DEVELOPMENT OF HETEROGENEOUS BASE CATAYST FOR TRANSESTERIFICATION REACTION

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DEVELOPMENT OF HETEROGENEOUS BASE CATAYST FOR TRANSESTERIFICATION REACTION

SHARMILLA ARUMUGAM

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

Faculty of Chemical & Natural Resources Engineering
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I declare that this thesis entitled "Development of Potassium Nitrate with Alumina as Heterogeneous Base Catalyst for Transesterification" is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree."

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I dedicate this thesis to my family without whom none of these would have been worth a challenge…

Loving Mother;

Mrs. Pachammah@Ponni Arjunan

Also Sweetest siblings

This is for all of you…

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ABSTRACT

In this study of heterogeneous base catalyst of potassium nitrate with alumina support was investigated for transesterification of vegetable oil which is palm oil to methyl ester. The environmental problem could be overcome by using heterogeneous base catalyst because the separation of catalyst from final product is easier without use of any solvent and the catalyst is recyclable. The objective of this study is to characterise the developed heterogeneous base catalyst and test it in transesterification reaction at different operating parameters such as molar ratio of methanol to oil, reaction temperature and catalyst loading. After loading potassium nitrate of 35 wt.% on alumina followed by calcination at 773K for 5 h, the catalyst gave the highest basicity and the best catalytic activity for this reaction. The catalysts were characterized by using Fourier Transform Infrared Spectrometers (FTIR) and Scanning Electron Microscopy (SEM). It was found that KNO_3/ Al_2O_3 show high activity which converting 78.44% of palm oil to methyl ester with the optimum conditions which are at temperature 65°C, methanol to oil ratio of 15:1 and catalyst loading of 8.5% . Therefore, base heterogeneous catalyst of potassium on alumina of support has the potential to be used in biodiesel production processes due to its high activity on transesterification of palm oil.

ABSTRAK

Dalam kajian pemangkin alkali heterogen, nitrat kalium dengan alumina diselidiki untuk pengtransesteran minyak kelapa sawit kepada biodiesel. Masalah persekitaran dapat diatasi dengan menggunakan pemangkin alkali heterogen kerana pemisahan pemangkin dari produk lebih mudah tanpa menggunakan pelarut dan pemangkin ini dapat dikitar semula. Tujuan dari penelitian ini adalah untuk mengkarakterisasi pemangkin alkali untuk mengujinya dalam pengtransesteran pada parameter operasi yang berbeza seperti nisbah molar methanol terhadap minyak, reaksi suhu dan loading pemangkin. Apabila menggunakan sebanyak 35% nitrat kalium /alumina dan diikuti dengan kalsinasi pada 773K selama 5 jam, pemangkin memberikan kebesan tertinggi dan menunjukkan pemangkin terbaik untuk tindak balas ini. pemangkin ini dikaji dengan menggunakan Transformasi Fourier Spektrometer (FTIR) dan Mikroskop Elektron (SEM). KNO_3/ Al_2O_3 menunjukkan aktiviti tertinggi; iaitu ia dapat biodiesel sebanyak 78,44% dari minyak sawit dengan keadaan optimum yang pada suhu 65 ° C, metanol terhadap minyak 15:1 dan loading pemangkin 8.5%. Oleh kerana itu, pemangkin heterogen iaitu KNO_3/alumina munjukkan ia mempunyai berpotensi untuk menggunakan dalam pengeluaran biodiesel kerana dapat hasilkan banyak biodiesel.

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LIST OF ABREAVIATION

IICA	-	Inter-American Institute for Cooperation on Agriculture
PME	-	Palm oil methyl ester
WCO	-	Waste Cooking Oil
FFA	-	Free Fatty Acid
BSP	-	Biomass Support Particles
FTIR	-	Fourier transform Infrared Spectrometer
GC	-	Gas Chromatography

LIST OF SYMBOLS

T	-	Temperature
°C	-	Degree Celcius
Ml	-	Mililiter
Min	-	Minute
K	-	Kelvin
w/w	-	Weight per weight
kg	-	Kilogram
g	-	Gram
%	-	Percentage
Rpm	-	Revolutions per minute
M	-	Molar (mol/dm3)
FFA	-	Free Fatty Acid

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CHAPTER 1.0

INTRODUCTION

The recent increases in crude oil prices have created unprecedented opportunities to displace petroleum-derived materials with biodiesel. Biodiesel, as an alternative fuel, has many merits and made from renewable biological sources such as vegetable oils and animal fats. It is biodegradable and nontoxic has low emission profiles and so is environmentally beneficial. Apart from that, biodiesel is a renewable fuel, helping to achieve the European Union (EU) renewable energy target of 12% of total energy output to consist of renewable energy by 2010 (European Commission, 1997). Carbon dioxide produced by combustion of biodiesel can be recycled by photosynthesis, thereby minimizing the impact of biodiesel combustion on the greenhouse effect (Keorbitz, 1999; Agarwal and Das, 2001). Additionally biodiesel has a relatively high flash point (150 °C), which makes it less volatile and safer to transport or handle than petroleum diesel (Krawczyk, 1996).

In support of this increasing consumption there have been substantial increases in biodiesel production in recent years, a trend that is expected to continue. The EIA (Energy Information Administration) foreseeable that demand for biodiesel will be at least 6.5 million gallons in 2010 and 7.3 million gallons in 2020. Based on

biodiesel's potential as a lubricity additive, demand could reach as much as 470 million gallons in 2010 and 630 million gallons in 2020. Now the major producer of biodiesel in the world is Germany. It has produced 2539 million ton in 2009 whilst Malaysia nearly exported 76 million gallons of biodiesel in 2009. So far 91 biodiesel licences issued to date, 15 plants with a combined 1.6 million tonnes capacity have been built. The plant in Johor have a capacity to produce 180 000 tonnes of biodiesel per year.

A mixture with 10% vegetable oil has been used in pre-combustion chamber engines to maintain total power without any alterations or adjustments to the engine in Brazil. At that point, it was not practical to substitute 100% vegetable oil for diesel fuel, but a blend of 20% vegetable oil and 80% diesel fuel was successful. Some short-term experiments used up to a 50/50 ratio also provide good solution for well maintain engine (Fangrui et al., Ma, 1998).

1.1 Background of Study

A renewable diesel fuel that is produced from fats and oils is known as biodiesel. It consists of the simple alkyl esters of fatty acids, most typically the methyl esters. It environmentally benign substitute instead of petroleum based fuels (Zabeti et al., 2009). The biodiesel would reduce emissions of CO, $SO_{X,}$ unburned hydrocarbons and particulate matter during the combustion process. So it is very advantageous in environmentally sensitive areas such as large cities and mines. Moreover, it is biodegradable, non-toxic, and better lubricity (Demirbas et al., 2008). The demand of biodiesel is very high now these days due to the increase in number of population and environmental concern.

Transesterification is crucial reaction that takes place during convert the vegetable oil to biodiesel which is with alcohol to form esters and glycerol. Excess alcohol has been used to shift the equilibrium to the products since the reaction is reversible (Helwani et al., 2009). Only simple alcohol can be used for

transesterification process such as methanol, ethanol, propanol and amyl alcohol. However, methanol is most selective choice in industries due to its chemical and physical nature such as shortest alcohol chain and polar.

Many researchers have been introduced heterogeneous catalyst as magnificent catalyst for their experiment. Example of heterogeneous catalyst commercially used are CaO, SrO, BaO, and $Ca(OCH_3)_2$. Homogeneous catalyst has been widely used in industries such are KOH, NaOH, and CH_3ONa (Liu et al., 2007). Alkali metal hydroxides or alkoxides can be used as transesterification catalysts. Hydroxides are cheaper than alkoxides, but must be used in higher concentrations to achieve good reaction (Freedman et al., 1984). Particulate heterogeneous catalysts can be readily separated from products following reaction allowing the catalyst to be reused, generating less waste, and consuming less energy. Recycling and reactivating the catalyst have been studied and found to maintain efficiency for use in industrials.

1.2 Problem Statement

Due to the fact that the supply of fossil fuel is limited while energy demand continues rise, biodiesel has been introduced as alternative renewable energy. The International Energy Outlook, an annual forecast by the U.S. Energy Information Administration forecast due to the driven by population and economic growth in developing countries, the world in 2035 would be more dependent on fossil fuels than ever, it finds. Countries overall would be consuming 49 percent more energy and spewing 43 percent more carbon dioxide into the atmosphere in 2035 than in 2007. To get rid from this problem, biodiesel plays essential role in manner to reduce the emissions of carbon dioxide and reduce the consumption fossil fuel.

The employment of homogeneous catalyst in the production of biodiesel has brought several disadvantages. Since homogeneous catalyst can be dissolved in the methanol; the separation of catalyst from the product is difficult. Therefore, the catalyst recycling may be more costly and challenging. Thus, the manufacturing cost increases. Other disadvantage of homogeneous base catalyst is soap formation which could reduce the catalytic efficiency.

Considering the disadvantageous of the homogeneous catalyst, vegetable oil transesterification using heterogeneous catalyst, potassium nitrate with alumina has been studied in the present research.

1.3 Research Objectives

1. To synthesize and characterize potassium nitrate with alumina
2. To identify the optimum operating condition for the reaction

1.4 Scope of Study

This study was carried out by using palm oil with Al_2O_3/KNO_3 as base heterogeneous catalyst for the tansesterification reaction. In this study three parameters have been investigated which are temperature, molar ratio of alcohol to oil, and catalyst ratio.

The range of studying for operating are:-

1. Temperature : 35°C - 65°C
2. Mass ratio of catalyst to oil : 4.5% - 9.5%
3. Molar ratio of methanol to oil : 15:1 to 18:1

1.5 Rationale & Significance

The contributions of the present research are:

a) It could overcome environmental issue such as reduce global warming gas emission and displace imported petroleum. Besides that the catalyst could be easily recycled.

b) The cost of manufacturing will be reduced due to the simple process which is the purification process.

CHAPTER 2.0

LITERATURE REVIEW

2.1 Biodiesel

With the exception of electricity and nuclear energy, the majority of the worlds energy needs are supplied through petrochemical sources, coal and natural gas. All these sources are finite and at current usage rates will be consumed by the end of the next century (C. Sookman et al., 1999). The depletion of world petroleum reserves and increased environmental concerns has stimulated recent interest in alternative sources for petroleum-based fuels. Biodiesel has arisen as a potential candidate for a diesel substitute due to the similarities it has with the petroleum-based diesel.

The use of vegetable oils as alternative fuel has been around since 1990 when the inventor of the diesel engine Rudolph Diesel first tested them, in his compression engine (Foglia, Jones,Haas, & Scott, 2000). Biodiesel also has been known as oxygenated fuel, meaning that it emit low amount of carbon to the environment because it's contain higher hydrogen and oxygen than carbon (Armas et al., 2008).

Furthermore, the sulphur contents of vegetal oils are close to zero and consequently, the environmental damage caused by sulphuric acid is reduced (Vicente et al., 1998)

2.1.1 Raw material

Basically biodiesel have been produced by using vegetable oil and animal fats. But commonly biodiesel derived from vegetable oil.

2.1.2 Animal fat

Apart from the vegetable oils, it is worth mentioning the possibility of producing biodiesel from animal fats which is an interesting option for the meat packing industries, by increasing the value of usefulness of marginal by products like tallow (Noordam and Withers, 1996). The potential of biodiesel production, from bovine cattle only taken into account, 64 million animals were slaughtered in 2007 in South Africa, where Brazil, Argentina and Uruguay are particularly highlighted. According to estimations of IICA- Paraguay (Souto 2008), if 50% of the production of bovine tallow from slaughtering, there would be a volume of about 9.5 million litres of biodiesel annually, enough quantity to complete the 1% established blend (Federico Ganduglia, 2002). One of the studies was investigated of transesterification on animal fat. At the end of these experiments, the maximum yield of 89% was obtained in two steps which is 0.35 (w/w) methanol/fat was used at reaction temperature of 62 °C for 2 h reaction period and by catalysing with 0.08 (w/w) H_2SO_4/fat and 0.01 (w/w) NaOH/fat ratios (Atilla Koca et al., 2009).

2.1.3 Vegetable oil

Vegetable oil has been used widely in the industrial to produce biodiesel. It gives more efficient of product which is biodiesel than animal fats. Different countries are looking for different types of vegetable oils as substitutes for diesel fuels. Generally, the most abundant vegetable oil in a particular region is the most common feedstock. Thus, rapeseed and sunflower oils are predominantly used in Europe; soybeans are commonly used in the United States for food products which has led to soybean biodiesel becoming the primary source for biodiesel in this country. In India, jatropha oil is used as a significant fuel source, palm oil in the South-East Asia (mainly Malaysia and Indonesia) and coconut oil are being considered in the Philippines (Barnwal and Sharma, 2005; Demirbas, 2007). The worldwide consumption of soybean oil is this highest in 2003 which about 27.9 million metric tonnes and followed by palm oil with 27.8 million metric tonnes of worldwide consumption. The table 2.1 shows that the different fatty acid in their own oil.

Table 2.1: The composition of fatty acids in vegetables oil (Jackson et al., 2006)

Fatty acid	Soybean	Cottonseed	Palm	Coconut oil
Lauric	0.1	0.1	0.1	46.5
Myristic	0.1	0.7	1.0	19.2
Palmitic	10.2	20.1	42.8	9.8
Stearic	3.7	2.6	4.5	3.0
Oleic	22.8	19.2	40.5	6.9
Linoleic	53.7	55.2	10.1	2.2
Linolenic	8.6	0.6	0.2	0.0

2.2.2.1 Palm oil as biodiesel feedstock

Palm oil biodiesel is produced from the edible vegetable oil obtained from the fruit of the oil palm tree. Biodiesel from palm oil are taking on renewed global importance as countries seek to substitute the soaring price of conventional oil and also cut hazardous emissions. Palm oil methyl ester (PME), differs from other types of biodiesel in its grade of molecule unsaturation, this is because each type of oil contain different amount of fatty acid and properties. Table 2.2 shows the properties of palm oil.

Table 2.2: The physical properties of palm oil

Physical state and appearance	Liquid
Molecular weight (g/mol)	846.1
Colour	Light yellow
Viscosity	57.85 @ 30°C
Heat Capacity KJ/kg-C	1.875 @ 30°C
Conductivity W/m-C	0.1717
Density kg/m3	885
Flash points (°C)	162

2.2.2.2 Waste cooking oil

The increasing production of waste cooking oils (WCOs) from household and industrial sources is a growing problem in all around the world. Waste edible oils and fats pose significant disposal problems in many parts of the world and resulting problems for wastewater treatments plants and energy loss, or are integrated into the food chain through animal feeding, thus becoming a potential cause of human health problems (Felizardo et al., 2006). So in the past much of this waste cooking oil have been used in the production of biodiesel (Kulkarni and Dalai, 2006). Compared to petroleum-based diesel, the high cost of biodiesel is a major barrier to its commercialization. It costs approximately one and a half times that of petroleum-based diesel depending on feedstock oils (Prokop, 2002; Lott, 2002). It is reported that approximately 70–95% of the total biodiesel production cost arises from the cost of raw material; that is, vegetable oil or animal fats (Krawczyk, 1996; Connemann and Fischer, 1998). Therefore, the use of waste cooking oil should greatly reduce the cost of biodiesel because waste oil is available at a relatively low price.

Based on estimates from seven countries, a total of about 0.4 Mt is collected within the EU, mainly from the catering industry, while the amount that could be collected is estimated to be considerably higher, possibly from 0.7 to 1 Mt. Its price is variable, but in general is approximately half that of virgin oil (Gomez et al., 2002).

