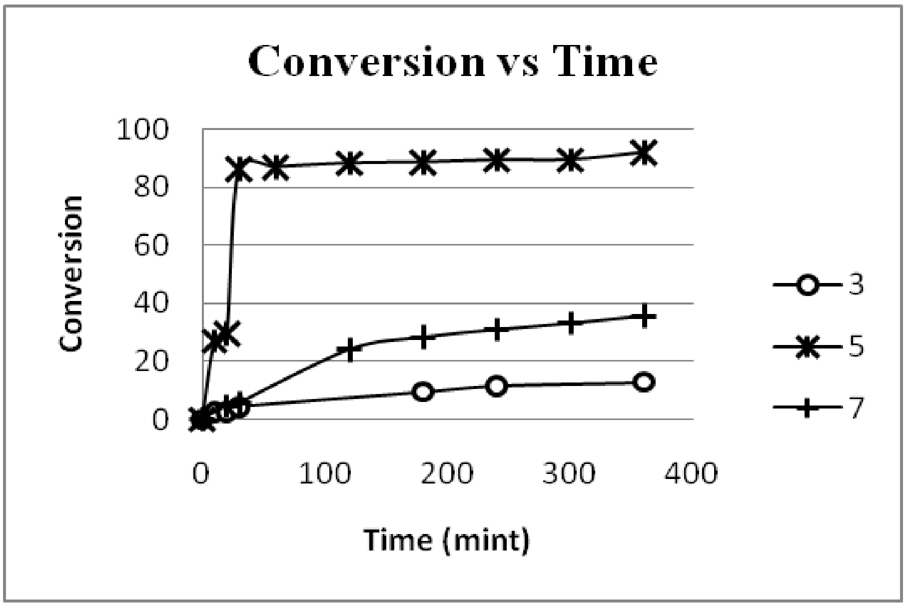


Figure 4.11: Conversion profile of effect of catalyst concentration to conversion of oil for operating conditions using 12:1 molar ratio and 100°C of reaction temperature.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

By performing the research studies based on the scope of study that has been proposed, the best operating condition for biodiesel fuel production via homogeneous Lewis acid catalyzed transesterification with methanol has been determined.

The molar ratio that results in highest conversion of methyl ester is 12:1 methanol to oil. Since the transesterification process is a reversible process, high amount of methanol needed to shift the equilibrium to the right hand side. This result bringing forward to the study of varying the reaction temperature which are 70ºC, 85ºC and 100ºC. The most feasible temperature for this reaction is 100ºC in order to achieve high conversion. The best amount of molar ratio and reaction temperature then brought forward to the studies of varying the amount of catalyst with 3 g, 5 g and 7 g. As the result, 5 g of catalyst seems to be the suitable amount to catalyze the reaction. The reaction under optimum conditions has produced 91% conversion of oil using transesterification process and methanol as solvent.

5.1 Recommendations

To improve the study, immobilize aluminium chloride on the support might be another way to make the catalyst become more sufficient. Instead of using batch reactor, continuous reactor can be used to study the effect of residence time.

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APPENDIX A

Experimental Diagram

Figure A.1: Biodiesel production using heating mantle

Figure A.2: Biodiesel production using oil bath

Figure A.3: Gas Chromatography used to analyze biodiesel

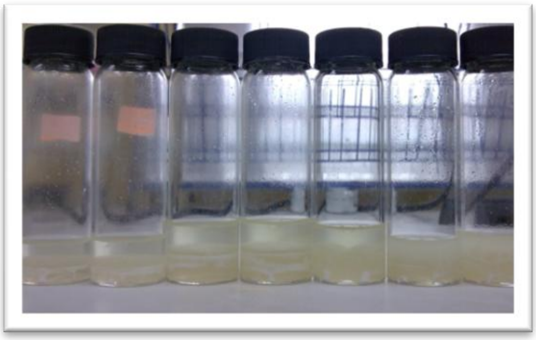

Figure A.4: Samples taken in time interval

APPENDIX B

Calculation of methyl ester conversion

From the calibration curve,

For methyl oleate,	y=0.1187x
For methyl palmitate,	y=0.1878x
For methyl linoleate	y=0.0617x

$$\mathrm{Conversion} = \frac{\mathrm{m_e}}{\mathrm{M_T}} \times 100$$

Where,

m_T = mass total

m_e = mass of methyl ester

$$\mathrm{M_T} = \frac{\text{Mass of oil}}{\text{MW of oil}} \times 3 \times (\text{Percentage of fatty acid in a palm oil}) \times \text{Molar mass of fatty acid}$$

Details	Linoleic Acid	Oleic Acid	Palmitic Acid
Molar mass	280	256	282
Percentage in sunflower oil	55%	7%	38%

MW of oil = 817g/L

Example: Calculation of methyl ester for effect of molar ratio 12:1 of methanol to oil

For Sample 1:

Area obtained at GC analysis is y= 89.52905 for methyl linoleate

Thus, y = 0.0617x

x = 1451.038 µg/mL

Mass of methyl linoleate in a 10mL volumetric flask,

$$\frac{1451.038\ \text{□g}}{\text{mL}} = \frac{1.4510\ \times\ 10^{-3}\ \text{g}}{1\ \times\ 10^{-3}\text{L}} \times 0.01\text{L}$$

$$= 1.451\ \times\ 10^{-2}\ \text{g}$$

$$\%\ \text{scaling up} = \frac{1.451\ \times\ 10^{-2}\ \text{g}}{0.05} \times 100$$

$$=\ 29.02\ \%$$

Mass of oil + Mass of alcohol = 183 g

$$\%\ \text{scaling up} =\ 29.02\ \% \times 183\text{g}$$

$$=\ 53.07\ \text{g}$$

$$\mathrm{M_T} = \frac{100\ \mathrm{g}}{817} \times 3 \times (55\ \%) \times 280 = 56.5483\ \mathrm{g}$$

$$\mathrm{Conversion} = \frac{53.07}{56.5483} \times 100$$

$$= 93.85\ \%$$

Table B.1: Effect of Molar Ratio Methanol to Oil

Experiment 1		Experiment 2		Experiment 3		Experiment 4	
Molar ratio : 6 Temperature : 70°C Catalyst Concentration : 5 g Time : 6 hours		Molar ratio : 9 Temperature : 70°C Catalyst Concentration : 5 g Time : 6 hours		Molar ratio : 12 Temperature : 70°C Catalyst Concentration : 5 g Time : 6 hours		Molar ratio : 24 Temperature : 70°C Catalyst Concentration : 5 g Time : 6 hours	
Conversion	t (min)	Conversion	t (min)	Conversion	t (min)	Conversion	t (min)
0	0	0	0	0	0	0	0
0.645	10	2.481	10	26.366	10	4.077	10
0.685	20	4.093	20	33.877	20	7.683	20
0.873	30	4.517	30	37.847	30	8.983	30
1.211	60	6.893	60	38.801	60	10.212	60
1.553	120	21.892	120	41.308	120	10.443	120
1.597	180	23.447	180	43.583	180	10.181	180
1.988	240	25.135	240	47.670	240	10.456	240
2.125	300	25.988	300	59.494	300	11.320	300
2.952	360	26.040	360	63.011	360	11.292	360

