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Al₂O₃ – SUPPORTED ALKALI METAL OXIDES (LINO₃) FOR TRANSESTERIFICATION OF PALM OIL

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

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JANUARY, 2012

SUPERVISOR'S DECLARATION

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To my beloved family

ACKNOWLEDGEMENT

In the name of Allah S.W.T the Most Beneficent and the Most Merciful. The deepest sense of gratitude to the Almighty for the strength and ability to complete this project. Infinite thanks I brace upon Him.

I would like to take this opportunity to express my sincere appreciation to my supervisor Dr Chin Sim Yee, for encouragement, guidance, morale support, and critics in bringing this project fruition. Without her outstanding support and interest, this thesis would not been at the best it would right now.

I would also like to express my deepest appreciation to my mother whom always support me and motivate me to complete this final year project.

Last but not least, I am also indebt to Faculty of Chemical and Natural Resources Engineering for the usage of workstation lab for my research. My sincere appreciation also extends to all my colleagues, housemates, and friends whom had provided assistance at various occasions.

Finally to individuals who has involved neither directly nor indirectly in succession of this thesis. Indeed I could never adequately express my indebtedness to all of them. Thank you.

ABSTRACT

Transesterification of palm oil with methanol is investigated under a heterogeneous catalysis system. Biodiesel or biofuel is a great solution in greenhouse problems emitted by petroleum diesel. The supported alkali metal catalysts, LiNO₃/Al₂O₃, with active metal oxides formed at calcinations temperatures of 550 °C. The catalysts will be characterized using the Fourier Transform Infra Red (FT-IR), Atomic Absorption Spectrophotometer (AAS) and Thermo Gravimetric Analysis (TGA). The Palm oil and methanol will be mixed with LiNO₃/Al₂O₃ in a 250-mL three-neck round bottom flask equipped with a condenser and an overhead stirring motor. The methanol/oil molar ratios will be varied between 6.5. The mixture will be heated to a controlled temperature by water bath at 40 to 60 °C and the stirring speed is at 400rpm. The sample from the reaction mixture will be collected and kept in overnight. After been kept overnight the samples is settled into two layers. Finally, gas chromatography is used to analyze the product and the desired peak obtained from the GC analysis is compared with the standard calibration. The suitable conditions for the transesterification of palm oil with methanol/oil ratio 6.5, temperature 60°C, and reaction time are 3 hours and loading lithium nitrate 10wt%, respectively in conversion of 93 %.

ABSTRAK

Proses pengesteran minyak sawit dengan metanol menggunakan pemangkinan heterogen. Biodiesel atau bahan bakar biologi adalah satu jalan penyelesaian kepada masalah rumah hijau yang disebabkan oleh minyak petroleum. Disokong pemangkin logam alkali, LiNO3/Al2O3, dengan oksida logam yang aktif yang terbentuk pada suhu 550 ° C. Pemangkin akan dicirikan menggunakan penjelmaan Fourier Transform Infra Red (FT-IR), Penyerapan Spectrophotometer Atom (AAS) dan Termo gravimetrik Analisis (TGA). Minyak sawit dan metanol akan bercampur dengan LiNO3/Al2O3 dalam 250-mL tiga leher bahagian bawah kelalang bulat yang dilengkapi dengan pemeluwap dan kacau magnet. Nisbah molar metanol / minyak adalah 6.5. Campuran akan dipanaskan kepada suhu terkawal dengan mandi air pada 40 hingga 60 oC dan kelajuan kacau di 400 rpm. Sampel daripada campuran tindak balas akan dikumpul dan disimpan semalaman. Selepas disimpan semalaman sampel akan terbentuk dua lapisan. Akhirnya, kromatografi gas yang digunakan untuk menganalisis produk dan puncak yang diingini yang diperolehi daripada analisis GC berbanding dengan penentukuran piawai. Keadaan yang sesuai untuk transesterification minyak sawit dengan metanol / nisbah minyak 6.5, 60oC suhu, dan masa tindak balas adalah 3 jam dan jumlah digunakan LiNO₃ ialah 10 wt%, dengan peratus penghasilan ialah sebanyak 93.00%.

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LIST OF ABBREVIATION/ TERMINOLOGY/ SYMBOLS

Т	-	Temperature
°C	-	Degree Celcius
m	-	Meter
mg	-	Milligram
ul	-	Micro liter
ug	-	Micro gram
um	-	Micro meter
ml	-	Mililiter
kJ	-	KiloJoule
h	-	Hour
min	-	Minute
Κ	-	Kelvin
w/w	-	Weight per weight
kg	-	Kilogram
g	-	Gram
%	-	Percentage
kHz	-	Kilohertz
rpm	-	Revolutions per minute
М	-	Molar (mol/dm3)
FFA	-	Free Fatty Acid
wt	-	Percentage by Weight
TG	-	Triglyceride
PAHs	-	Polycyclic Aromatic Hydrocarbons
C _{FAo}	-	Initial Concentration
C _{FA}	-	Final Concentration
X _{FA}	-	Conversion
S 1	-	Sample 1
CC	-	Catalyst Concentration
MR	_	Molar Ratio