One of the paper review revealed that biodiesel could be produced from waste cooking oil via two-step catalyzed process. First, free fatty acid (FFA) of the WCO with an acid value of 66.40 was esterified with methanol catalyzed by polyferric sulfate (PFS). Second, the esterified WCO was transesterified with methanol catalyzed by potassium hydroxide to produce crude biodiesel. The crude biodiesel was purified by molecular distillation to produce purified biodiesel (fatty acid methyl ester, FAME). The highest yield of FAME by molecular distillation from the crude biodiesel was 98.32% ± 0.17% at an evaporator temperature of 120 °C (Shuze Tang et al., 2010).

Other than that, another study investigated production biodiesel from waste cooking oil via acid catalysed. Albeit, the acid catalysed cause slow reaction, but it has been suggested best way to produce efficient biodiesel (Freedman et al. 1984). The most advantage of producing biodiesel via acid catalysed rather than base catalysed is it prevents form soap. Soap formation reduces catalyst efficiency, causes an increase in viscosity, leads to gel formation and makes the separation of glycerol difficult (Guo and Leung, 2003). The reaction conditions were set to a 50:1 molar ratio of methanol to oil, a 1.3:1 molar ratio of sulphuric acid to waste oil, a reaction temperature of 80 °C and a pressure of 400 kPa (M. Kates et al,. 2003).

2.2 Process

There are some feasible process could solve the problem which to reduce viscosity in the virgin oil. The eminent process that most of industries prefer is transesterification which is most easy and economical. Whilst, other process could be used are direct use and blend, micro emulsion, thermal cracking and with critical methanol.

2.2.1 Direct use and blend

The direct use of vegetable oils in diesel engines is problematic and has many inherent failings due to its high viscosity. Although some diesel engines can run pure vegetable oils engine, turbocharged direct injection engines such as trucks are prone to many problems (BTCE, 1994). The term use ratio of 1:10 to 1:20 oil to diesel has been found successful (Ma, 1999). According to the study of (Ma, 1999), the canola oil and diesel are very similar except the viscosity. Viscosity of canola is six times than diesel, it creates such a huge problem with flow of oil from fuel tank to the engine, blockages in filters, and subsequent engine power losses. Further, engines can suffer coking and gumming which leads to sticking of piston rings due to multi bonded compounds undergoing pyrolysis (Ma, 1999).

2.2.2 Micro emulsion

Micro emulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures, with dimensions generally in the 1-150nm range. These are formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphophiles (Schwab et al., 1987).

One of the studies conducted to reduce viscosity of vegetable oil by the process of micro emulsion. The optimized condition for micro emulsion formation was 57.6% (w/w) of n-pentanol, 20% (w/w) of biodiesel or vegetable oil, 14.4% (w/w) of Triton X-100 and 8% (w/w) of water (aqueous standard of KCl or NaCl in/or diluted HNO_3). The optimized instrumental parameters were aspiration rate of 2 mL min^{-1} and the flame composition of 0.131 of C_2H_2/air ratio (Maria Goreti R. Vale, 2007)

Further study has been investigated using the ternary phase equilibrium diagram and the plot of viscosity versus solvent fraction to determine the emulsied fuel formulations. All micro emulsions with butanol, hexanol and octanol met the maximum viscosity requirement for No. 2 diesel. No. 2 diesel is the fuel that used for trucks and some cars and leading to the name "road diesel". In the micellar solubilisation of methanol the 2-octanol was an effective amphiphile in triolein and soybean oil. Regularly methanol has been used due to its economic benefit over ethanol (Schwab et al, .1987).

2.2.3 Thermal cracking (Pyrolysis)

Pyrolysis is the conversion of one substance into another by means of applying heat such heating in the absence of air of oxygen with temperatures ranging from 450°C-850°C (Sonntag, 1979). In some situations this is with the aid of a catalyst leading to the cleavage of chemical bonds to yield smaller molecules (Weisz et al., 1979). By this method, the fats can be cracked to produce many smaller chain

compounds. To tackle shortage of petroleum deposits, some countries used pyrolysis method on fats has been investigated for over a hundred years.

Typical catalysts that can be employed in pyrolysis are SiO_2 and Al_2O_3. Copra oil and palm oil stearin were pyrolysed over a standard petroleum catalyst SiO_2/Al_2O_3 at 450°C to produce gases, liquids and solids with lower molecular weights (Pioch et al., 1993). To produce a mixture of methyl esters, the rapeseed oil was cracked in a tubular reactor between 500 and 850°C and in nitrogen (Billaud et al., 1995).

2.2.4 Transesterification

There are a lot of researchers conducts their own studies to achieve high conversion of biodiesel by transesterification on vegetable oil. By using calcium oxide as catalyst and alumina as support soybean oil has been converted to biodiesel. It could achieve the conversion of 98.6% with methanol to oil ratio of 1:1 of volume. Within 2 hr the excellent yield of biodiesel obtained. The other optimum parameter values were catalyst content of 5.97%, alcohol/oil molar ratio of 12.14:1 and the reaction temperature of 64.29°C. From the results, calcium methoxide showed it has strong basicity and high catalytic activity as base heterogeneous solid base catalyst and it can be reused for 2 cycles (Liu et al., 2007).

CaO/SBA-14 has been chosen as base catalyst to convert sunflower oil to biodiesel, the yield of biodiesel exceeds 95% within 5hr. The speciality of CaO/SBA-14 demonstrated from the study is the catalyst is insoluble in methanol and has strong basicity and long lifetime of catalyst. For the best result achieved with the optimum condition needed are 12:1 molar ratio of methanol to oil, addition of 3% SrO catalyst and temperature reaction of 70°C. With mild temperature and pressure condition, the reaction has been completed within short time (Montes et al., 2006). Deng et al., (2006) conducted a study by using Mg-Al HT as solid catalyst for transesterification of rapeseed oil to biodiesel. These researchers achieved the

excellent yield of 90.5% biodiesel. The optimum conditions are to achieved high yield are the ratio of methanol to oil of 6, the reaction about 65°C and takes 4 hr for complete the reaction. Another researcher had studied on transesterification of jatropha curcas catalyzed by CaO as a solid base catalyst. When the a molar ratio of methanol to jatropha curcas oil of 9:1 with the reaction time 3 hr, and the reaction temperature is 70°C, the highest conversion reached is 93% (Ping et al., 2005).

2.2.4.1 Supercritical Methanol

The study of the transesterification of rapeseed oil with supercritical methanol has achieved high conversion which 95% above within 4 min. A reaction temperature of 350 °C, pressure 30Mpa and a ratio of 42:1 of methanol to rapeseed oil for 240s were found to be the best conditions. The rate was substantially high from 300 °C to 500 °C but at temperatures above 400°C it was found that thermal degradation takes place. Supercritical treatment of lipids with a suitable solvent such as methanol relies on the relationship between temperature, pressure and the thermo physical properties such as dielectric constant, viscosity specific weight and polarity (Kushdiana, 2000).

2.2.5 Esterification

By esterification reaction the biodiesel was produced from oleic acid and methanol, using sulphuric acid as catalyst. The results showed that the yield produced is up to 99.7% biodiesel. The best operating condition was found when the reactor was operated at 100 °C, 1% catalyst (w/w), and with an oleic acid to methanol ratio of 3:1 (Lucena et al., 2008). Another study revealed, the esterification of palmitic acid with ethanol in a solvent-free system was carried out by synthesis ethyl hexadecanoate. A lipase of Lipozyme RM-IM was mixed with the reagents, in a closed batch reactor with constant stirring. The effect of palmitic acid/ethanol

molar ratio was 0.50, reaction temperature nearly to 67^{o}C and enzyme concentration about 4.50% w/w. The yield produced under these following experimental conditions is 93% (Silva et al., 2006). Production of fatty acid methyl ester from palm fatty acid distillate (PFAD) having high free fatty acids (FFA) was investigated and batch esterifications of PFAD were carried out to this study. The optimum condition for the continuous esterification process (CSTR) was molar ratio of methanol to PFAD at 8:1 with 1.834 wt% of H_2SO_4 at 70 °C under its own pressure with a retention time of 60 min. The amount of FFA was reduced from 93 wt% to less than 2 wt% at the end of the esterification process (Chongkhong et al., 2006)

2.3 Catalyst

Fatty acid methyl esters are products of the transesterification (also called methanolysis) of vegetable oils and fats with methanol in the presence of a suitable catalyst. The transesterification reaction can be catalysed by both homogeneous and heterogeneous catalysts.

2.3.1 Homogeneous Catalyst

Alkaline metal alkoxides the most active homogeneous catalysts being tested in laboratories is as CH_3ONa for the methanolysis. The high yield obtained is 98% in short reaction time of 30 min even if they are applied at low molar concentrations. Alkaline metal hydroxides such KOH and NaOH are alternative sources to base catalysts, cheaper than metal alkoxides, but less active. Nevertheless, they can give sufficiently high conversions of vegetable oils to biodiesel by increasing the catalyst concentration to 1 or 2 mol% (Schuchardta et al., 2009). Another study conducted by using sodium methoxide, potassium methoxide, sodium hydroxide and potassium hydroxide for methanolysis on sunflower oil. About, 100 wt% biodiesel yields were only obtained with the methoxide catalysts only. (Vicente, et al., 2003)

2.3.2 Heterogeneous Catalyst

Application of heterogeneous catalysts improves biodiesel production by eliminating separation steps. Furthermore, high conversions could be achieved at temperatures ranging from 40 to 65 °C in a few hours by using heterogeneous catalysts. Table 2.3 below shows the various base heterogeneous catalysts had been developed for transesterification reaction.

Table 2.3: Various Basic Heterogeneous catalysts of Reaction Conditions and Conversion

Vegetable oil	**Catalysts**	**X[a]:1**	**t[b] ,h**	**T [c], °C**	**X [d], %**	**References**
Soybean	Na/NaOH/γ-Al_2O_3	6:1	2	60	77	(kim 2004)
Soybean	KI/ZrO_2	15:1	8	65	78.3	(Xie 2006)
Soybean	KNO_3/Al2O_3	15:1	8	65	67.4	(Xie 2006)
Soybean	KF/ZnO	10:1	9	65	87	(Huang 2006)
Soybean	KOH/ZnO	10:1	9	65	82	(Huang 2006)
Jatropha curcas	CaO	9:1	2.5	70	93.5	(Zongbin 2006)
Rapeseed	KNO_3/CaO	6:1	3	60	99.8	(MacLeod 2008)
Rapeseed	$Ca_2Fe_2O_5$	10:1	10	60	92	(Kawashima 2008)

(**Note:** a = Ratio methanol; b= Time, hr; c= Temperature, °C; d= Conversion, %)

2.3.3 Bio catalysed

The active enzyme known as Pseudomonas Cepacia lipase resulted to be reaching 100% of conversion after 6 h. Different operative conditions such as reaction temperature, water activity, and reagent stoichiometric ratio were investigated and optimised. Methanol and 2-butanol were the worst alcohols cause the former, probably, due to its low miscibility with the oil and the latter because secondary alcohols usually are less reactive than primary alcohols. Conversely, linear and branched primary alcohols with short alkyl chains (C_2–C_4) showed high reaction rate and conversion. (Vincenzo Solinas et al., 2005).

Other than that ,biomass support particles(BSP) –immobilized cells was used for investigated with methanolysis was carried out with in the presence of 15% water the methyl esters (MEs) content in the reaction mixture reached 90% conversion. (Hideki Fukuda et al., 2000).

Further, another experiment was carried out on jatropha oil by using Rhizopus oryzae (ROL), The maximum methyl esters found in the reaction mixture reaches 80 wt.% after 60 h whereas it is 76% after 90 h using Novozym 435. Both the lipases can be used for repeated batches and both lipases exhibit more than 90% of their initial activities after five cycles (Hideki Fukuda et al., 2007). Other various bio catalysts have been used for production biodiesel showed in table 2.4 below.

Table 2.4: Various Bio Ctalysts Used for Biodiesel Production

Oil	**Catalyst**	**solvent**	**T ,°C**	**Other condition**	**X,%**	**References**
Sunflower oil	Candida antarctica	Propanol	45	24 h	93.2	Deng et al. (2005)
Jatropha oil	Candida antarctica	Hexane	50	8 h, 150 rpm	93.4	Modi et al. (2006)
Cottonseed oil	Candida antarctica	Butanol	50	7hr, 120 rpm	97	Royon et al. (2007)
Jatropha oil	Pseudomonas cepacia	None	50	8h, 200 rpm	98	Shah and Gupta (2007)
Soybean oil	Pseudomonas fluoresces	Heptane	45	Use of 92 re combinant Lip B68	92	Lou et al. (2006)
Sunflower oil	Rhizomucor miehei	Heptane	40	24 h	79.1	Soumanou (2003)
Sunflower oil	Thermomyces lanuginose	None	40	24 h	89.8	Deng et al. (2005)
Jatropha oil	Chromobacteri-m viscosum	None	40	8 h, 200 rpm,	92	Shah et al. (2004)
Tallow	Mucormiehei	Hexane	45	8 h	94.8	Nelson et al. (1996)

(**Note**: T= Temperature in ℃, X=Conversion in %)

2.4 Alcohol

For biodiesel production, alcohol plays essential role to transfer oil to biodiesel. The feasible alcohols that could be used for biodiesel are methanol, ethanol, propanol, and butanol. However, methanol is chosen as best solvent to produce biodiesel technically and economically. Other than that, it also low cost and it have physical and chemical advantages such as polar and shortest chain alcohol (Ma and Hanna, 1999).

The alcohol has been used for the production of biodiesel to increase the yields of the alkyl esters and to allow its phase separation from the glycerol to be formed (Schuchardt, et al., 1998). Methyl, rather than ethyl, ester production was modelled because methyl esters are the predominant commercial products, and the downstream recovery of unreacted alcohol is much easier (Zhou and Boocock, 2003). Ethanol maintains its capability of being renewable as an advantage. It can be produced from agricultural renewable resources, thereby attaining total independence from petroleum-based alcohols (Saifuddin and Chua, 2004; Encinar, et al., 2007). Most of the world's methanol is being produced using natural gas as a feedstock. However, the ability to produce methanol from renewable biomass resources is growing in interest.

CHAPTER 3.0

METHODOLOGY

3.1 Introduction

This chapter will cover the experimental detail such as chemical substances, apparatus, equipment used during the experiment, experimental procedure, catalyst preparation, and sample analysis with gas chromatography.

3.2 Chemical Substances

The chemical that will be used for carrying out the experimental are potassium nitrate, alumina, anhydrous methanol, n-hexane and palm oil. Table 3.1 below shows the chemicals will be used and its function.

Table 3.1 Chemicals and Its Function

No	Chemicals	Functions
1	Palm oil	Reactant
2	Potassium nitrate	To synthesis alumina
3	Alumina	As support to potassium nitrate to give high basicity
6	Anhydrous methanol	For transesterification process
7	N-hexane	For GC column

3.3 Apparatus & Equipments

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 3.2 shows the equipments that have been used in this research studies and its function.

Table 3.2: The Equipments and Its Function

No	Equipments	Functions
1	Furnace	For calcinations purpose
2	Three – necked glass flask	For mixing the catalyst and reactant
3	Water- cooled condenser	To remove the water from the mixture
4	Thermometer	To observe the temperature
5	Magnetic stirrer	To stir the mixture vigorously
6	Reflux condenser	To reflux the methanol and to reuse
7	Rotary evaporator	To evaporate the methanol from product
8	Heating mantal	To heat the mixture below 100°C
9	Retort stand	To support condenser

3.3.1 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**.** In this case, the combination of 3 neck flask with magnetic stirrer, condenser and heating mantel act as batch reactor. The figure 3.1 shows the batch reactor used for carrying out experiments in the analytical lab.

Figure 3.1: Batch Reactor used for experiment

3.3.1.1 Condenser

The condenser has been attached with the three neck flask because the methanol could be condensing during the reaction to maintain the amount of methanol used.