Table B.2: Effect of Reaction Temperature

Experiment 3		Experiment 5		Experiment 6	
Molar ratio : 12 Temperature : 70°C Catalyst Concentration : 5 g Time : 6 hours		Molar ratio : 12 Temperature : 85°C Catalyst Concentration : 5 g Time : 6 hours		Molar ratio : 12 Temperature : 100°C Catalyst Concentration : 5 g Time : 6 hours	
Conversion	t (mint)	conversion	t (mint)	conversion	t (mint)
0	0	0	0	0	0
26.366	10	25.679	10	26.789	10
33.877	20	29.641	20	29.399	20
37.847	30	42.522	30	86.187	30
38.801	60	64.734	60	86.865	60
41.308	120	65.547	120	88.153	120
43.583	180	67.838	180	88.474	180
47.670	240	80.596	240	89.281	240
59.497	300	81.937	300	89.337	300
63.017	360	82.903	360	91.851	360

Table B.3: Effect of Catalyst Concentration

<table>
<tr><th>Experiment 6</th><th>Experiment 7</th><th>Experiment 8</th></tr>
<tr>
<td>Molar ratio : 12
Temperature : 70°C
Catalyst
Concentration : 5 g
Time : 6 hours
<table>
<tr><th>Conversion</th><th>t (mint)</th></tr>
<tr><td>0</td><td>0</td></tr>
<tr><td>26.789</td><td>10</td></tr>
<tr><td>29.399</td><td>20</td></tr>
<tr><td>86.187</td><td>30</td></tr>
<tr><td>86.856</td><td>60</td></tr>
<tr><td>88.153</td><td>120</td></tr>
<tr><td>88.474</td><td>180</td></tr>
<tr><td>89.281</td><td>240</td></tr>
<tr><td>89.337</td><td>300</td></tr>
<tr><td>91.851</td><td>360</td></tr>
</table>
</td>
<td>Molar ratio : 12
Temperature : 70°C
Catalyst
Concentration : 3 g
Time : 6 hours
<table>
<tr><th>Conversion</th><th>t (mint)</th></tr>
<tr><td>0</td><td>0</td></tr>
<tr><td>2.358</td><td>10</td></tr>
<tr><td>2.363</td><td>20</td></tr>
<tr><td>4.258</td><td>30</td></tr>
<tr><td>9.403</td><td>180</td></tr>
<tr><td>11.509</td><td>240</td></tr>
<tr><td>12.689</td><td>360</td></tr>
</table>
</td>
<td>Molar ratio : 12
Temperature : 70°C
Catalyst
Concentration : 7 g
Time : 6 hours
<table>
<tr><th>conversion</th><th>t (mint)</th></tr>
<tr><td>0</td><td>0</td></tr>
<tr><td>4.498</td><td>20</td></tr>
<tr><td>5.602</td><td>30</td></tr>
<tr><td>23.964</td><td>120</td></tr>
<tr><td>28.237</td><td>180</td></tr>
<tr><td>30.870</td><td>240</td></tr>
<tr><td>33.028</td><td>300</td></tr>
<tr><td>35.565</td><td>360</td></tr>
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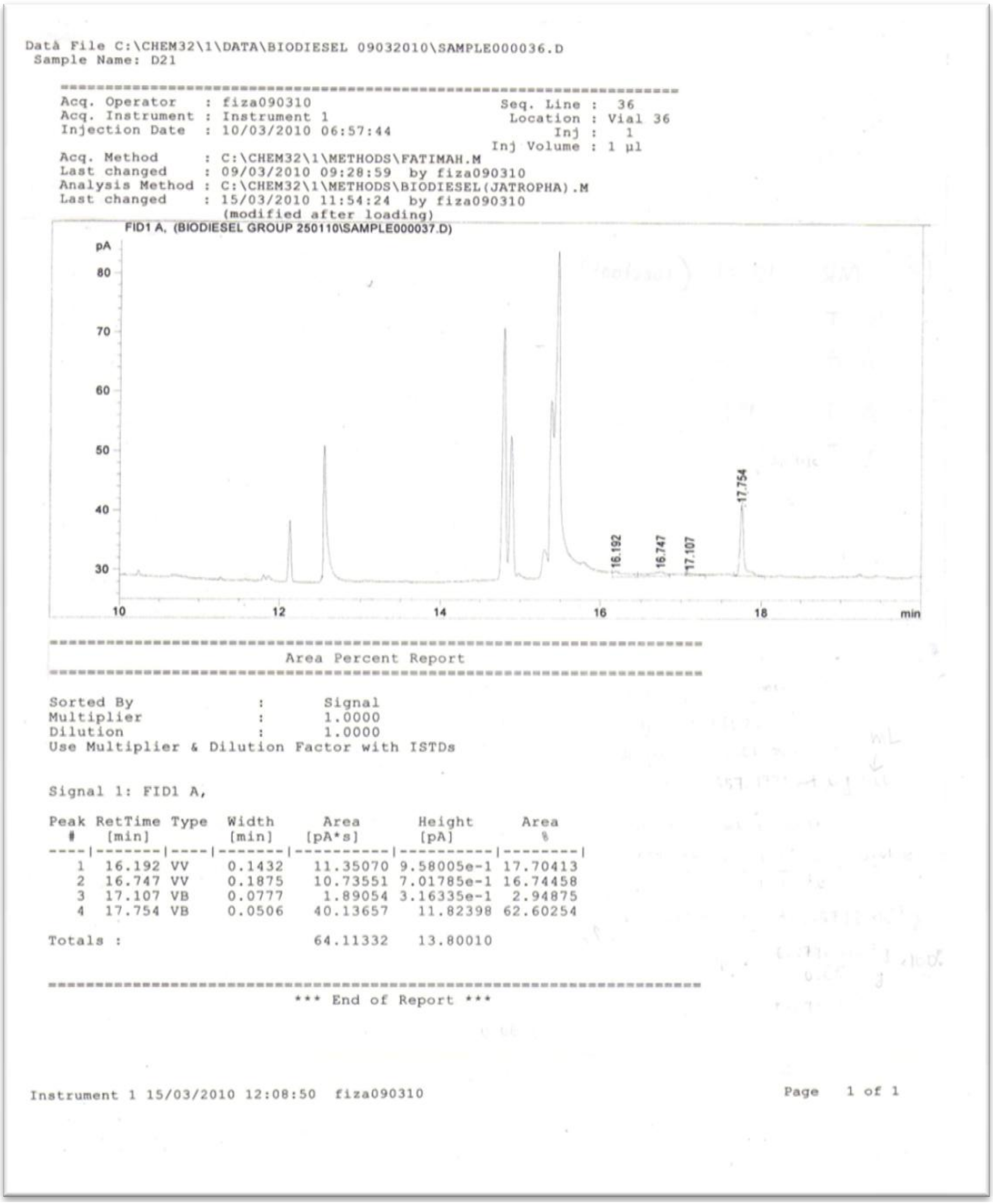
APPENDIX C