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CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND OF STUDY

Biodiesel, derived from vegetable oil or animal fats by transesterification with alcohol like methanol and ethanol, is recommended for use as a substitute for petroleum based diesel mainly because biodiesel is an oxygenated, renewable, biodegradable and environmentally friendly biofuel with similar flow and combustion properties and also low emission profile (Altin and Selim, 2001). It helps to reduces global warming gas emissions such as carbon dioxide. Biodiesel has no aromatics, almost no sulfur and contains 11% oxygen by weight. These characteristics of biodiesel reduce the emissions of carbon monoxide, hydrocarbon and particulate matter in the exhaust gas compared to petroleum based diesel fuels (Peterson and Hustrulid, 1998).

Due to the good properties and the environment improvement, many countries pay much attention to research and development (R&D) of biodiesel industry and constitute favorable legislation for it. More than 2.7 million tons biodiesel in 2003 was made in Europe, and 8-10 million tons is expected in 2010 (Altin and Selim, 2001).

Unfortunately, many of these feedstocks contain large amounts of free fatty acids (FFAs). These FFAs react with alkali catalysts to produce soaps that inhibit the fatty acid methyl esters (FAMEs) formation (Gerpen *et al*, 2004). In the case of the vegetable oils that contain up to 5% FFAs, the transesterification reaction can still be catalyzed with an alkali catalyst. However, additional catalyst must be added to compensate for the catalyst lost to soap. This soap can prohibit the separation of the

methyl ester and glycerol and also contribute to emulsion formation during the washing step (Gerpen, 2005).

Currently, compared to petroleum based diesel, the high cost of biodiesel is a major barrier to its commercialization. It is reported that approximately 70%-85% of the total biodiesel production cost arises from the cost of the raw material (Fukuda *et al*, 2001). Use of low cost feedstock such as waste cooking oil (WCO) should help make biodiesel competitive in price with petroleum diesel. Everywhere in the world, there is an enormous amount of waste lipids generated from restaurants, food processing industries and fast food shops everyday (Mittlebach and Gangl, 2001).

1.2 PROBLEM STATEMENT

Petroleum price is undoubtedly agreed to be very unstable. At some point the price roars to maximum price. This sort of trend has affected the world economic growth. Each human being in this mother earth can feel the effect of economic crisis that is mainly caused by unstable price of petroleum. Thus, by using biodiesel as alternative, the problem could be tackle.

Malaysia is famously known as one of the producer of palm oil. It has the potential to lead the way in biofuel production looking at its vast production of palm oil. By using palm oil, Malaysian would have a consistent supply and provision to replace the usage of diesel petroleum. Besides palm oil is also one of the most highly efficient feedstock for biodiesel compared to other vegetable oils.

A conventional operation of biodiesel usually uses alkali metal such as Lithium Nitrate (LiNO₃) as catalyst and palm oils as raw material. These homogeneous catalysis systems have many drawbacks. The homogeneous catalyst is very sensitive to FFAs and water in the oil feedstock's and alcohols because the reaction of FFAs with basic homogeneous catalyst will forms soaps. The soaps formation will complicates the glycerol separation. In addition, Lithium Nirate (LiNO₃) is the alkali metal group are generally water-soluble. The catalysis over these support alkali metal oxides has been

1.3 OBJECTIVE

The objective in the present study is:

• To determine the best condition in producing biodiesel using Lithium Nitrate (LiNO₃) supported by Aluminum Oxide (Al₂O₃).

1.4 SCOPE OF RESEARCH

The scope of research includes:

- To characterization LiNO₃/Al₂O₃ catalyst with various loading LiNO₃.
- To study the effect of important parameters on the transesterification of palm oil:
 - Effect loading of Lithium Nitrate (LiNO₃) in LiNO₃/Al₂O₃ catalyst.
 - Effect of temperature (°C).

1.5 SIGNIFICANCE OF STUDY

The rationales and significances of this study are:

- Creating a new development technology (catalyst technology) in biodiesel from palm oil.
- LiNO₃/Al₂O₃ catalyst alkali heterogeneous, it is noncorrosive, environmentally benign, fewer disposal problem, easily separation, higher selectivity and longer catalyst higher.