3.3.1.2 Thermometer

Thermometer was placed in the three neck flask to measured temperature time to time. The temperature has been observed all the time because the thermometer has been used was cant set the actual temperature.

3.3.1.3 Heating Mantle

In this experiment, heating mantel has been used because it can heat up maximum until 100°C. Since, the temperature of this reaction chosen is about 65°C, the heating mantle is suitable to be used for this experiment. The three neck flask has placed inside of this heating mantle and heats it up to 65°C. The magnetic stirrer was placed in three neck flask to agitate the mixture to increase the rate reaction.

3.3.2 Gas Chromatography

A gas chromatographic method for the simultaneous determination of glycerol, mono-glycerides , di-glycerides , and triglycerides in vegetable oil methyl esters has been developed. Gas chromatography is often used as the analytical method of choice for free and total glycerine since it is simple, sensitive and reliable, requiring only a small amount of sample preparation.

3.4 Raw Material Preparation

The raw material has been used in this experiment is edible palm oil. The extracted palm oil was purchased for the purpose of this experiment. Since, methanol also contributes for this experiment, so it also has been purchased from the chemical supplier.

3.5 Catalyst Preparation

The catalyst has been introduced in this experiment is KNO_3 on alumina which is known as base heterogeneous base catalyst. Before the impregnation, the alumina was calcined at 500°C for 1 hr. Then the aqueous potassium nitrate loaded on alumina and stirs it for 4 hrs. The purpose of stirring is to make sure the catalyst well distributed on support. Further, the catalyst was dried for 16 hr at 120°C. Prior to each reaction, the catalyst were calcined at 500°C for 5hr in furnace. The catalyst were prepared to different KNO_3 loading amounts of 15, 25, 35, and 45wt%, were designed as 15% KNO_3/Al_2O_3, 25% KNO_3/Al_2O_3, 35% KNO_3/Al_2O_3 and 45% KNO_3/Al_2O_3 respectively. The figure 3.2 below shows the catalyst preparation.

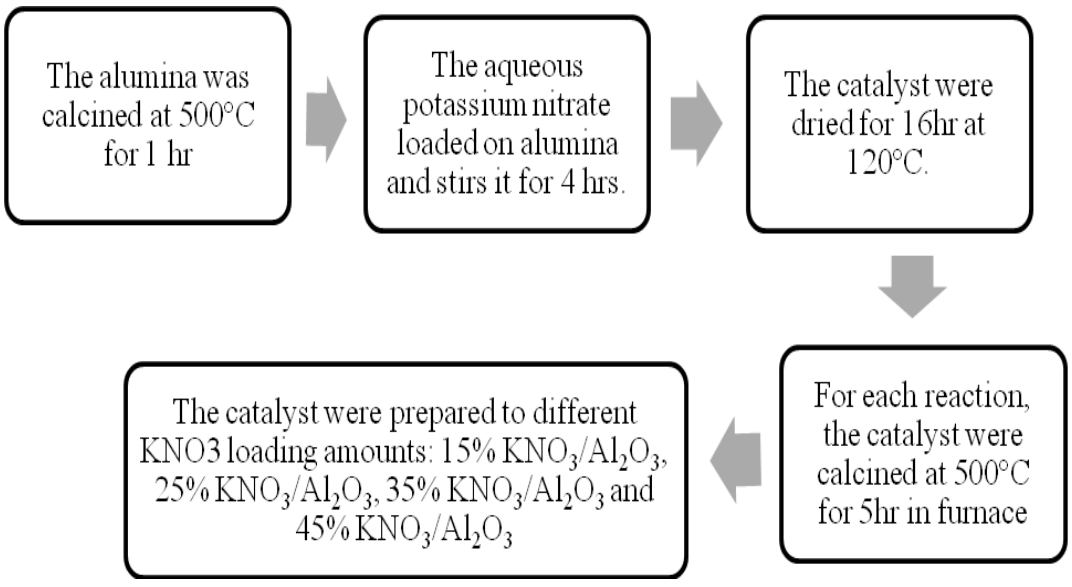

Figure 3.2: The procedure for prepare catalyst

3.6 Experimental Procedure

The experimental procedure for production of biodiesel through this experiment involves several steps which are transesterification and removal of glycerine from product. All of these steps need to be followed in order to make a produce efficient biodiesel.

3.6.1 Transesterification

The transesterification process is carried out in labscale. The procedure is shown in figure 3.3.

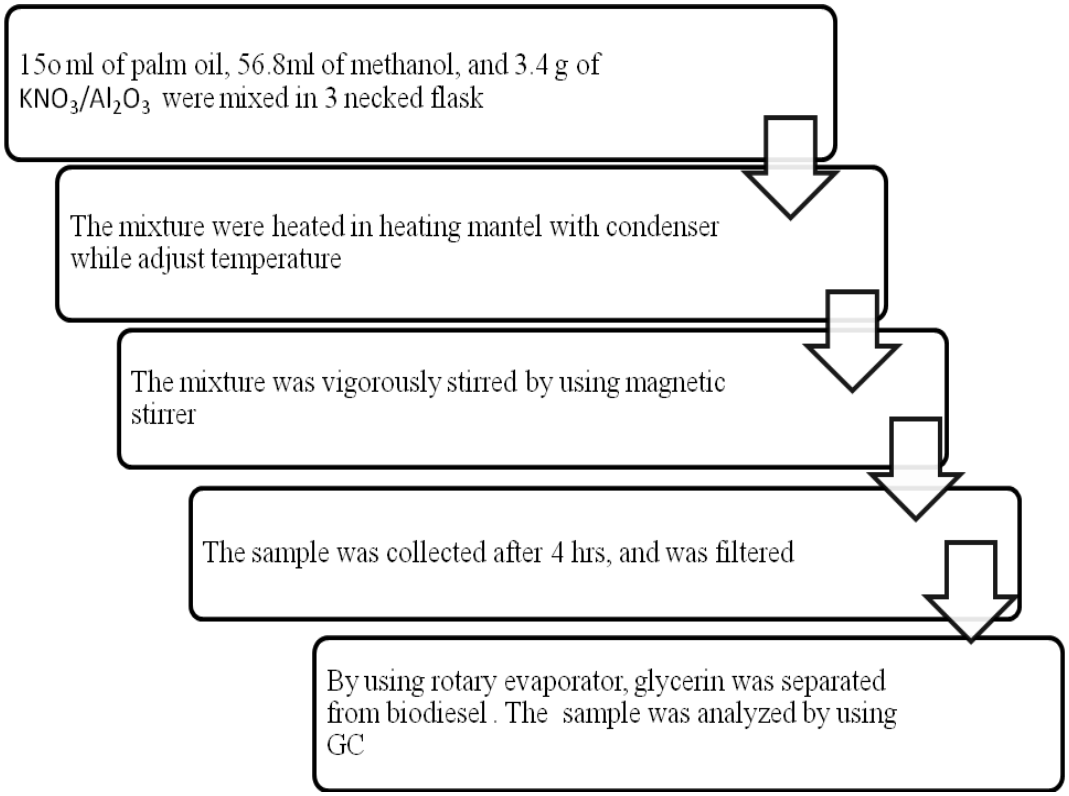

Figure 3.3: The procedure of transesterification process.

3.6 The Experimental Procedure for Sample with Different Manipulated Variable

In this heterogeneous catalyzed transesterification process, the effect of three parameters has been studied. These parameters are the catalyst loading, the methanol to oil molar ratio and the reaction temperature. For the catalyst concentration, the experiment was carried out for 4.5%, 6.5%, 8.5% and 9.5% of KNO_3/Al_2O_3 while for methanol to oil molar ratio 15:1; 16:1; 17:1; 18:1 and for the reaction temperature are 35°C, 45°C , 55°C and 65°C. The experiment is done by step by step which the optimal value for each parameter was determined while for other parameters must keep constant. Therefore, the conversion could be investigated at various parameters.

For the 1st experiment is carried out to study the effect of molar ratio methanol to oil. The molar ratio was set to different value while the other two parameters were fixed 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

Sample	Temperature, °C	Catalyst loading % KNO_3/Al_2O_3	Methanol to oil ratio
1	65	6.5	15:1
2	65	6.5	16:1
3	65	6.5	17:1
4	65	6.5	18:1

For 2nd experiment, the main objective is to study the effect of temperature. The temperature value has to be different while for molar ratio value was taken from the optimal value from the 1st experiment which is 18:1 as shown in Table 3.4 below:

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

Sample	Temperature, °C	Catalyst loading % KNO_3/Al_2O_3	Methanol to oil ratio
1	35	6.5	18:1
2	45	6.5	18:1
3	55	6.5	18:1
4	65	6.5	18:1

For 3rd experiment, the catalyst loading was taken into account to analyse the effect on reaction. Therefore, the catalyst loading value have been varied while for molar ratio value will constant for all reaction which is 18:1 and the reaction temperature was set to 65°C as shown in Table 3.5 below.

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

Sample	Temperature, °C	Catalyst loading % KNO_3/Al_2O_3	Methanol to oil ratio
1	35	4.5	18:1
2	45	6.5	18:1
3	55	8.5	18:1
4	65	9.5	18:1

3.7 Analytical Method

Generally, there are various analytical methods that can analyze the biodiesel produced by transesterification process using heterogeneous catalyst.

3.7.1 Procedure for Stock Standard

0.05 g of methyl palmitate was weighed out the appropriate amount of standard required in a 10ml volumetric flask for a concentration of 0.005 mg/ml. Then, it was diluted in 10ml volumetric flask with n-Hexane; reagent grade. Table 3.6 below shows the procedure for Stock Standard.

Table 3.6: Procedure for Stock Standard Preparation

Component	Concentration (mg/ml)	Volumetric flask (ml)	Mass of sample (g)
Methyl palmitate	0.625	10	6.25
Methyl oleate	0.625	10	6.25
Methyl linoleate	0.625	10	6.25

3.7.2 Procedure for Working Standard

Appropriate volumes of stock solution of methyl palmitate, methyl oleate and methyl linoleate were pipette into a 10ml volumetric flask and it was diluted with n-Hexane. By using 0.5µ filter, the solution were filtered and kept in vial for GC analysis. Table 3.7 below shows the preparation of working standards.

Table 3.7: Preparation Working Standards Preparation

Component	S1	S2	S3	S4	S5
Methyl palmitate	0.0025	0.005	0.01	0.02	0.025
Methyl oleate	0.0025	0.005	0.01	0.02	0.025
Methyl linoleate	0.0025	0.005	0.01	0.02	0.025

3.7.3 Calibration Curve

A calibration curve was plotted by using result from GC and it is an area under each peak vs. concentration for each homogeneous group. By using this calibration curve the concentration of each homogeneous group which contain in sample (biodiesel) could be determined.

3.7.4 Procedure for Samples

0.05g of the sample was weighed into a 10ml volumetric flask and the samples were diluted with n-Hexane. Further, the samples have to filter by using filter of 0.5µ and kept in vial for GC analysis.

3.7.5 Analysis with Gas Chromatography

The samples were sent to GC analysis and of each samples injected into this equipment. The components in products obtained are in form of chromatogram which contains peaks. Each of peaks represents the area of our component. Finally, the conversion was calculated using the calibration curve as references. Table 3.8 the operating condition of the GC that has been used in this study.

Table 3.8: Operating Condition of GC

Detector type	Flame ionization detector (FID)
Injector temperature	240°C
Detector temperature	240°C
Injection size	1µL(10:1 split)
Nitrogen flow	2mL/min
Nitrogen make up	30mL/min
Type of GC column	HP 5 with capillary column 30m×0.15mm×0.2µm

CHAPTER 4.0

RESULTS AND DISCUSSIONS

4.1 Catalyst Characterization

Knowledge of catalyst structure is essential to the understanding of the chemistry actually occurring in catalysis. This makes structure characterization crucial throughout the life cycle of the catalyst, from the preparation step to the use in reaction conditions. Catalyst could be characterising by physical properties such as morphology, porosity and texture. In this study, the catalyst has been used was characterised by using Fourier Transform Infrared Spectrometers (FTIR) and Scanning Electron Microscopy (SEM).

4.1.1 Fourier Transform Spectrometers (FT-IR)

The powder form of KNO_3/ Al_2O_3 was placed on the plate of FTIR and analyse it. The range of wavelength chosen was 500-4000cm^{-1} The FT-IR spectrum of the catalyst was shown in Figure 4.1. All the samples showed a very intense broad band at around 3500cm^{-1} could be partly assigned to the vibration of Al-O-K group. On the surface of fully hydroxylated alumina K^+ ion replaced the protons of isolated hydroxyl groups to form Al-O-K groups ($2KNO_3 + 2Al\text{-}OH \longrightarrow N_2O_3 + 2\ Al\text{-}O\text{-}K + H_2O$), which were considered to be the active basic sites. The absorption band is at 1384 cm^{-1} that could be attributed to the vibration of N-O of KNO3, while this N-O absorption band was not observed on alumina without loaded KNO_3. Further, the intensity of1384 cm^{-1} band grew as the amount of loaded KNO_3 rose. There are no bands ascribed to NO_2 (1550, 1320 cm^{-1}), were detected, demonstrating that the resultant ok KNO_3 decomposition was K_2O instead of KNO_3. Additionally, a weaker and broader absorption at about 1532 cm^{-1}, assigned to carbonates, was observed on calcined samples.

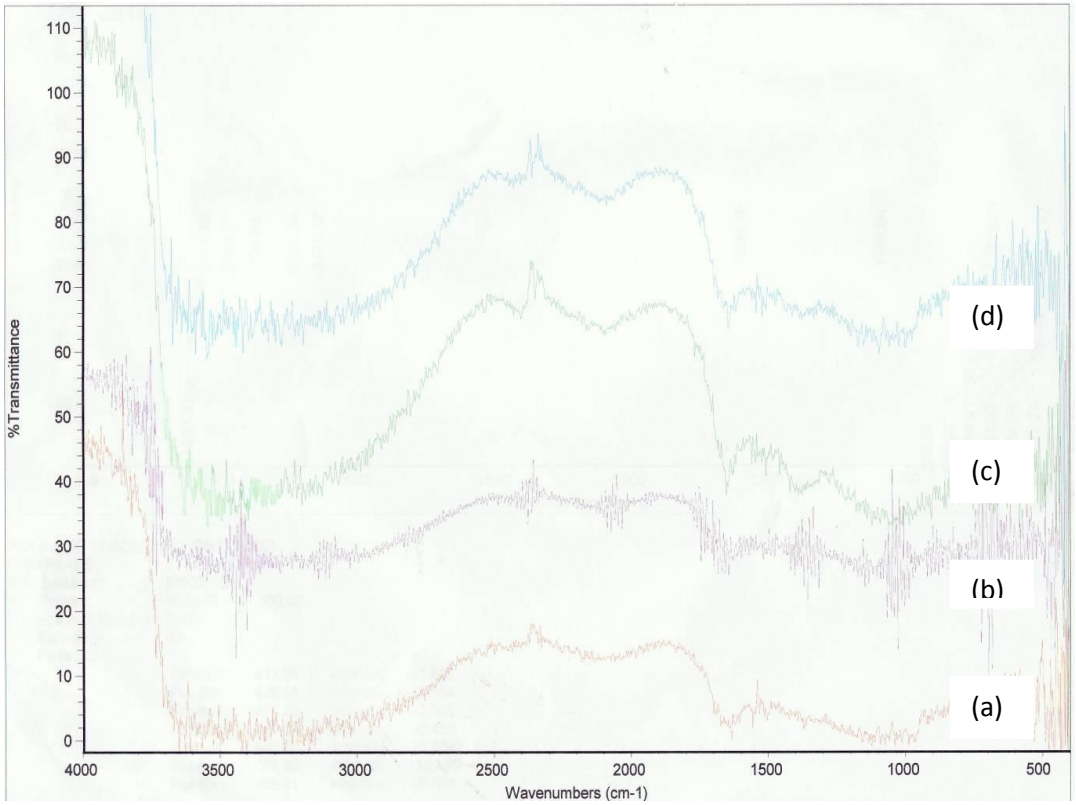

Figure. 4.1: FTIR spectra of KNO_3/ Al_2O_3 (a) 15% KNO_3/ Al_2O_3, (b) 25% KNO_3/ Al_2O_3, (c) 35% KNO_3/ Al_2O_3, (d) 45% KNO_3/ Al_2O_3

4.1.2 Scanning Electron Microscope (SEM)

The scanning electron micrographs of the samples are presented in Figure. 4.2. The SEM photographs shows 15%, 25%, 35%, and 45% of KNO_3 on Al_2O_3 samples which were calcined at 773K for 5 h. They are with crystallites size; nearly of hexahedron shape and porosity depends on the different KNO_3 loading amounts. As shown in figure 4.2 the porosity was hard to be seen for the figure 4.2(a) and (b). The porosity can be seen clearly in the figure of 4.2(c). Based on this image observation, after loading 35% of KNO_3 on Al_2O_3 it showed number of porosity increased. Nevertheless, 45% of KNO_3 on alumina couldn't observe much porosity as seen on 35% KNO_3/ Al_2O_3.