Chromatogram for Optimum Conditions



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                                                    Inj Volume : 1 µl
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    Last changed    : 09/03/2010 09:28:59  by fiza090310
    Analysis Method : C:\CHEM32\1\METHODS\BIODIESEL(JATROPHA).M
    Last changed    : 15/03/2010 11:54:24  by fiza090310
                      (modified after loading)
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                            Area Percent Report
   =================================================================

   Sorted By             :      Signal
   Multiplier            :      1.0000
   Dilution              :      1.0000
   Use Multiplier & Dilution Factor with ISTDs


   Signal 1: FID1 A,

   Peak RetTime Type  Width      Area       Height      Area
     #   [min]        [min]    [pA*s]        [pA]         %
   ----|-------|----|-------|----------|----------|--------|
     1  16.192 VV    0.1432   11.35070 9.58005e-1 17.70413
     2  16.747 VV    0.1875   10.73551 7.01785e-1 16.74458
     3  17.107 VB    0.0777    1.89054 3.16335e-1  2.94875
     4  17.754 VB    0.0506   40.13657   11.82398 62.60254

   Totals :                   64.11332   13.80010


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 Instrument 1 15/03/2010 12:08:50  fiza090310                     Page   1 of 1
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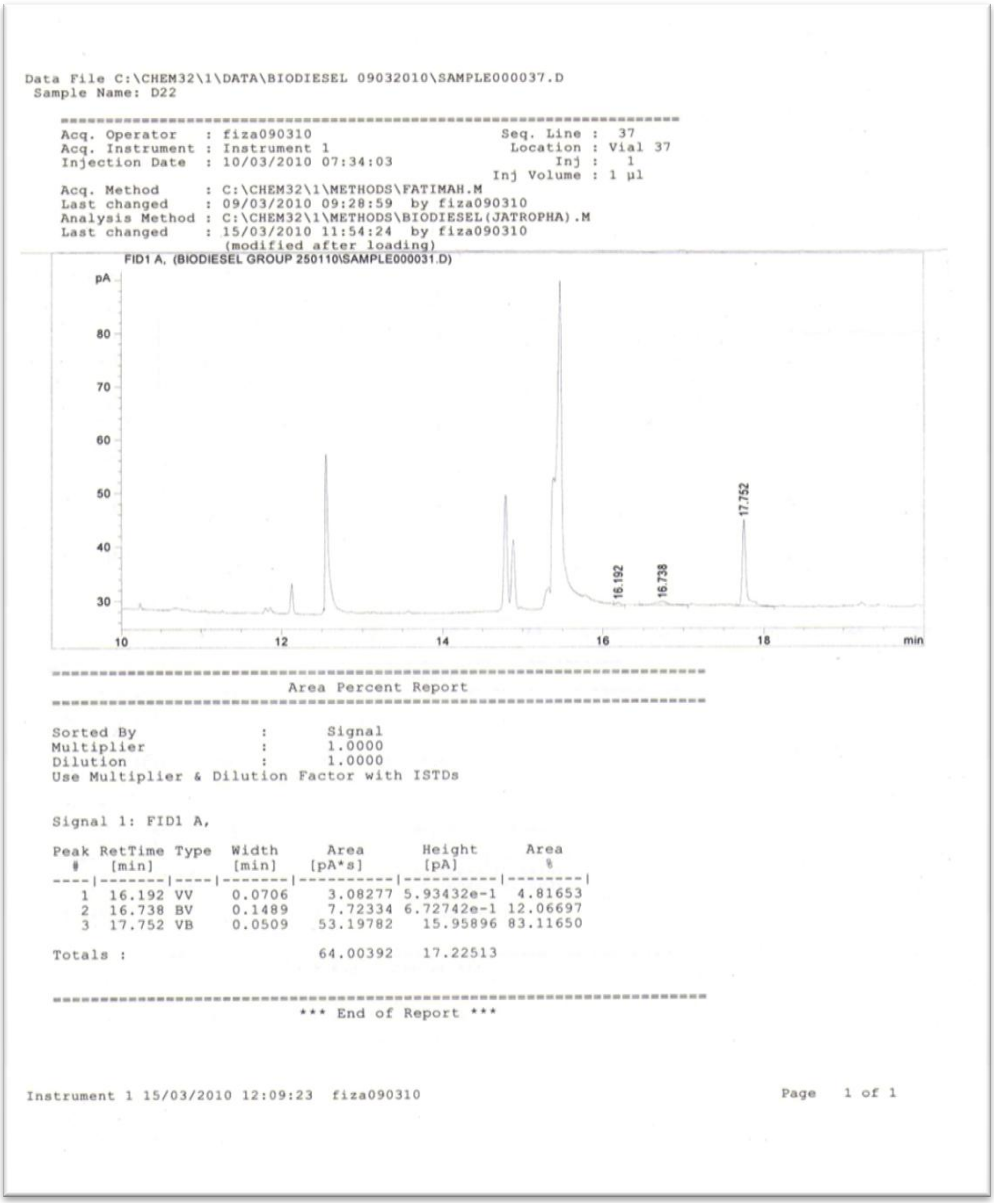
Figure C.1: Figure for Sample 1



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                                                       Inj Volume : 1 µl
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    Last changed    : 09/03/2010 09:28:59  by fiza090310
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    Last changed    : 15/03/2010 11:54:24  by fiza090310
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   =====================================================================

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   Dilution              :      1.0000
   Use Multiplier & Dilution Factor with ISTDs


   Signal 1: FID1 A,

   Peak RetTime Type  Width      Area      Height      Area
     #   [min]        [min]    [pA*s]      [pA]          %
   ----|-------|----|-------|----------|----------|--------|
      1  16.192 VV    0.0706    3.08277 5.93432e-1  4.81653
      2  16.738 BV    0.1489    7.72334 6.72742e-1 12.06697
      3  17.752 VB    0.0509   53.19782   15.95896 83.11650

   Totals :                    64.00392   17.22513


   =====================================================================
                          *** End of Report ***



Instrument 1 15/03/2010 12:09:23  fiza090310                     Page   1 of 1
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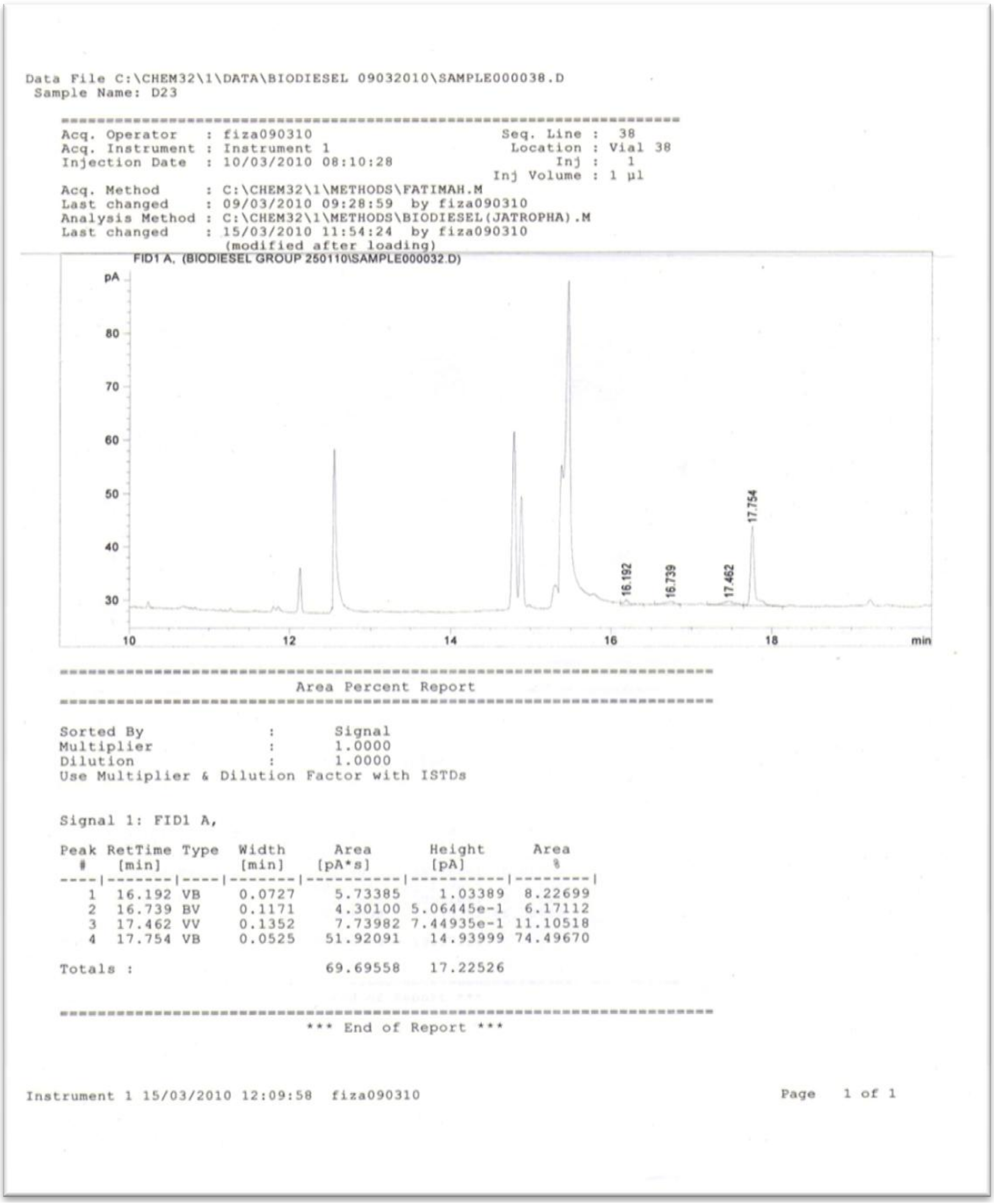
Figure C.2: Figure for Sample 2



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                                                     Inj Volume : 1 µl
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    Analysis Method : C:\CHEM32\1\METHODS\BIODIESEL(JATROPHA).M
    Last changed    : 15/03/2010 11:54:24  by fiza090310
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                             Area Percent Report
    =====================================================================

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    Multiplier             :      1.0000
    Dilution               :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID1 A,

    Peak RetTime Type  Width     Area      Height     Area
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    ----|-------|----|-------|----------|----------|--------|
       1  16.192 VB    0.0727    5.73385    1.03389   8.22699
       2  16.739 BV    0.1171    4.30100 5.06445e-1  6.17112
       3  17.462 VV    0.1352    7.73982 7.44935e-1 11.10518
       4  17.754 VB    0.0525   51.92091   14.93999  74.49670

    Totals :                    69.69558   17.22526

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                              *** End of Report ***


Instrument 1 15/03/2010 12:09:58  fiza090310                        Page   1 of 1
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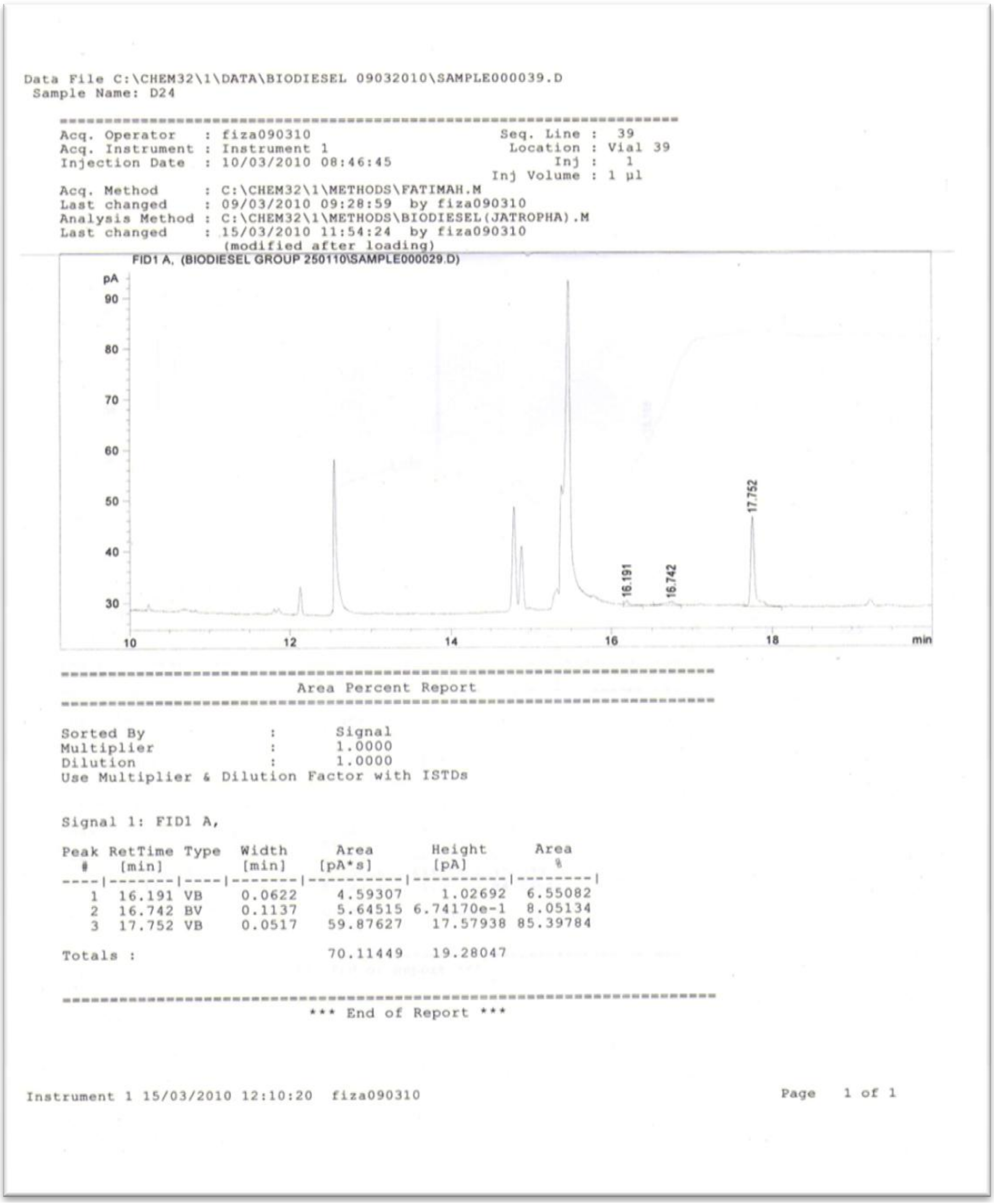
Figure C.3: Figure for Sample 3