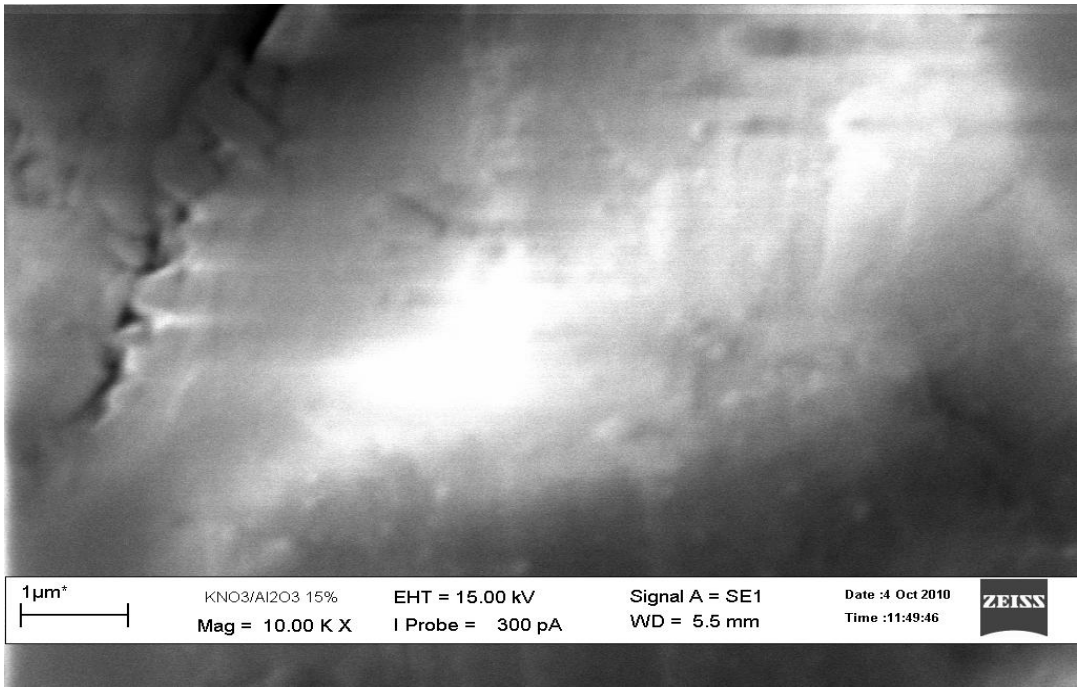

Figure 4.2(a): Typical SEM images of 15% KNO_3 on Al_2O_3

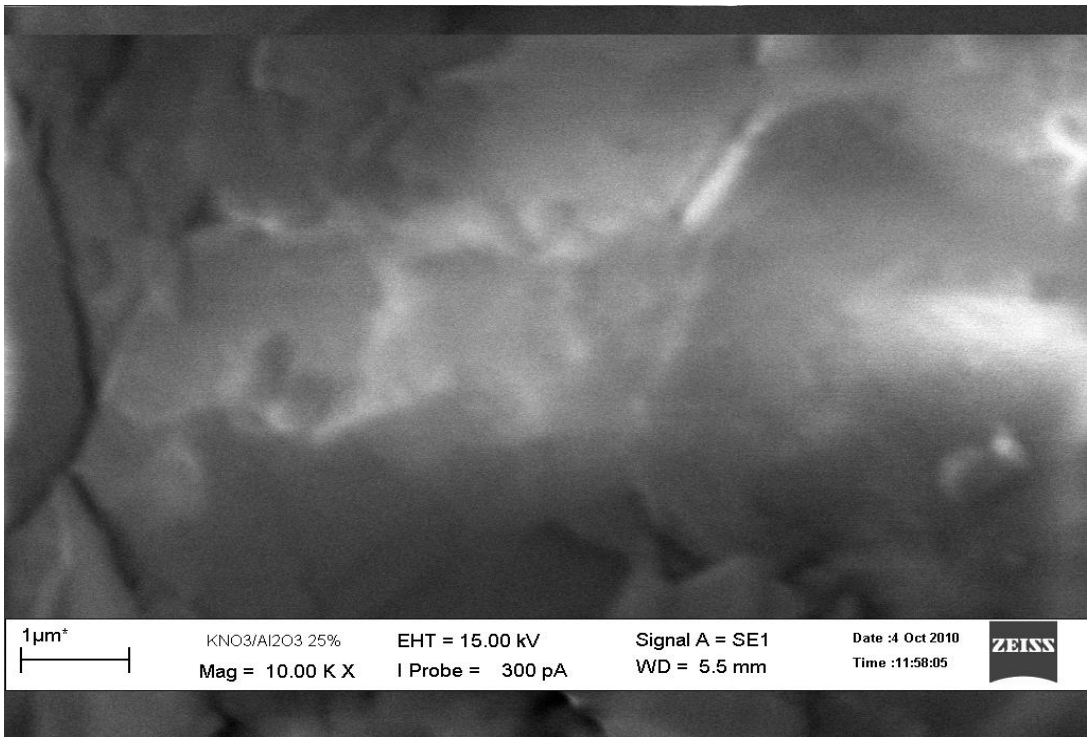

Figure 4.2(b): Typical SEM images of 25% KNO_3 on Al_2O_3

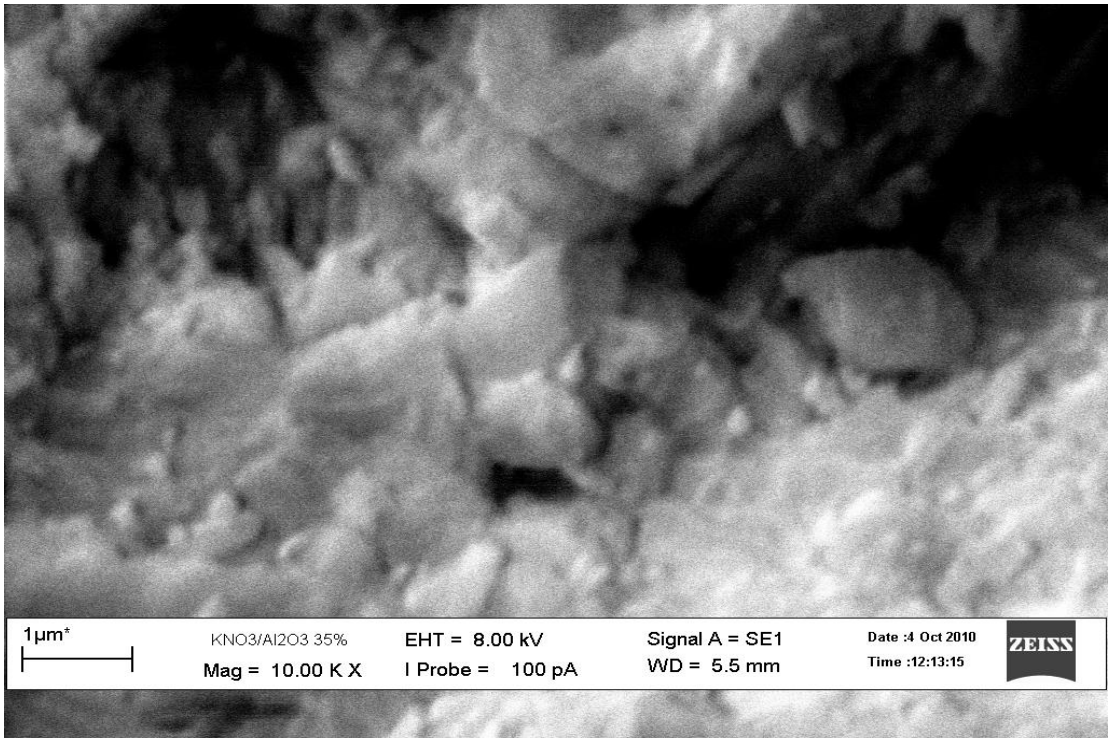

Figure 4.2(c): Typical SEM images of 35% KNO_3 on Al_2O_3

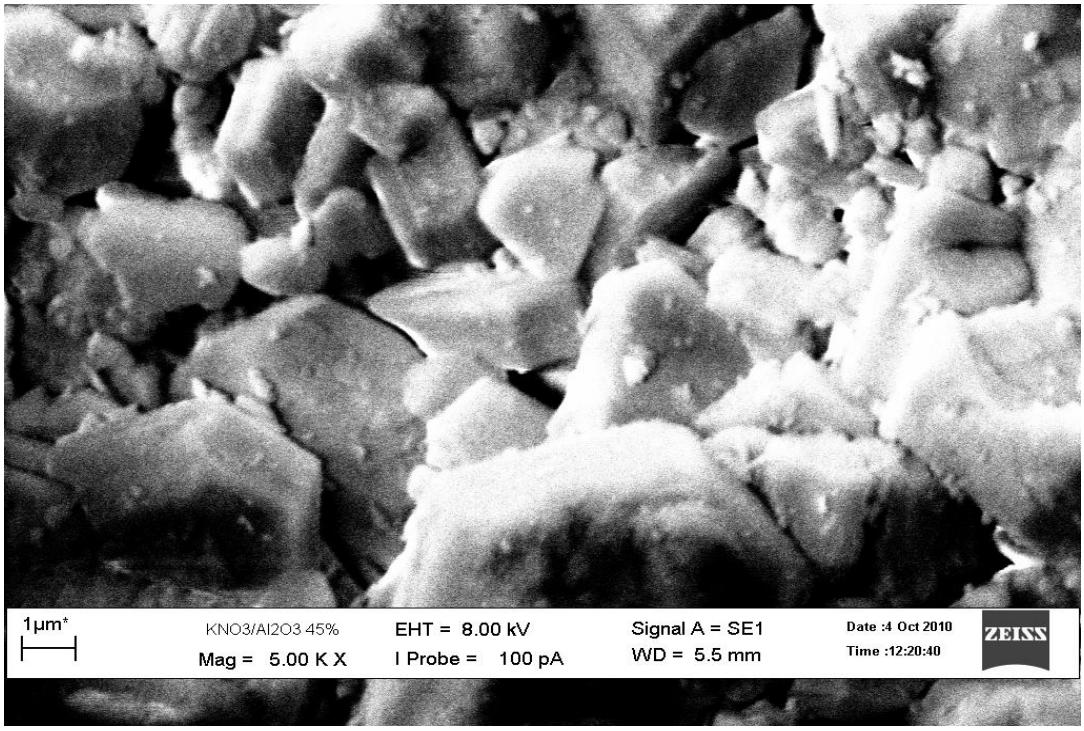

Figure 4.2(d): Typical SEM images of 45% KNO_3 on Al_2O_3

4.2 Gas Chromatography (GC) Analysis

The biodiesel purity means the methyl ester concentration (wt. %) in the biodiesel and is calculated by gas chromatography. This method also allows for the quantification of the monoglyceride, diglyceride and triglyceride contents in the biodiesel (Vicente et al., 1998). In this study, GC has been used to identify three different methyl esters according to their retention time which illustrated in table 4.1. There are three important major methyl found in palm oil biodiesel which are methyl palmitate, methyl linoleate and methyl oleate. The other small peaks found were ignored as insignificant.

Table 4.1 Retention Time for Methyl ester

Methyl Ester	Retention Time (minutes)
Methyl Palmitate	11.9
Methyl Linoleate	15.1
Methyl Oleate	15.7

4.2.1 Calibration Curves of the Methyl Esters

Three methyl esters calibration curves plotted as shown in figure 4.3, 4.4 and 4.5. They were found to be linear over the range 0.0025-0.025 mg/mL.