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                                                       Inj Volume : 1 µl
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    Last changed    : 09/03/2010 09:28:59  by fiza090310
    Analysis Method : C:\CHEM32\1\METHODS\BIODIESEL(JATROPHA).M
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                      (modified after loading)

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                             Area Percent Report
    =====================================================================

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    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID1 A,

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [pA*s]      [pA]        %
    ----|-------|----|-------|----------|----------|--------|
       1  16.191 VB    0.0622    4.59307    1.02692  6.55082
       2  16.742 BV    0.1137    5.64515 6.74170e-1  8.05134
       3  17.752 VB    0.0517   59.87627   17.57938 85.39784

    Totals :                    70.11449   19.28047

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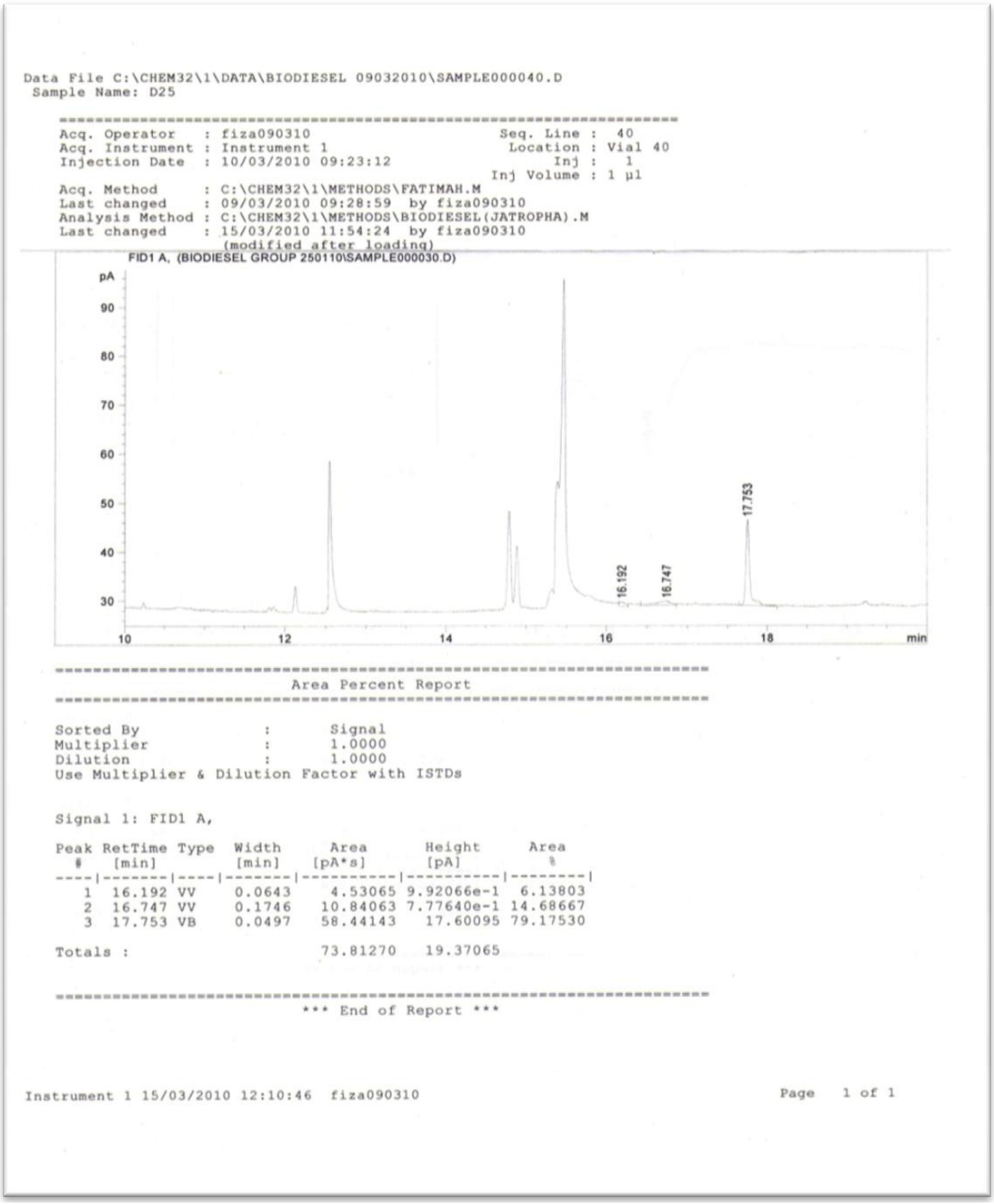
                              *** End of Report ***


Instrument 1 15/03/2010 12:10:20  fiza090310                    Page    1 of 1
```

Figure C.4: Figure for Sample 4



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                                                        Inj Volume : 1 µl
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    Analysis Method : C:\CHEM32\1\METHODS\BIODIESEL(JATROPHA).M
    Last changed    : 15/03/2010 11:54:24  by fiza090310
                      (modified after loading)
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                         Area Percent Report
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Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
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   1  16.192 VV    0.0643    4.53065 9.92066e-1  6.13803
   2  16.747 VV    0.1746   10.84063 7.77640e-1 14.68667
   3  17.753 VB    0.0497   58.44143   17.60095 79.17530

Totals :                    73.81270   19.37065


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                         *** End of Report ***


Instrument 1 15/03/2010 12:10:46  fiza090310                    Page   1 of 1
```
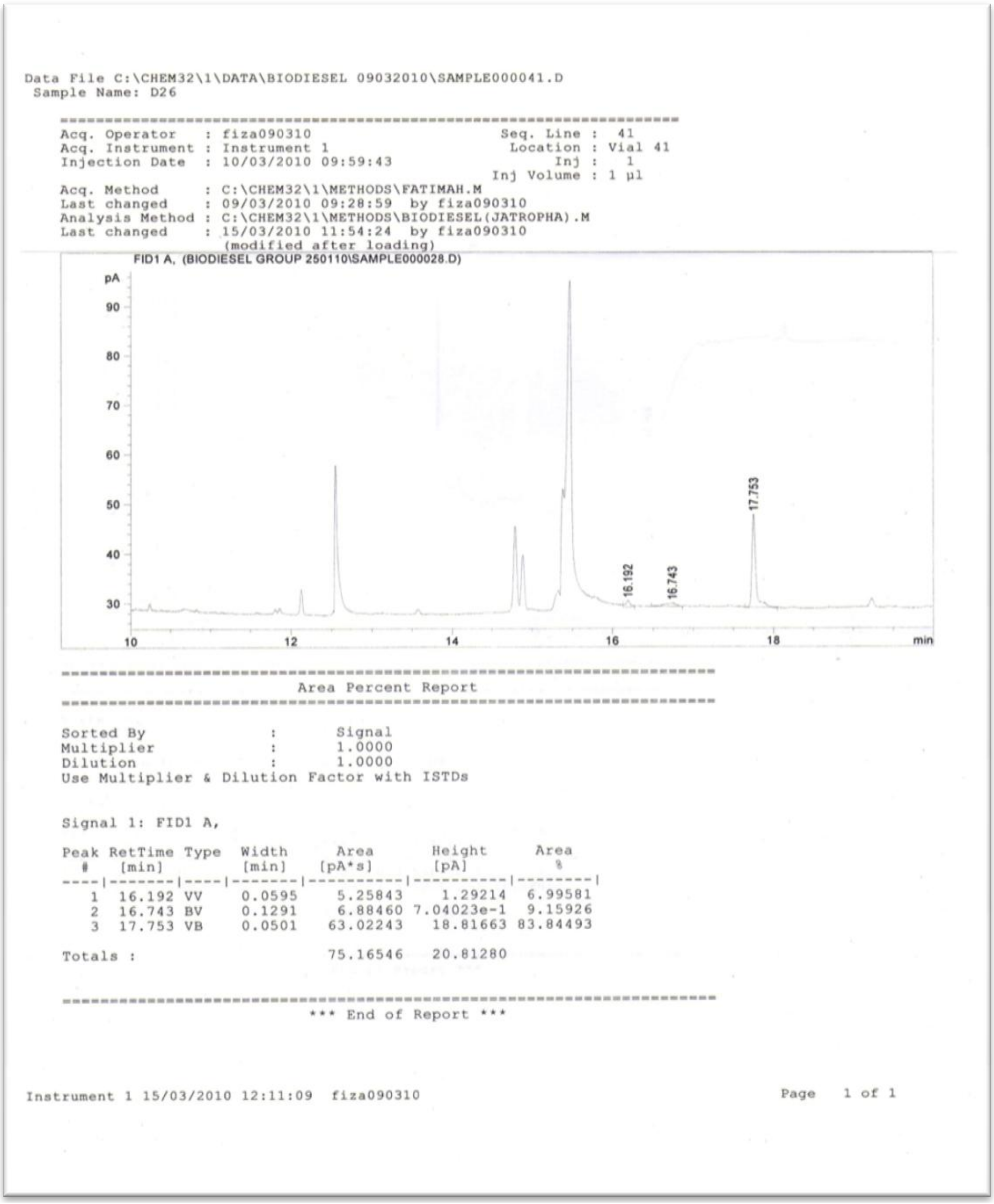
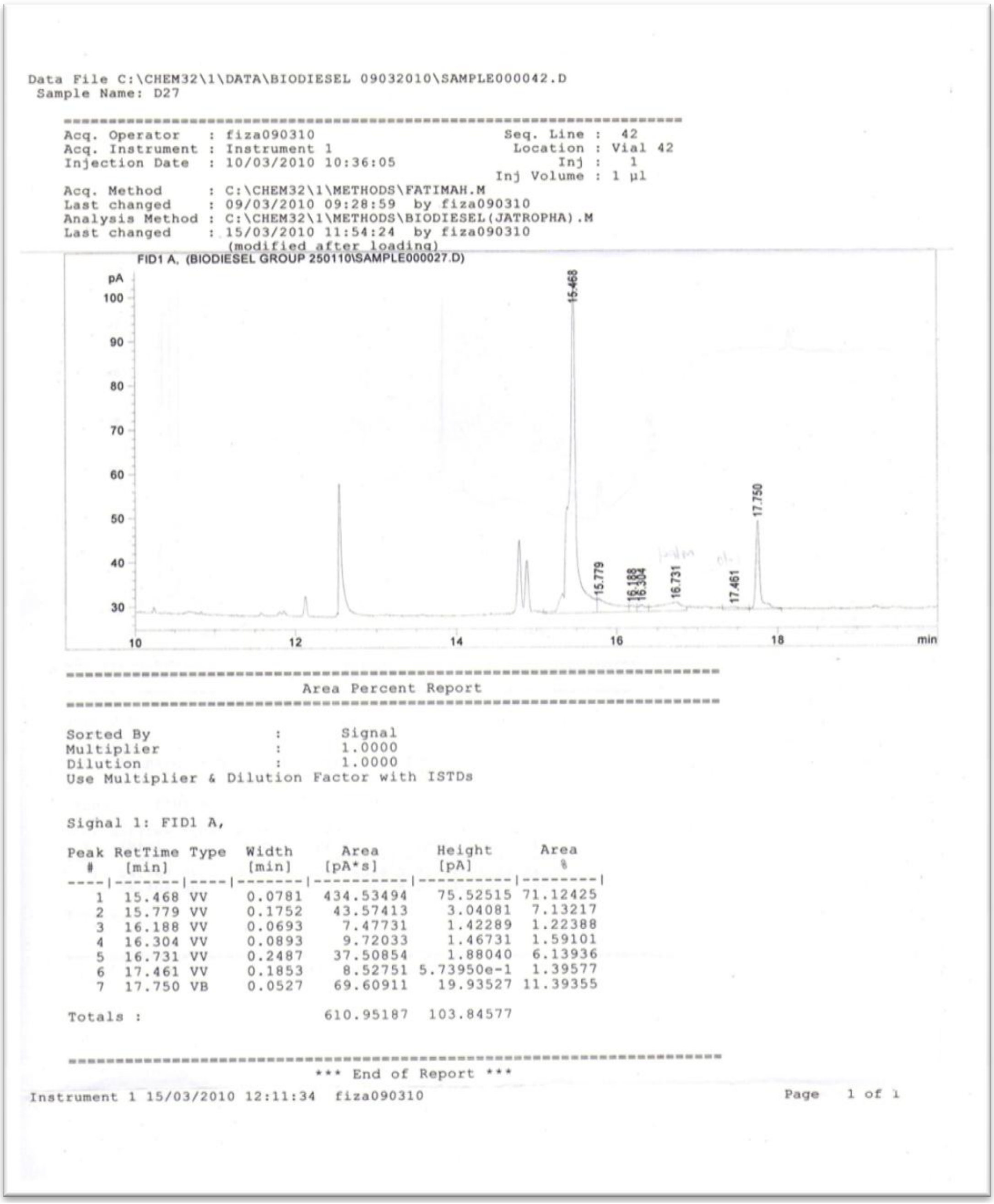