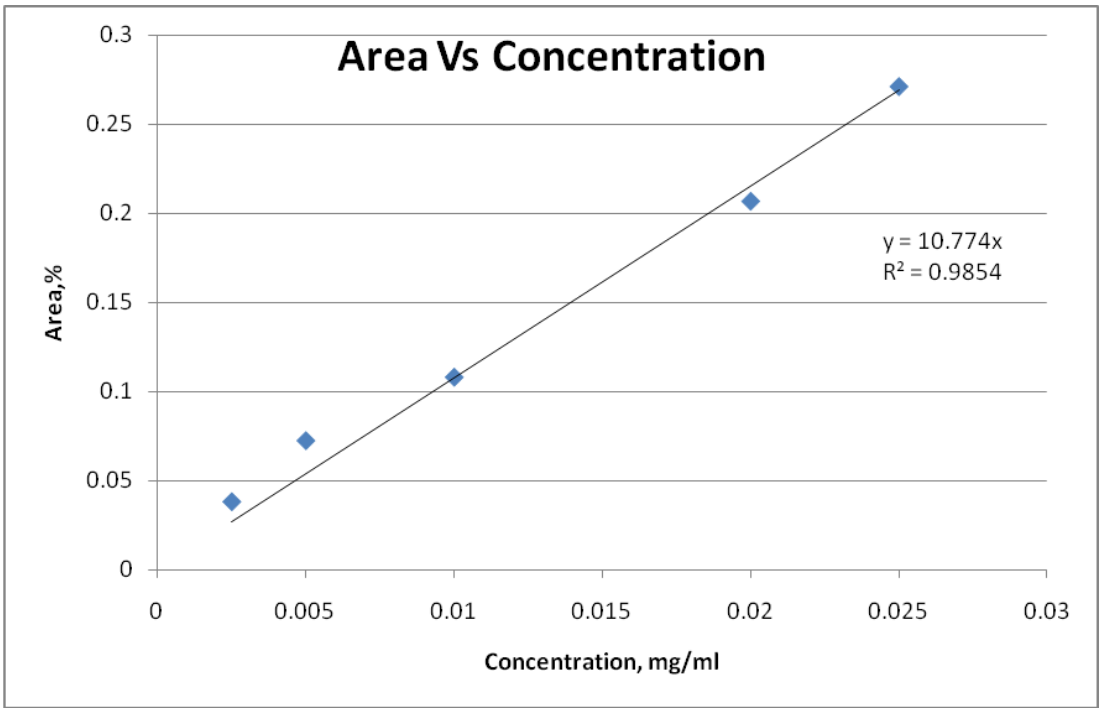

Figure 4.3: Calibration curve for methyl palmitate

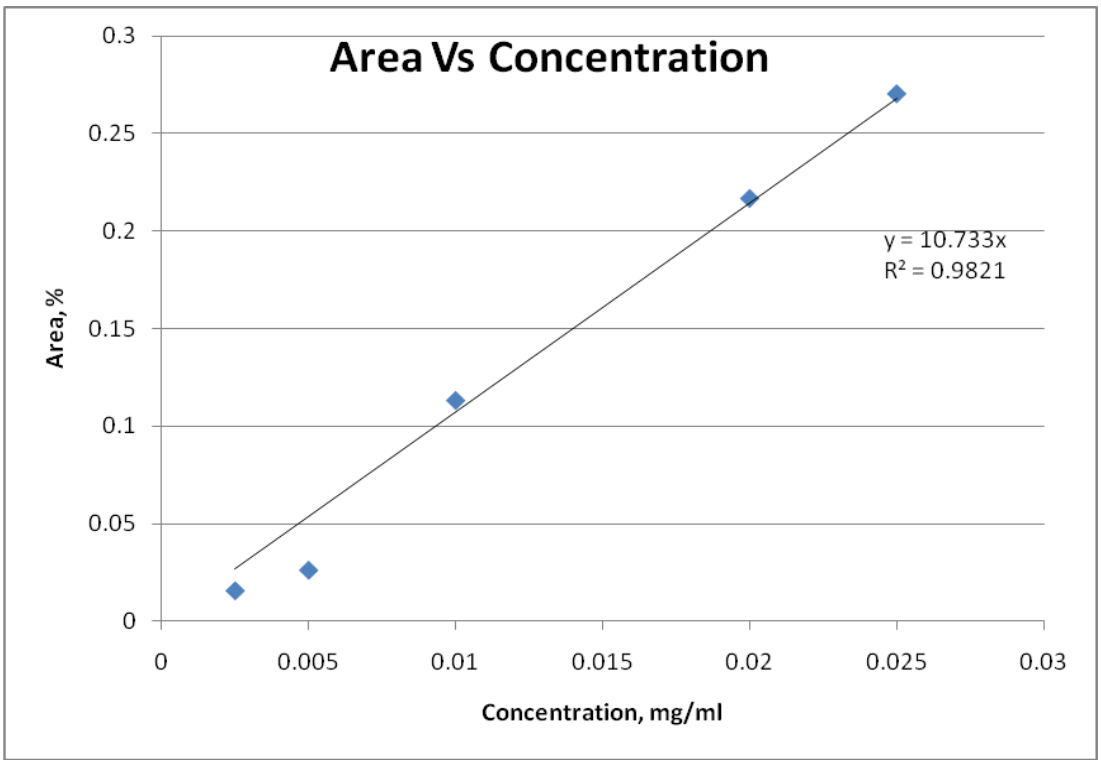

Figure 4.4: Calibration curve for methyl linoleate

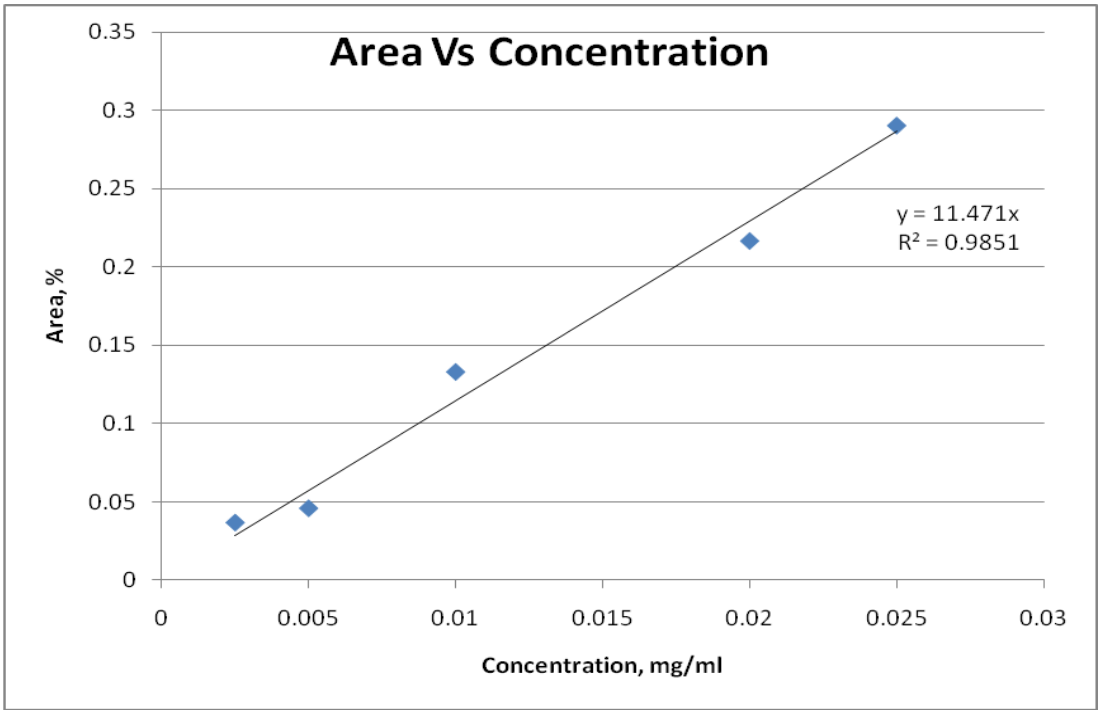

Figure 4.5: Calibration curve for methyl oleate

4.3 Important Operating Parameters for the Reaction

The reaction could be speed up to convert palm oil to biodiesel by various parameters. This study was carried out to determine the best operating condition for the production of methyl ester. A various parameter studied are reaction molar ratio of methanol to oil, temperature, and amount of catalyst. The typical analysis calculation is shown in Appendix A.

4.3.1 Effect of Molar Ratio

This stoichiometry of this reaction requires 3 mol methanol per mol triglyceride to convert 3 mol biodiesel and 1 mol glycerol. The biodiesel conversion could be elevated by introducing an excess amount of methanol to shift the equilibrium to the right-hand side. The effect of molar ratio of methanol to oil on biodiesel conversion illustrated in figure 4.6 which shows the reaction rate increased when the molar ratio of methanol to oil was increased. The biodiesel conversion increased from 16% to 60% as the molar ratio increased from 15:1 to 18:1.this is because due to the presence of heterogeneous solid catalysts, the reaction mixture initially constitutes a three-phase system, oil-ethanol-catalyst, which for diffusion reasons inhibits the reaction. When the mass transfer is limited, the rate of mass transfer seems to be much slower than the reaction rate. Therefore, the usage of excess methanol is one of the better options for improving the rate of reaction. So, the maximum conversion of about 60 % was obtained when the molar ratio was 18:1 from a study range of 15:1-18:1.

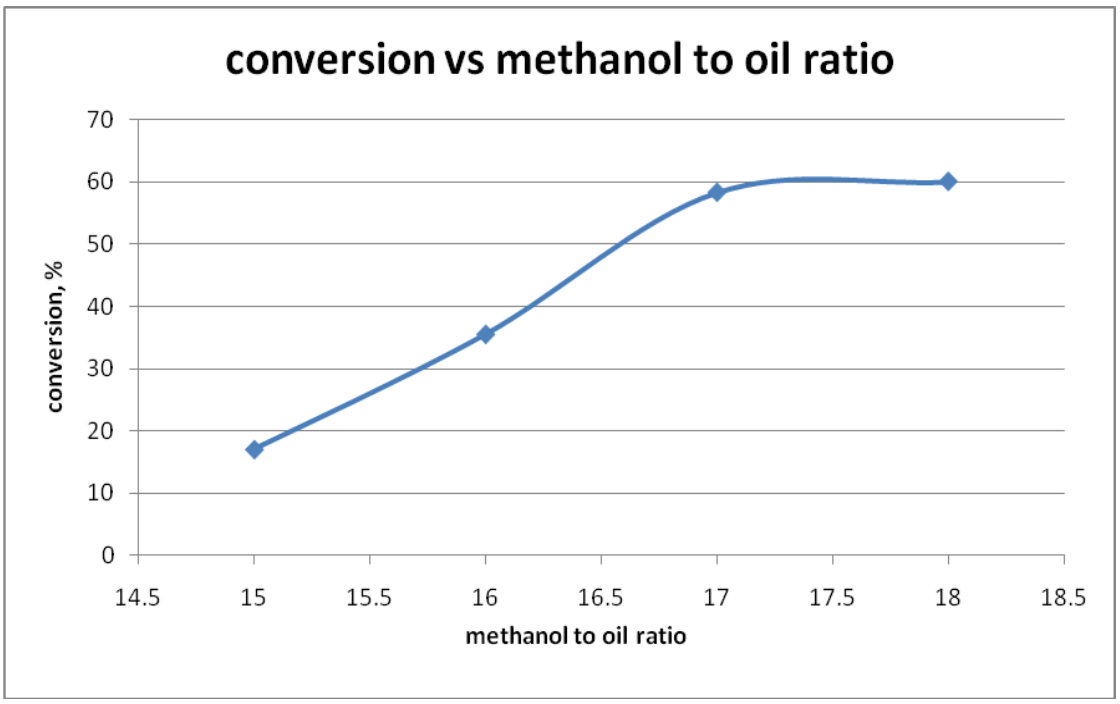

Figure 4.6: Effect of molar ratio of methanol to oil on biodiesel conversion when catalyst loading of 6.5% and the reaction temperature at 65 °C.

4.3.2 Effect of the Temperature

Reaction temperature can influence the reaction rate and biodiesel conversion. In this present work, the reaction temperature was varied within range from 35°C to 65°C. The experimental results are shown in figure 4.7. The biodiesel conversion increased with the increased of reaction temperature to 63% at 65°C. The results indicate that the reaction rate was slow at low temperature and biodiesel was converting only 11% at 35°C after 4 hrs of reaction. The advantage of higher temperatures is a shorter reaction time. However, if the reaction temperature exceeds the boiling point of methanol, the methanol will vaporise and form a large number of bubbles, which inhibit the reaction on the three phase interface. Therefore, the optimum reaction temperature is considered to be around 65°C. When the

temperature increased the kinetic energy also increased. Thus the number of colloidal particles increased. Therefore, the conversion increased.

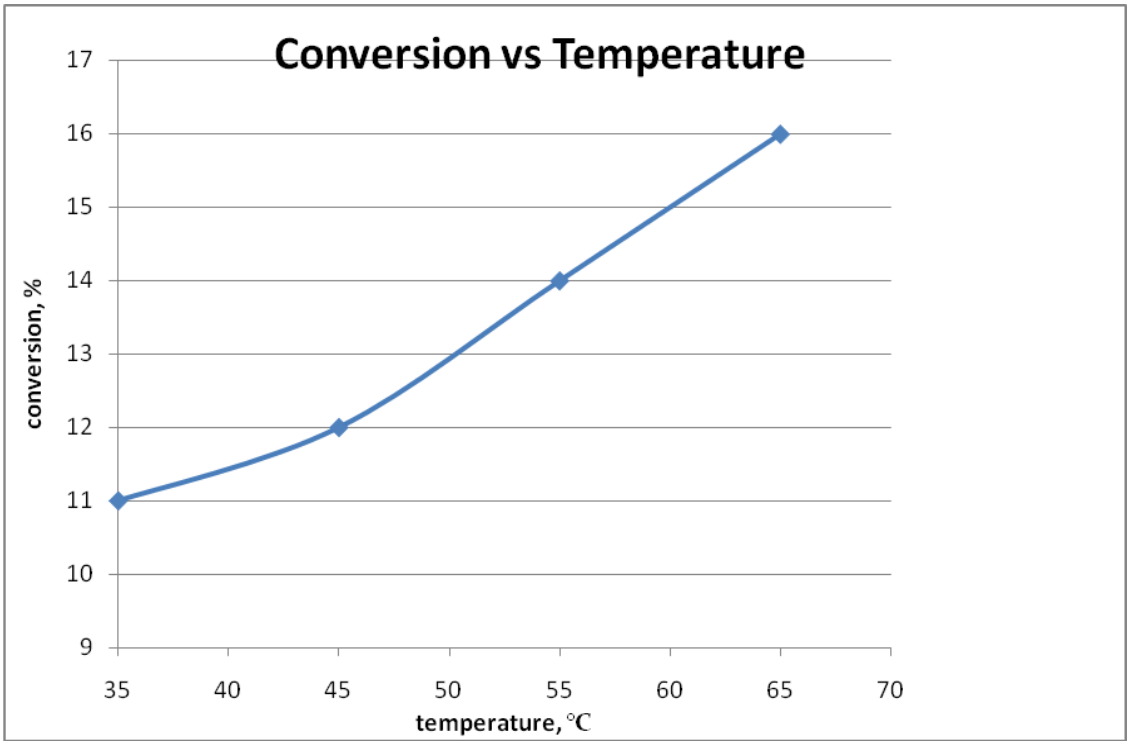

Figure 4.7: Effect of temperature on biodiesel conversion when catalyst loading of 6.5% and the molar ratio methanol to oil of 15:1.

4.3 Effect of Catalyst Loading

A catalyst possessing strong basic sites and a large surface area should exhibit high activity. In this study, mass of KNO_3/ Al_2O_3 to palm oil was varied within a range of 4.5-9.5%. These percentages are the weight fractions of the palm oil used in the reaction. As shown in figure 4.8, the conversion increased with the increase of catalyst amount from 4.5-8.5% but if further increase catalyst concentration of 9.5%, the conversion decreased. This is because the larger amount of catalyst disturbs the mixing of methanol, oil, and catalyst separation which is leads the solution become more viscous.

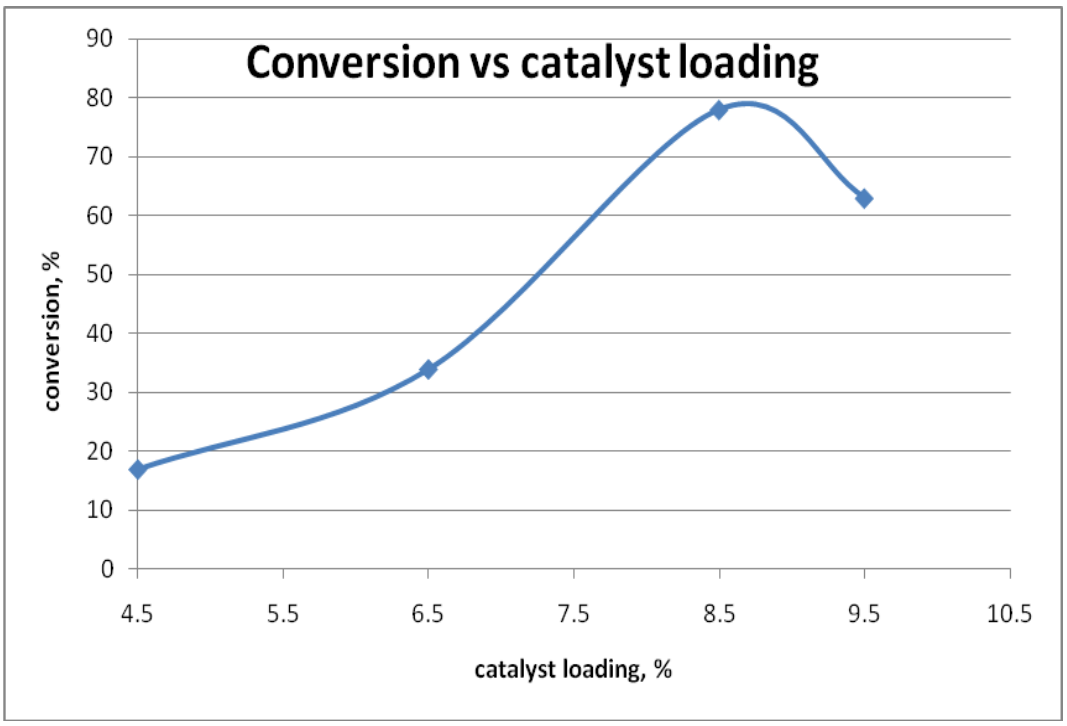

Figure 4.8: Effect of catalyst loading on biodiesel conversion when temperature at 65° C and methanol to oil molar ratio of 15:1.