Figure C.5: Figure for Sample 5



```
Data File C:\CHEM32\1\DATA\BIODIESEL 09032010\SAMPLE000041.D
 Sample Name: D26

    =================================================================
    Acq. Operator   : fiza090310                       Seq. Line :  41
    Acq. Instrument : Instrument 1                      Location : Vial 41
    Injection Date  : 10/03/2010 09:59:43                    Inj :   1
                                                      Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\METHODS\FATIMAH.M
    Last changed    : 09/03/2010 09:28:59  by fiza090310
    Analysis Method : C:\CHEM32\1\METHODS\BIODIESEL(JATROPHA).M
    Last changed    : 15/03/2010 11:54:24  by fiza090310
                      (modified after loading)
```

```
    =====================================================================
                             Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs

    Signal 1: FID1 A,

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [pA*s]      [pA]         %
    ----|-------|----|-------|----------|----------|--------|
       1  16.192 VV    0.0595    5.25843    1.29214  6.99581
       2  16.743 BV    0.1291    6.88460 7.04023e-1  9.15926
       3  17.753 VB    0.0501   63.02243   18.81663 83.84493

    Totals :                    75.16546   20.81280

    =====================================================================
                              *** End of Report ***


Instrument 1 15/03/2010 12:11:09  fiza090310                       Page    1 of 1
```

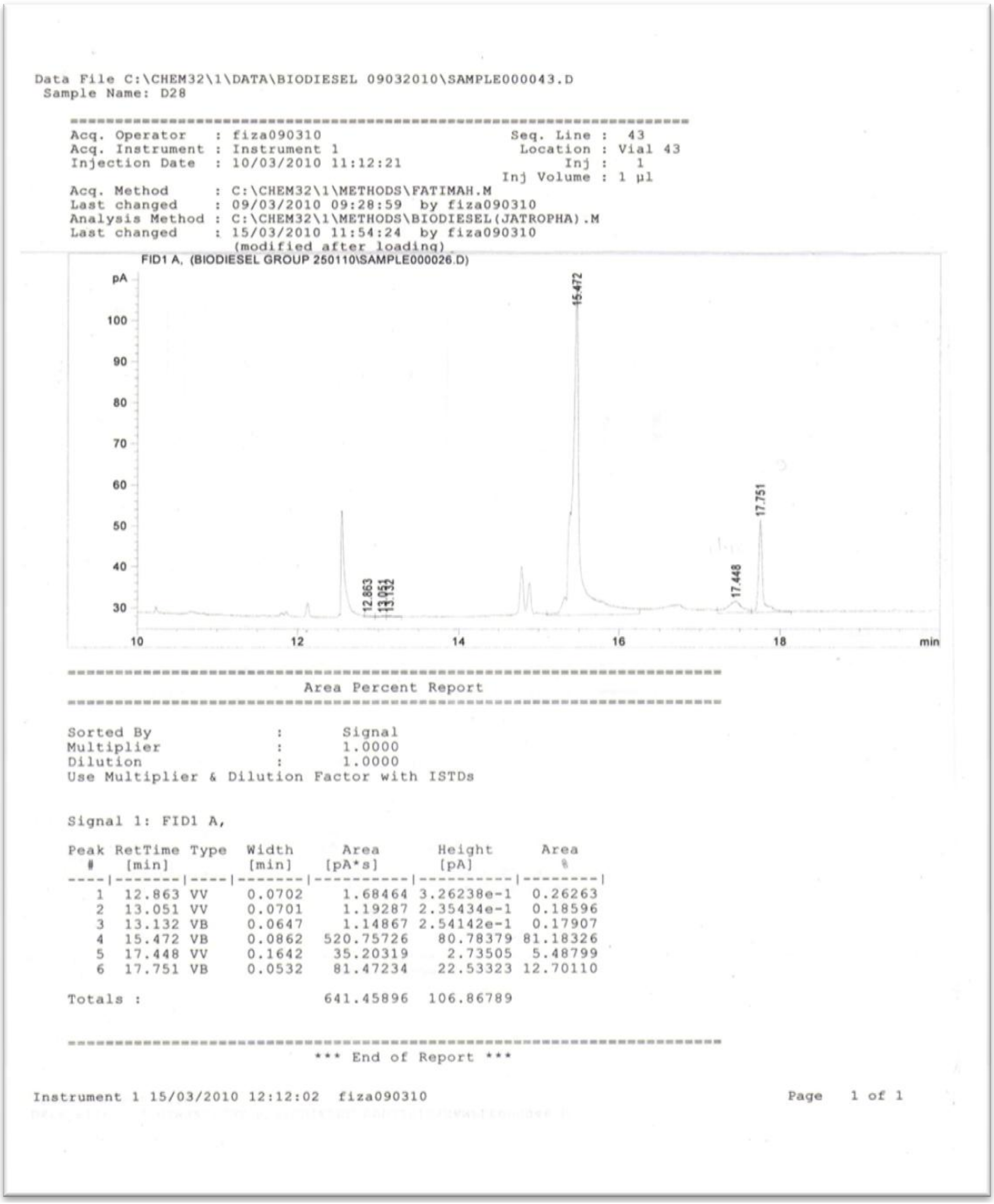
Figure C.6: Figure for Sample 6



```
Data File C:\CHEM32\1\DATA\BIODIESEL 09032010\SAMPLE000042.D
 Sample Name: D27

    =====================================================================
    Acq. Operator   : fiza090310                     Seq. Line :  42
    Acq. Instrument : Instrument 1                    Location : Vial 42
    Injection Date  : 10/03/2010 10:36:05                   Inj :   1
                                                    Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\METHODS\FATIMAH.M
    Last changed    : 09/03/2010 09:28:59  by fiza090310
    Analysis Method : C:\CHEM32\1\METHODS\BIODIESEL(JATROPHA).M
    Last changed    : 15/03/2010 11:54:24  by fiza090310
                      (modified after loading)
```

```
    =====================================================================
                          Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID1 A,

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [pA*s]      [pA]        %
    ----|-------|----|-------|----------|----------|--------|
       1  15.468 VV    0.0781  434.53494   75.52515 71.12425
       2  15.779 VV    0.1752   43.57413    3.04081  7.13217
       3  16.188 VV    0.0693    7.47731    1.42289  1.22388
       4  16.304 VV    0.0893    9.72033    1.46731  1.59101
       5  16.731 VV    0.2487   37.50854    1.88040  6.13936
       6  17.461 VV    0.1853    8.52751 5.73950e-1  1.39577
       7  17.750 VB    0.0527   69.60911   19.93527 11.39355

    Totals :                   610.95187  103.84577


    =====================================================================
                          *** End of Report ***
Instrument 1 15/03/2010 12:11:34  fiza090310                    Page   1 of 1
```

Figure C.7: Figure for Sample 7

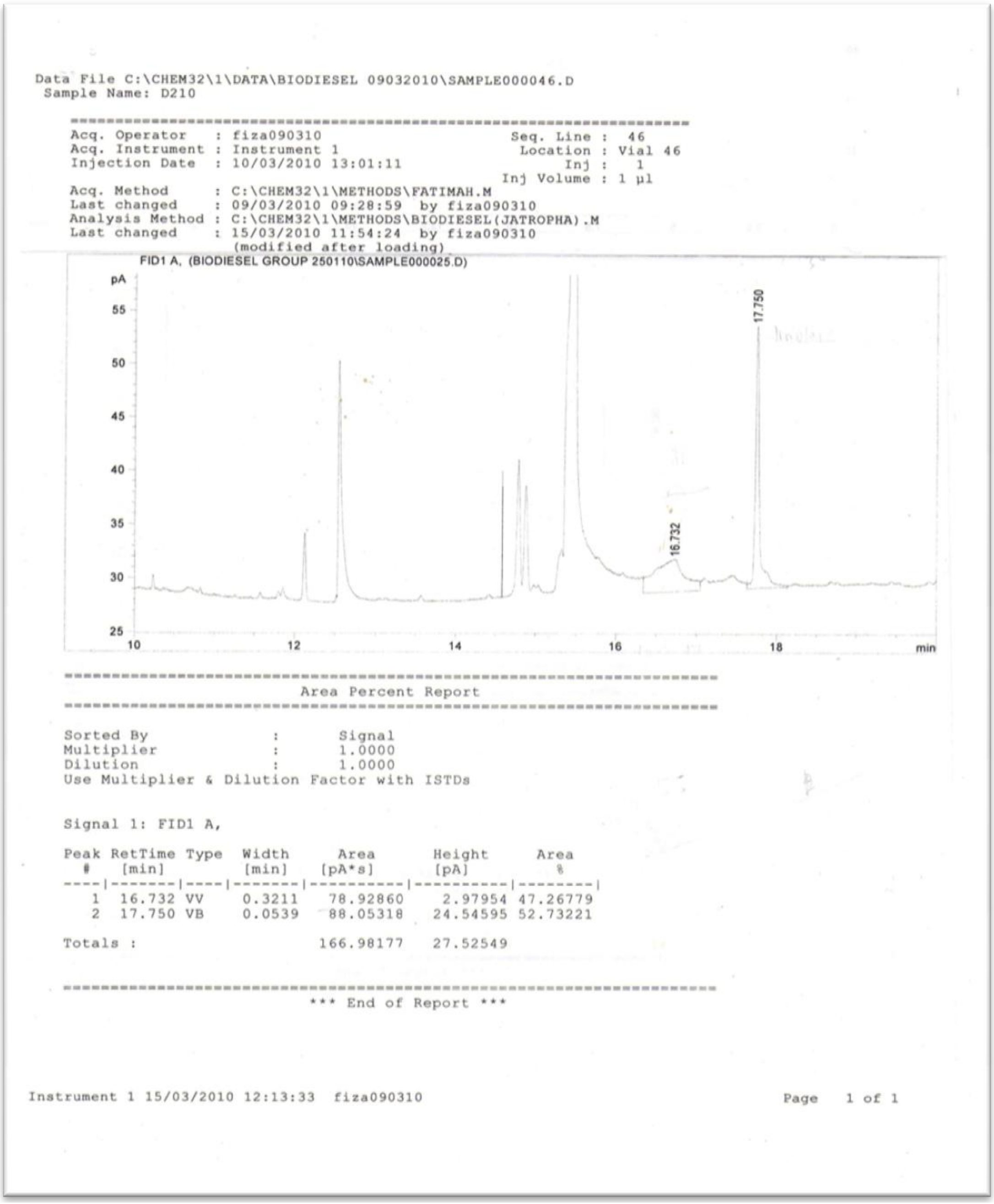


```
Data File C:\CHEM32\1\DATA\BIODIESEL 09032010\SAMPLE000043.D
 Sample Name: D28

    =================================================================
    Acq. Operator   : fiza090310                     Seq. Line :  43
    Acq. Instrument : Instrument 1                    Location : Vial 43
    Injection Date  : 10/03/2010 11:12:21                  Inj :   1
                                                Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\METHODS\FATIMAH.M
    Last changed    : 09/03/2010 09:28:59  by fiza090310
    Analysis Method : C:\CHEM32\1\METHODS\BIODIESEL(JATROPHA).M
    Last changed    : 15/03/2010 11:54:24  by fiza090310
                      (modified after loading)
```

FID1 A, (BIODIESEL GROUP 250110\SAMPLE000026.D)

```
    =====================================================================
                          Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID1 A,

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [pA*s]      [pA]         %
    ----|-------|----|-------|----------|----------|--------|
       1  12.863 VV    0.0702    1.68464 3.26238e-1  0.26263
       2  13.051 VV    0.0701    1.19287 2.35434e-1  0.18596
       3  13.132 VB    0.0647    1.14867 2.54142e-1  0.17907
       4  15.472 VB    0.0862  520.75726   80.78379 81.18326
       5  17.448 VV    0.1642   35.20319    2.73505  5.48799
       6  17.751 VB    0.0532   81.47234   22.53323 12.70110

    Totals :                   641.45896  106.86789


    =====================================================================
                          *** End of Report ***

Instrument 1 15/03/2010 12:12:02  fiza090310                         Page    1 of 1
```

Figure C.8: Figure for Sample 8



```
Data File C:\CHEM32\1\DATA\BIODIESEL 09032010\SAMPLE000046.D
 Sample Name: D210

    =====================================================================
    Acq. Operator   : fiza090310                        Seq. Line :  46
    Acq. Instrument : Instrument 1                       Location : Vial 46
    Injection Date  : 10/03/2010 13:01:11                     Inj :   1
                                                       Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\METHODS\FATIMAH.M
    Last changed    : 09/03/2010 09:28:59  by fiza090310
    Analysis Method : C:\CHEM32\1\METHODS\BIODIESEL(JATROPHA).M
    Last changed    : 15/03/2010 11:54:24  by fiza090310
                      (modified after loading)
```

```
   =====================================================================
                          Area Percent Report
   =====================================================================

   Sorted By              :      Signal
   Multiplier             :      1.0000
   Dilution               :      1.0000
   Use Multiplier & Dilution Factor with ISTDs

   Signal 1: FID1 A,

   Peak RetTime Type  Width     Area      Height     Area
     #   [min]        [min]   [pA*s]      [pA]        %
   ----|-------|----|-------|----------|----------|--------|
      1  16.732 VV    0.3211   78.92860    2.97954 47.26779
      2  17.750 VB    0.0539   88.05318   24.54595 52.73221

   Totals :                   166.98177   27.52549

   =====================================================================
                          *** End of Report ***


 Instrument 1 15/03/2010 12:13:33  fiza090310                     Page   1 of 1
```

Figure C.9: Figure for Sample 9