CHAPTER 5.0

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this study, the catalyst of KNO_3/Al_2O_3 was introduced as heterogeneous base catalyst. The catalyst with 35 wt.% KNO3 loading on Al_2O_3 and calcined at 773K for 5 h was found to be the optimum catalyst, which gave the highest basicity and the best catalytic activity.

Besides that, the various operating parameters were investigated in order to determine the highest conversion on optimum operating condition. The highest conversion was achieved when reaction carried out with catalyst loading of 8.5%, ratio methanol to oil of 15:1 and temperature at 65°C. The highest conversion resulted from this operation condition is 78.4% after 4 hrs reaction took place in reactor.

5.2 Recommendations

To improve this study, the characterization of catalyst should be increased. The various methods should be conducted to determine the catalyst basicity, the strength of catalyst in order to study the catalyst for the better reaction. Moreover, for the reaction part, the time of reaction should be increase to 8 hrs instead of 4 hrs to increase the conversion of the biodiesel. Other than that, more parameters could be varied to get the best and highest conversion for this catalyst.

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APPENDIX A

Calculation for Methyl Ester Conversion

From calibration curve,

For methyl Palmitate, Y= 10.77X

Conversion= $\frac{m_e}{m_T} \times 100$

where;

m_e=mass of methyl ester

m_T =mass total

$M_T = \frac{mass\ of\ oil}{MW\ of\ oil} \times 3 \times$ (% of fatty acid in palm oil) × molar mass of fatty acid

Details	Palmitic Acid	Oleic Acid	Linoleic Acid
Molar mass	256.42	282.46	280
Percentage in sunflower oil	44.4	38.7	10.5

Example 1: Calculation of methyl ester for effect of molar ratio methanol to oil of 18:1, at temperature 60°C and catalyst loading 6.5%

Area obtained at GC analysis is y= 0.03805 for methyl palmitate

Thus, y = 10.77x

$x = 3.532 \times 10^{-3}$ mg/mL

Mass of methyl linoleate in a 10mL volumetric flask,

$$= \frac{3.532 \times^{-3}}{1 \times^{-3}} \times 0.01L$$

$= 3.532 \times 10^{-5}$

$$\% \text{ of contration in sample} = \frac{0.03532}{0.05} \times 100$$

$= 0.07064\ \%$

Mass of oil + mass of methanol = 53.18 g

% of mass in sample = 0.07064 % × 53.18 g

$$M_T = \frac{15.38}{846.1} \times 3 \times (44.5\%) \times 256.42$$

$$\text{Conversion} = \frac{3.756}{6.22} \times 100$$

$$= 60.04\%$$

Table A.1 : Effect of Ratio Methanol to Oil

Sample	Ratio Me:oil	Conversion,%
1	15:1	34.9
2	16:1	35.5
3	17:1	58.3
4	18:1	60.04
At Temperature 65°C and catalyst concentration is 6.5%		

Table A.2: Effect of catalyst loading

Sample	Catalyst loading, %	Conversion,%
4	6.5	34.5
5	4.5	16.9
6	8.5	78.4
7	9.5	63.16
At Temperature 65°C and methanol to oil ratio is 18:1		

Table A.3: Effect of Reaction Temperature

Sample	Reaction temperature, °C	Conversion,%
7	35	11.9
8	45	12.71
9	55	14.2
10	65	34.5
For catalyst loading of 6.5% and methanol to oil ratio is 18:1		

APPENDIX B

Result of FTIR

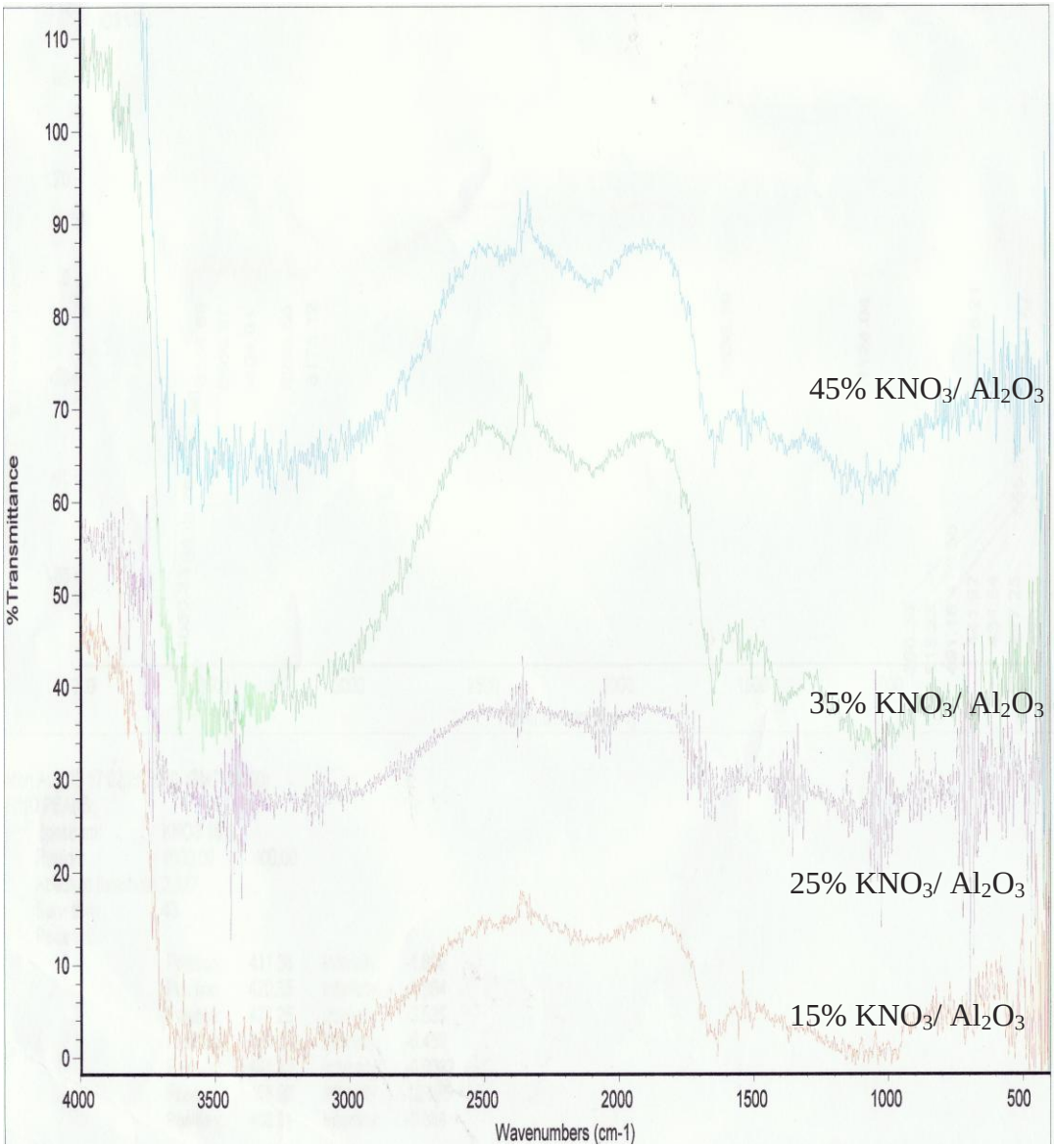


Figure B1: Spectrum of FTIR

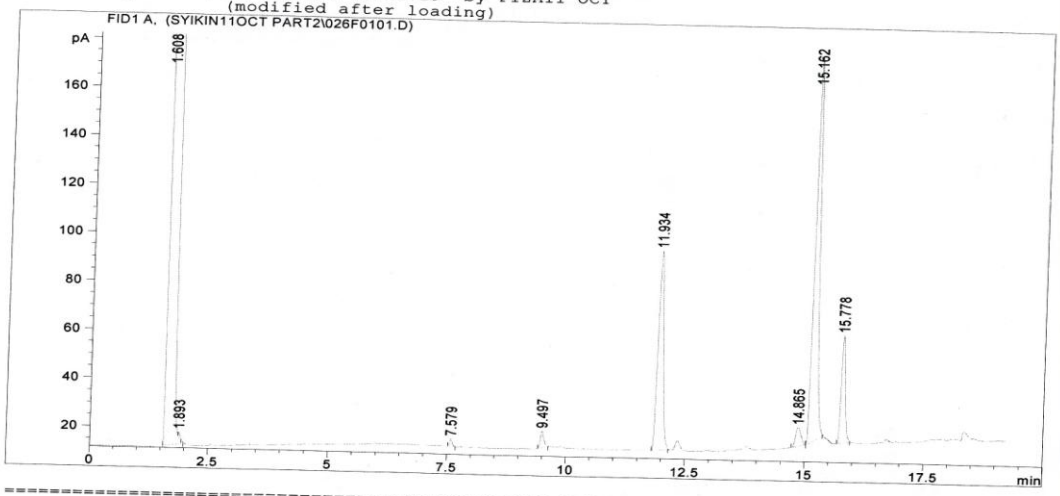
APPENDIX C

Chromatogram for samples

Data File C:\CHEM32\1\DATA\SYIKIN11OCT PART2\026F0101.D 2nd trial
Sample Name: KNO3 sample 1

Acq. Operator : FIZA11 OCT
Acq. Instrument : Instrument 1
Injection Date : 12/10/2010 16:32:27
Seq. Line : 1
Location : Vial 26
Inj : 1
Inj Volume : 1 µl

Acq. Method : C:\CHEM32\1\METHODS\BIODIESEL(JATROPHA).M
Last changed : 12/10/2010 16:30:54 by FIZA11 OCT
Analysis Method : C:\CHEM32\1\METHODS\BIODIESEL(JATROPHA).M
Last changed : 13/10/2010 11:32:19 by FIZA11 OCT
(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 [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	1.608	BB S	0.0457	1.63737e6	5.06692e5	99.87350
2	1.893	BB X	0.0300	4.21616	2.13587	0.00026
3	7.579	BB	0.0534	10.37052	2.99402	0.00063
4	9.497	BB	0.0762	34.20658	6.74426	0.00209
5	11.934	BB	0.1039	623.83679	81.85777	0.03805
6	14.865	BV	0.1060	59.06237	7.48778	0.00360
7	15.162	VB	0.0989	1084.61926	158.28148	0.06616
8	15.778	BB	0.0913	257.64288	44.00872	0.01572
Totals :				1.63945e6	5.06996e5	

*** End of Report ***

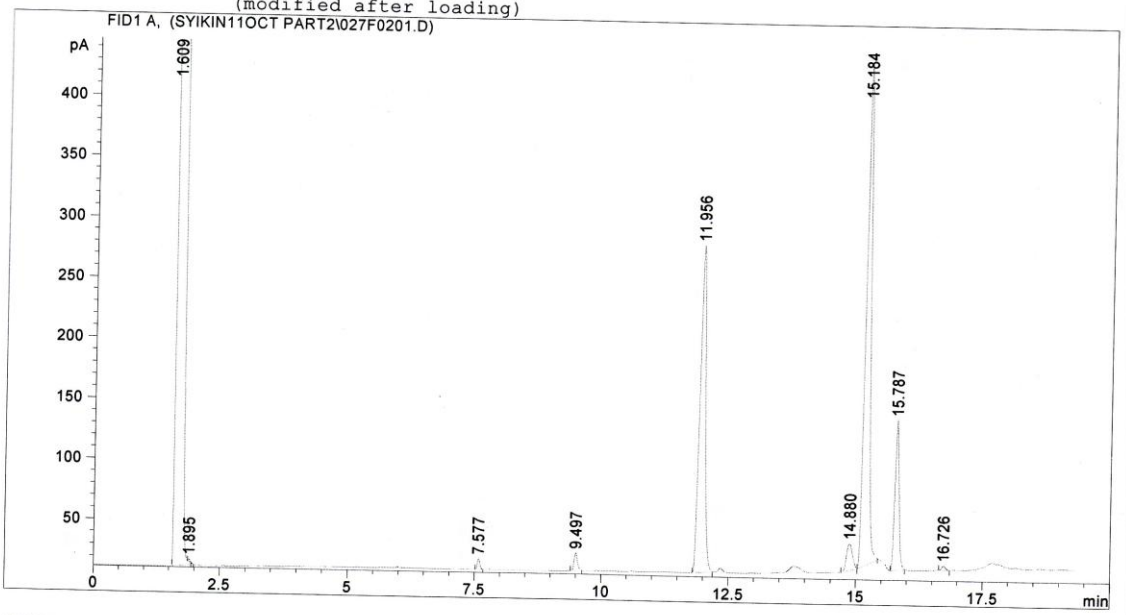
Instrument 1 13/10/2010 11:39:14 FIZA11 OCT

Page 1 of 1

Figure C1: sample 1

File C:\CHEM32\1\DATA\SYIKIN11OCT PART2\027F0201.D
Sample Name: KNO3 sample 2

Acq. Operator : FIZA11 OCT
Acq. Instrument : Instrument 1
Injection Date : 12/10/2010 17:05:42
Seq. Line : 2
Location : Vial 27
Inj : 1
Inj Volume : 1 µl
Acq. Method : C:\CHEM32\1\METHODS\BIODIESEL(JATROPHA).M
Last changed : 12/10/2010 17:05:12 by FIZA11 OCT
(modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\BIODIESEL(JATROPHA).M
Last changed : 13/10/2010 11:32:19 by FIZA11 OCT
(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 [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	1.609	BB S	0.0453	1.62203e6	5.07091e5	99.64009
2	1.895	BB X	0.0304	4.93574	2.46089	0.00030
3	7.577	BB	0.0532	30.99527	9.00118	0.00190
4	9.497	BB	0.0719	66.52384	14.40436	0.00409
5	11.956	BB	0.1149	2075.98633	269.38202	0.12753
6	14.880	BV	0.1051	178.26396	21.86260	0.01095
7	15.184	VB	0.0965	2790.38257	414.59393	0.17141
8	15.787	BB	0.0826	692.70398	123.11047	0.04255
9	16.726	BB	0.0807	19.09757	3.55076	0.00117
Totals :				1.62789e6	5.07949e5	

*** End of Report ***

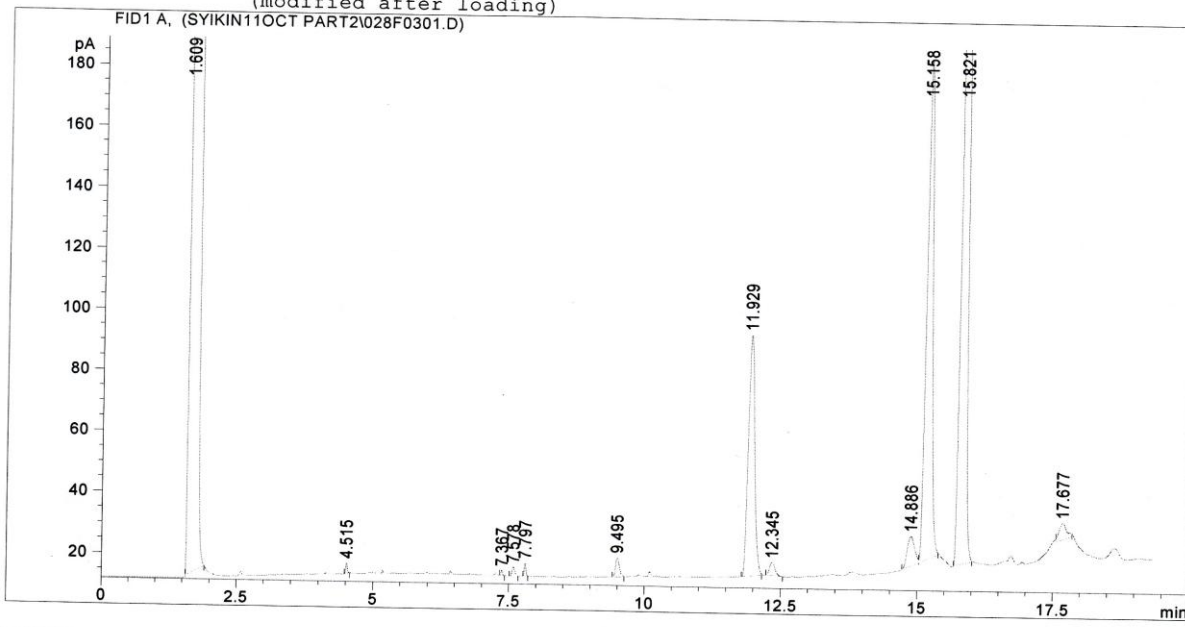
Instrument 1 13/10/2010 11:39:32 FIZA11 OCT

Page 1 of 1

Figure C 2: sample 2

File C:\CHEM32\1\DATA\SYIKIN11OCT PART2\028F0301.D
Sample Name: KNO3 sample 3

Acq. Operator	: FIZA11 OCT	Seq. Line	: 3
Acq. Instrument	: Instrument 1	Location	: Vial 28
Injection Date	: 12/10/2010 17:50:43	Inj	: 1
		Inj Volume	: 1 µl
Acq. Method	: C:\CHEM32\1\METHODS\BIODIESEL(JATROPHA).M		
Last changed	: 12/10/2010 17:05:12 by FIZA11 OCT (modified after loading)		
Analysis Method	: C:\CHEM32\1\METHODS\BIODIESEL(JATROPHA).M		
Last changed	: 13/10/2010 11:32:19 by FIZA11 OCT (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,

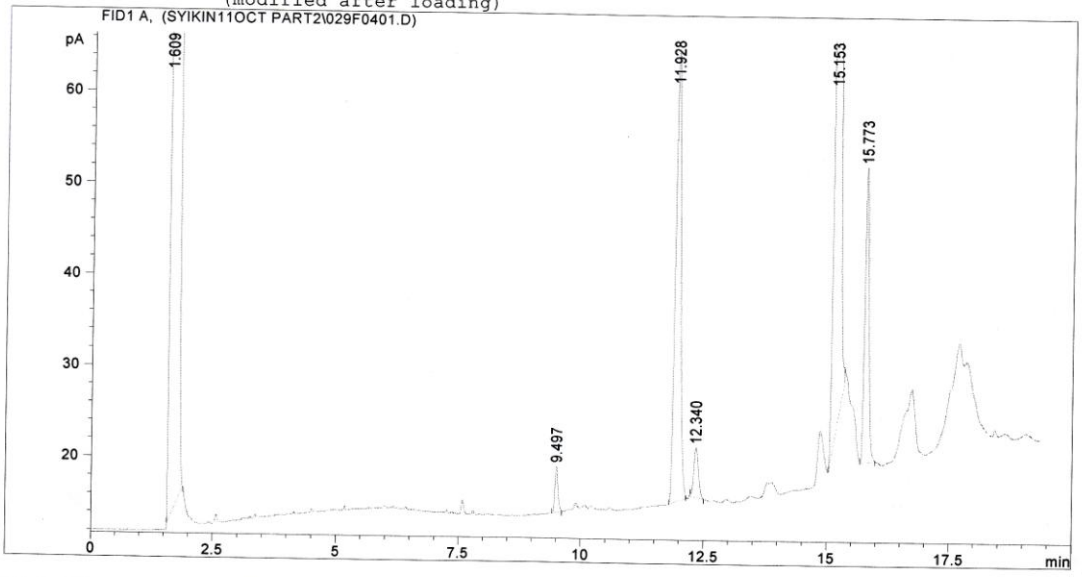
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	1.609	BB S	0.0454	1.61047e6	5.02723e5	99.70829
2	4.515	BB	0.0294	6.70420	3.48619	0.00042
3	7.367	BB	0.0296	2.94695	1.59034	0.00018
4	7.578	BB	0.0561	10.62231	2.94066	0.00066
5	7.797	BB	0.0319	8.84465	4.31511	0.00055
6	9.495	BB	0.0754	29.89789	6.29098	0.00185
7	11.929	BB	0.1139	641.67395	78.87843	0.03973
8	12.345	BB	0.1097	29.48566	4.26494	0.00183
9	14.886	BV	0.1168	88.69861	9.59604	0.00549
10	15.158	VB	0.1091	1235.20410	163.64658	0.07647
11	15.821	BB	0.0914	2605.77710	431.66885	0.16133
12	17.677	BB	0.1353	51.73532	5.37392	0.00320
Totals :				1.61518e6	5.03435e5	

Figure C 3: sample 3

Data File C:\CHEM32\1\DATA\SYIKIN11OCT PART2\029F0401.D
Sample Name: KNO3 sample 4

Acq. Operator : FIZA11 OCT
Acq. Instrument : Instrument 1
Injection Date : 12/10/2010 18:33:23
Seq. Line : 4
Location : Vial 29
Inj : 1
Inj Volume : 1 µl

Acq. Method : C:\CHEM32\1\METHODS\BIODIESEL(JATROPHA).M
Last changed : 12/10/2010 17:05:12 by FIZA11 OCT
(modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\BIODIESEL(JATROPHA).M
Last changed : 13/10/2010 11:32:19 by FIZA11 OCT
(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 [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	1.609	BB S	0.0452	1.61729e6	5.07134e5	99.90516
2	9.497	BB	0.0694	22.25092	4.95674	0.00137
3	11.928	BB	0.1075	381.65970	49.22011	0.02358
4	12.340	BB	0.1003	35.11609	5.37139	0.00217
5	15.153	BB	0.1035	907.57288	133.19547	0.05606
6	15.773	BB	0.0922	188.61388	32.28249	0.01165
Totals :				1.61882e6	5.07359e5	

*** End of Report ***

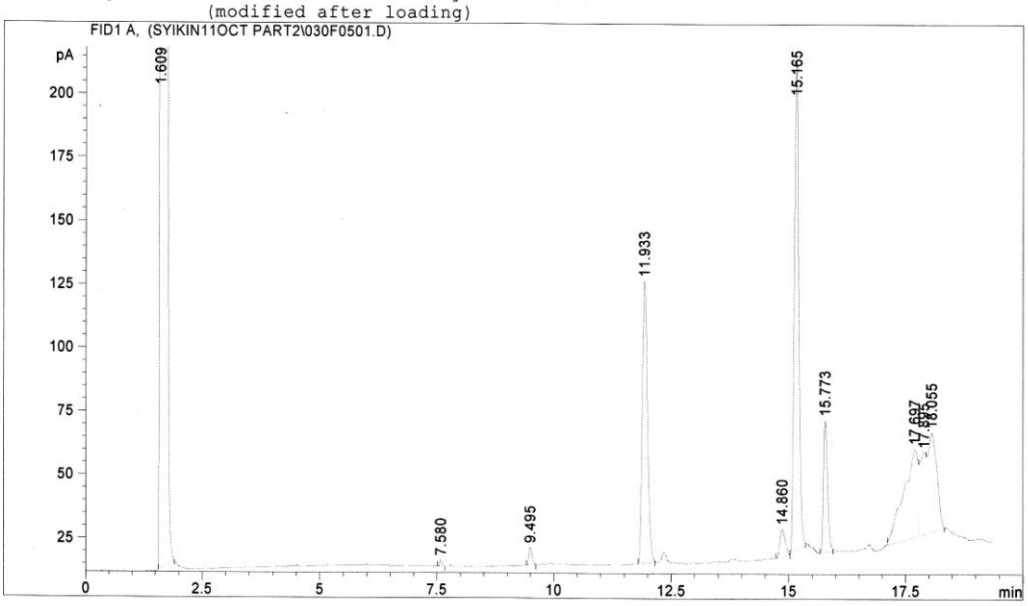
Instrument 1 13/10/2010 11:40:27 FIZA11 OCT

Page 1 of 1

Figure C 4: sample 4

File C:\CHEM32\1\DATA\SYIKIN11OCT PART2\030F0501.D
Sample Name: KNO3 sample 5

Acq. Operator : FIZA11 OCT
Seq. Line : 5
Acq. Instrument : Instrument 1
Location : Vial 30
Injection Date : 12/10/2010 19:16:31
Inj : 1
Inj Volume : 1 µl
Acq. Method : C:\CHEM32\1\METHODS\BIODIESEL(JATROPHA).M
Last changed : 12/10/2010 17:05:12 by FIZA11 OCT
(modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\BIODIESEL(JATROPHA).M
Last changed : 13/10/2010 11:32:19 by FIZA11 OCT
(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 [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	1.609	BB S	0.0453	1.61899e6	5.06251e5	99.74685
2	7.580	BB	0.0533	9.00966	2.60709	0.00056
3	9.495	BB	0.0693	31.80833	6.96259	0.00196
4	11.933	BB	0.1080	846.75409	111.01568	0.05217
5	14.860	BV	0.1019	81.12376	10.76969	0.00500
6	15.165	VB	0.0949	1270.67383	192.84254	0.07829
7	15.773	BB	0.0898	306.12317	51.90681	0.01886
8	17.697	BV	0.2620	729.99481	34.62162	0.04498
9	17.895	VV	0.1211	295.31644	32.16368	0.01819
10	18.055	VB	0.1774	538.01166	39.12569	0.03315
Totals :				1.62309e6	5.06733e5	

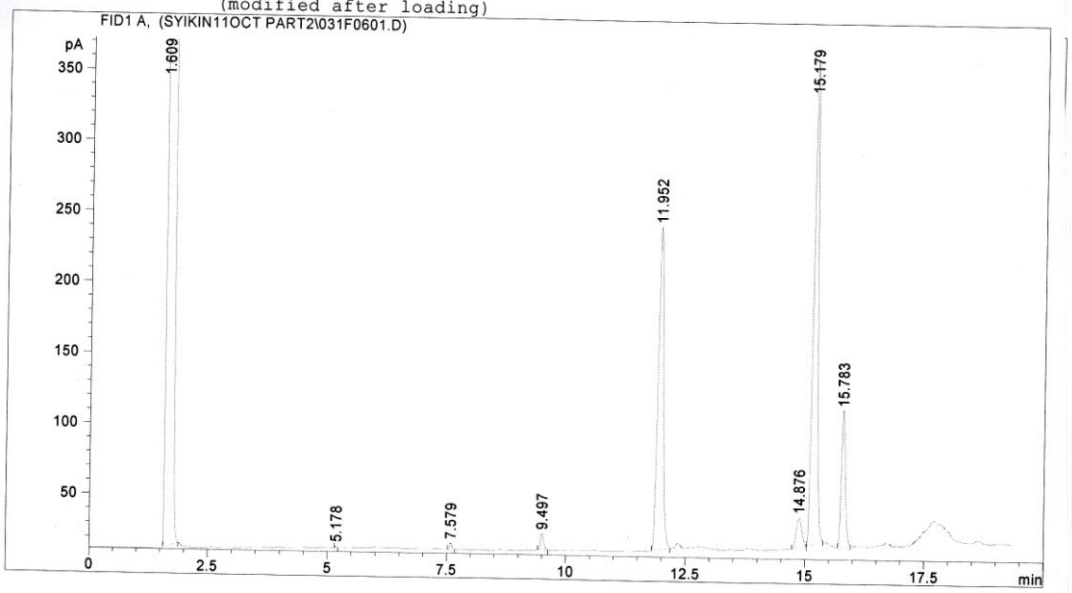
*** End of Report ***

Instrument 1 13/10/2010 11:40:42 FIZA11 OCT Page 1 of 1

Figure C 5: sample 5

File C:\CHEM32\1\DATA\SYIKIN11OCT PART2\031F0601.D
le Name: KNO3 sample 6

Acq. Operator : FIZA11 OCT
Acq. Instrument : Instrument 1
Injection Date : 12/10/2010 19:59:10
Seq. Line : 6
Location : Vial 31
Inj : 1
Inj Volume : 1 µl
Acq. Method : C:\CHEM32\1\METHODS\BIODIESEL(JATROPHA).M
Last changed : 12/10/2010 17:05:12 by FIZA11 OCT
(modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\BIODIESEL(JATROPHA).M
Last changed : 13/10/2010 11:32:19 by FIZA11 OCT
(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 [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	1.609	BB S	0.0453	1.61959e6	5.07119e5	99.70247
2	5.178	BB	0.0218	1.76289	1.22087	0.00011
3	7.579	BB	0.0551	16.05574	4.56040	0.00099
4	9.497	BB	0.0703	53.83893	11.56467	0.00331
5	11.952	BB	0.1079	1772.19458	227.39034	0.10910
6	14.876	BV	0.1031	165.25128	20.94349	0.01017
7	15.179	VB	0.0923	2269.12378	342.44635	0.13969
8	15.783	BB	0.0874	554.90442	96.11117	0.03416
Totals :				1.62442e6	5.07823e5	

*** End of Report ***

Instrument 1 13/10/2010 11:40:57 FIZA11 OCT

Page 1 of 1

Figure C 6: sample 6

ile C:\CHEM32\1\DATA\SYIKIN11OCT PART2\032F0701.D
le Name: KNO3 sample 7

```
======================================================================
Acq. Operator    : FIZA11 OCT                      Seq. Line :   7
Acq. Instrument  : Instrument 1                     Location : Vial 32
Injection Date   : 12/10/2010 20:41:51                 Inj :   1
                                                   Inj Volume : 1 µl
Acq. Method      : C:\CHEM32\1\METHODS\BIODIESEL(JATROPHA).M
Last changed     : 12/10/2010 17:05:12  by FIZA11 OCT
                   (modified after loading)
Analysis Method  : C:\CHEM32\1\METHODS\BIODIESEL(JATROPHA).M
Last changed     : 13/10/2010 11:32:19  by FIZA11 OCT
                   (modified after loading)
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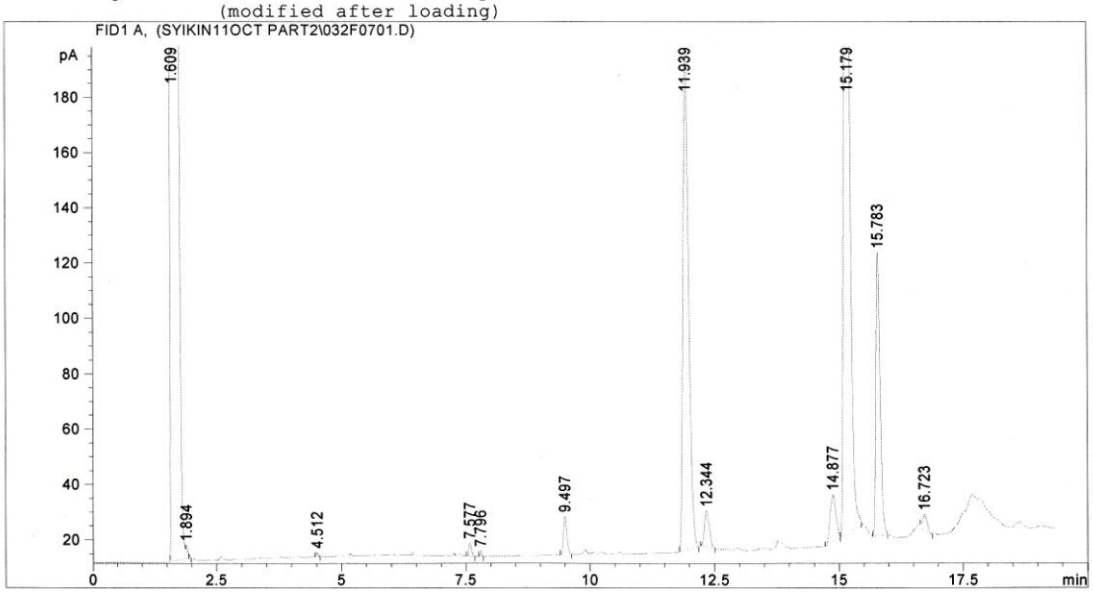


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======================================================================
                        Area Percent Report
======================================================================

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


Signal 1: FID1 A,
```
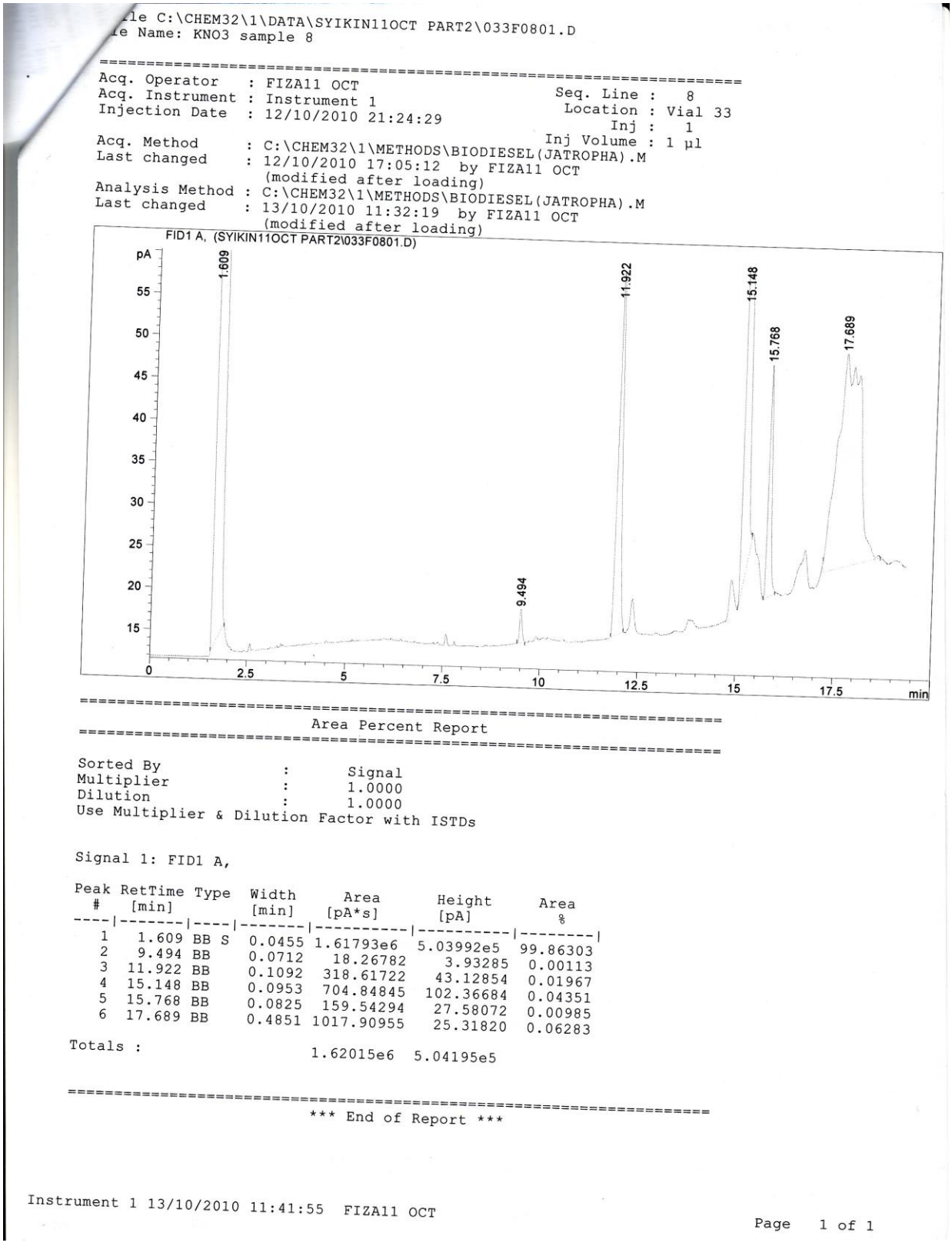

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	1.609	BB S	0.0453	1.60254e6	5.01409e5	99.67705
2	1.894	BB X	0.0331	4.16901	2.10209	0.00026
3	4.512	BB	0.0296	2.75786	1.49258	0.00017
4	7.577	BB	0.0578	17.36453	4.73808	0.00108
5	7.796	BB	0.0316	3.91915	1.93494	0.00024
6	9.497	BB	0.0761	66.92419	13.66405	0.00416
7	11.939	BB	0.1073	1410.02661	178.13239	0.08770
8	12.344	BB	0.0966	85.54288	12.86735	0.00532
9	14.877	BV	0.1008	135.45746	16.84633	0.00843
10	15.179	VB	0.1048	2825.57642	384.18094	0.17575
11	15.783	BB	0.0909	603.29260	102.16866	0.03752
12	16.723	BB	0.0943	37.12518	5.67499	0.00231
Totals :				1.60773e6	5.02133e5	

Figure C7: sample 7



```
le C:\CHEM32\1\DATA\SYIKIN11OCT PART2\033F0801.D
e Name: KNO3 sample 8

==================================================================
Acq. Operator    : FIZA11 OCT                    Seq. Line :   8
Acq. Instrument  : Instrument 1                  Location : Vial 33
Injection Date   : 12/10/2010 21:24:29              Inj :   1
                                                 Inj Volume : 1 µl
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Last changed     : 12/10/2010 17:05:12  by FIZA11 OCT
                   (modified after loading)
Analysis Method  : C:\CHEM32\1\METHODS\BIODIESEL(JATROPHA).M
Last changed     : 13/10/2010 11:32:19  by FIZA11 OCT
                   (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   1.609 BB S  0.0455 1.61793e6  5.03992e5  99.86303
   2   9.494 BB    0.0712   18.26782    3.93285  0.00113
   3  11.922 BB    0.1092  318.61722   43.12854  0.01967
   4  15.148 BB    0.0953  704.84845  102.36684  0.04351
   5  15.768 BB    0.0825  159.54294   27.58072  0.00985
   6  17.689 BB    0.4851 1017.90955   25.31820  0.06283

Totals :                  1.62015e6  5.04195e5

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

Instrument 1 13/10/2010 11:41:55  FIZA11 OCT                Page   1 of 1
```
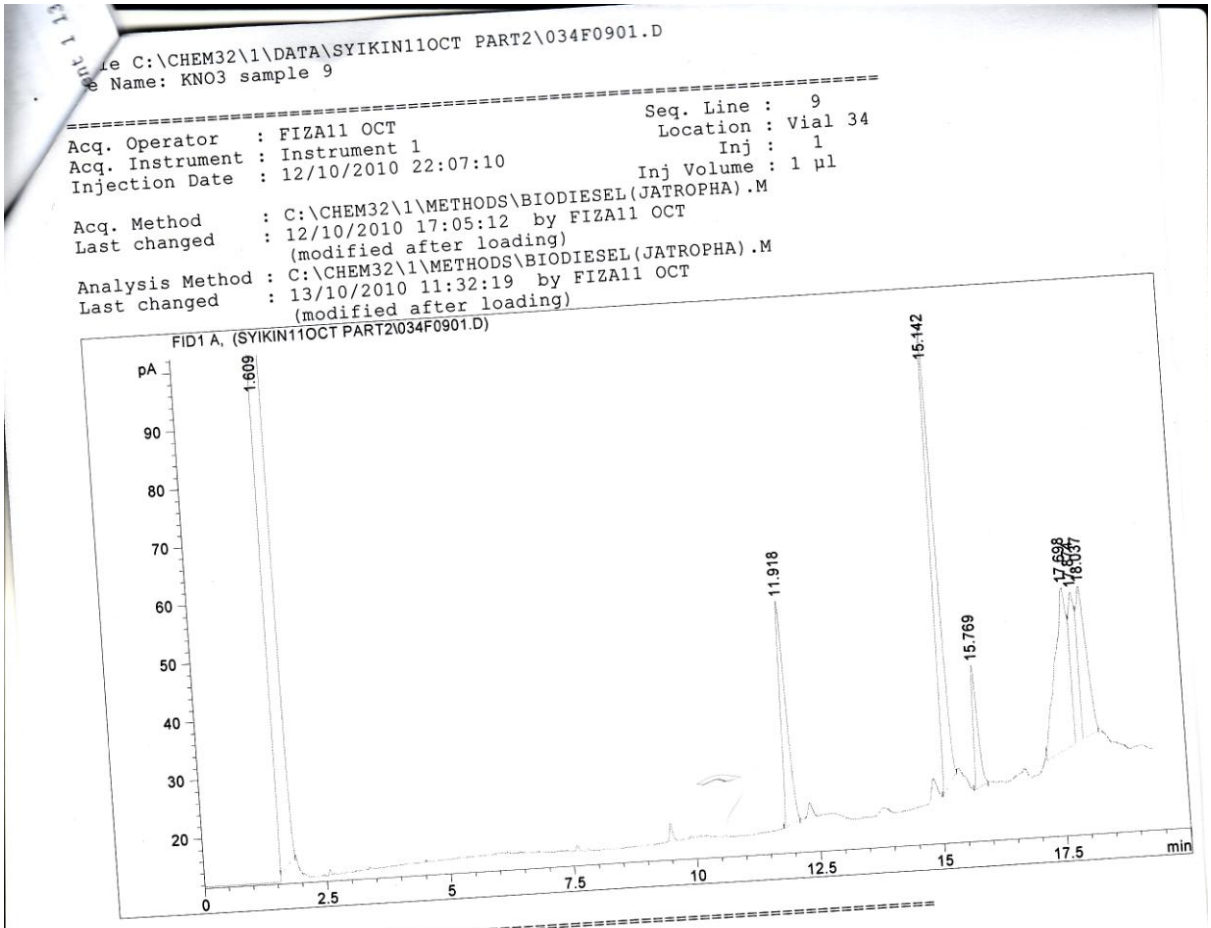
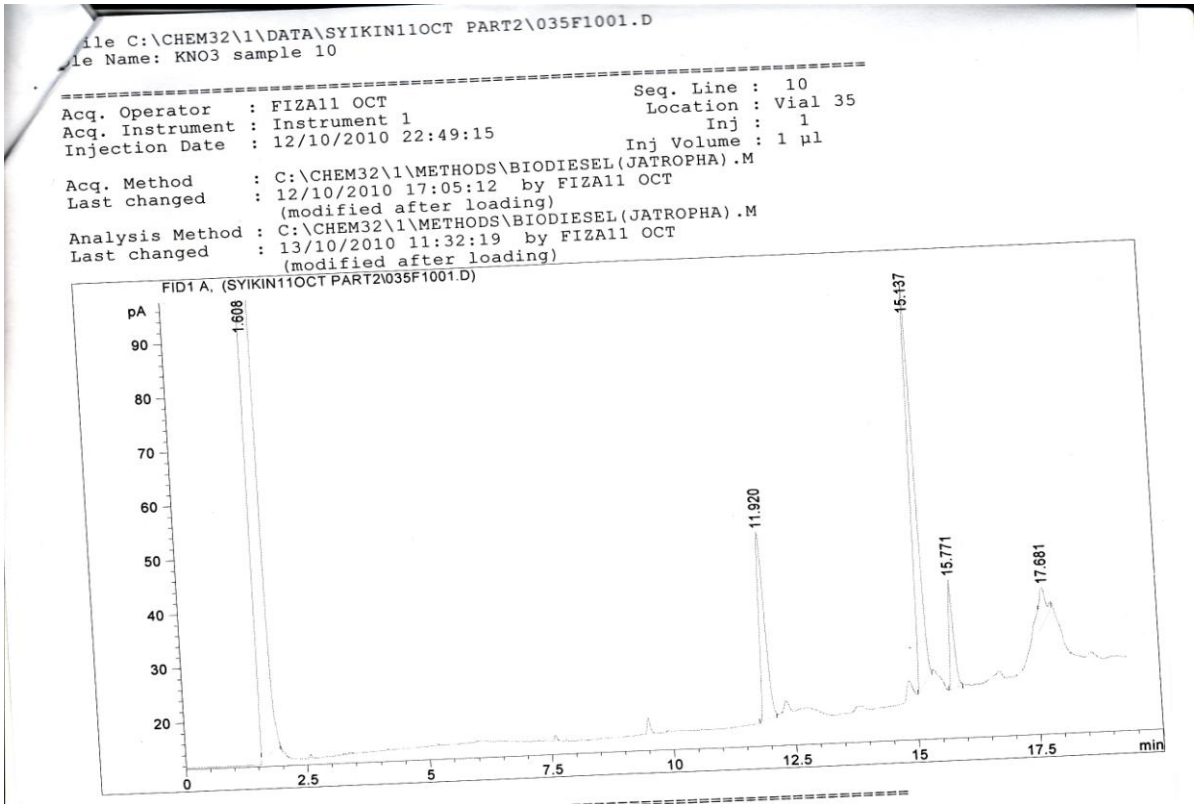

Figure C 8: sample 8




```
Data File C:\CHEM32\1\DATA\SYIKIN11OCT PART2\034F0901.D
Sample Name: KNO3 sample 9

Acq. Operator    : FIZA11 OCT                    Seq. Line :   9
Acq. Instrument  : Instrument 1                  Location  : Vial 34
Injection Date   : 12/10/2010 22:07:10           Inj       :  1
                                                 Inj Volume : 1 µl

Acq. Method      : C:\CHEM32\1\METHODS\BIODIESEL(JATROPHA).M
Last changed     : 12/10/2010 17:05:12  by FIZA11 OCT
                   (modified after loading)
Analysis Method  : C:\CHEM32\1\METHODS\BIODIESEL(JATROPHA).M
Last changed     : 13/10/2010 11:32:19  by FIZA11 OCT
                   (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   1.609 BB S  0.0467 1.63432e6  5.05475e5  99.87719
   2  11.918 BB    0.1051  289.20779   38.31639   0.01767
   3  15.142 BB    0.1030  530.81671   79.38351   0.03244
   4  15.769 BB    0.0921  125.92794   20.95790   0.00770
   5  17.698 BV    0.2516  552.05853   27.21892   0.03374
   6  17.874 VV    0.1118  220.85913   25.56045   0.01350
   7  18.037 VB    0.1429  290.77875   25.72328   0.01777

Totals :                  1.63633e6  5.05692e5

                      *** End of Report ***

Page   1 of 1

Instrument 1 13/10/2010 11:42:15  FIZA11 OCT
```

Figure C 9: sample 9



ile C:\CHEM32\1\DATA\SYIKIN11OCT PART2\035F1001.D
le Name: KNO3 sample 10

Acq. Operator : FIZA11 OCT
Acq. Instrument : Instrument 1
Injection Date : 12/10/2010 22:49:15
Seq. Line : 10
Location : Vial 35
Inj : 1
Inj Volume : 1 µl

Acq. Method : C:\CHEM32\1\METHODS\BIODIESEL(JATROPHA).M
Last changed : 12/10/2010 17:05:12 by FIZA11 OCT
(modified after loading)

Analysis Method : C:\CHEM32\1\METHODS\BIODIESEL(JATROPHA).M
Last changed : 13/10/2010 11:32:19 by FIZA11 OCT
(modified after loading)

FID1 A, (SYIKIN11OCT PART2\035F1001.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 [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	1.608	BB S	0.0457	1.62547e6	5.03138e5	99.94214
2	11.920	BB	0.1209	268.91809	34.49834	0.01653
3	15.137	BB	0.0942	493.50989	74.55930	0.03034
4	15.771	BB	0.0822	115.07075	19.97898	0.00708
5	17.681	BB	0.1177	63.59646	6.52776	0.00391
Totals :				1.62641e6	5.03273e5	

*** End of Report ***

Instrument 1 13/10/2010 11:42:39 FIZA11 OCT

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Figure C 10: sample 10