CHAPTER TWO

LITERATURE REVIEW

2.1 **BIODIESEL**

Biodiesel is mono-alkyl esters of fatty acids derived from vegetable oils and animal fats. It has received increasing levels of attention as a potential alternative green fuel due to its non-toxic, sulphur- and aromatic-free, biodegradable and renewable material status (Dunn and Knothe, 2001). The physical and fuel properties, i.e. kinematic viscosity, specific gravity, calorific value, flash point, and cetane number of biodiesel are categorized into the same range as that of petroleum-based diesel fuel. Thus, it can be applied to the mass of currently existing compression-ignition diesel engines with little or no modifications. The additional advantage is that, like any other biomass-derived fuels, the exhaust gas from biodiesel combustion contains no SOx and a relatively small amount of CO, unburnt hydrocarbons and particulate matter, compared to the combustion of conventional diesel fuel [Ma and Hanna, 1999; Ramadhas et al.,2005).

Conventional biodiesel production is performed through the transesterification of triglycerides from vegetable oils and animal fats with mono-alkyl alcohols, for example methanol and ethanol. The process is usually carried out in the presence of a homogeneous base or acid catalyst to reduce the reaction temperature and to control the product selectivity. Sodium or potassium hydroxides, carbonates or alkoxides are the common base catalysts (Encinar et al., 2002) and the often used acid catalysts are sulphuric and hydrochloric acids (Obibuzor et al., 2003). However, these homogeneous catalysis systems have many drawbacks. Removal of the catalysts to purify the biodiesel fuel and glycerol by-product is difficult and requires a large amount of water. Consequently, a considerable amount of wastewater is inevitably produced. To overcome these problems, the transesterification over environmentally benign solid catalysts is a promising route

2.2 TRANSESTERIFICATION

Transesterification is the general term used to describe the important class of organic reactions where an ester is transformed into another through interchange of the alkoxymoiety. When the original ester is reacted with an alcohol, the transesterification process is called alcoholysis (figure 2.1) (Otera, 1993). The term transesterification will be used as synonymous for alcoholysis of carboxylic esters, in agreement with most publications in this field. The transesterification is an equilibrium reaction and the transformation occurs essentially by mixing the reactants. However, the presence of a catalyst (typically a strong acid or base) accelerates considerably the adjustment of the equilibrium. In order to achieve a high yield of the ester, the alcohol has to be used in excess.

Figure 2.1: General Equation of Transesterification Reaction

The applicability of transesterification is not restricted to laboratory scale. Several relevant industrial processes use this reaction to produce different types of compounds1. An example is the production of PET (polyethylene terephthalate), which involves a step where dimethylterephthalate is transesterified with ethylene glycol in the presence of zinc acetate as catalyst (figure 2.2) (Weissermel, 1993). Furthermore, a large number of acrylic acid derivatives are produced by transesterification of methyl acrylate with different alcohols, in the presence of acid catalysts.



Figure 2.2: Transesterification of Dimethylterephthalate with Ethylene Glycol.

If the alcohol and the ester groups are present in the same molecule simple lactones or macrocycles are formed by an intermolecular transesterification, as shown in figure 2.3. Further transesterification reactions can be found in the literature, in which metal alkoxides, aluminium isopropoxide, tetraalkoxytitanium compounds and organotin alkoxides are applied as catalysts.



Figure 2.3: Examples of intermolecular transesterification reactions, forming lactones or macro cycles.

2.3 ESTERIFICATION

Esterification is simply the reaction between a carboxylic acid and an alcohol which is catalyzed, in this case, by a mineral acid, e.g., sulfuric or phosphoric acids. In general, the mechanism for esterification follows the following scheme: the compounds of the chemical structure R-COOR', where R and R' is either alkyl or aryl groups. The most common method for preparing esters is to heat a carboxylic acid, R-CO-OH, with an alcohol, R'-OH, while removing the water that is formed. Esters can also be formed by various other reactions. These include the reaction of an alcohol with an acid chloride (R-CO-Cl) or an anhydride (R-CO-OCR'). Concluded that the ester product (R-CO-OR') is the union of the acyl group (R-C= O-) from the acid, *RCO*-OH, with the alkoxide group (R'O-) from the alcohol, *R'-OH* rather than other possible combinations. Figure 2.4 were show mechanism for esterification.



Figure 2.4: Acid catalyzed esterification of fatty acid.

According to Ma and Hanna (1999), the free fatty acid (FFA) content in cheaper and lower-quality feedstock's such as waste cooking oil and some crude and recycled oils and greases can exceed 10 wt.%. Such FFA must first undergo acid-catalyzed esterification before transesterification of the larger triglycerides is carried out using a base catalyst.

Marchetti (2008) say the esterify FFA to alkyl esters in the presence of an acidic catalyst is a route to improving the use of high FFA oils on biodiesel production. Esterification is normally carried out in the homogeneous phase in the presence of acid catalysts such as sulfuric and p-toluene sulfonic acids. This pretreatment step has been successfully demonstrated using sulfuric acid.

2.4 PALM OIL

Palm oil, like other vegetable oils, can be used to create biodiesel, as either a simply processed palm oil mixed with petro diesel, or processed through transesterification to create a palm oil methyl ester blend, which meets the international EN 14214 specification. Glycerin is a by-product of transesterification. The actual process used to produce biodiesel around the world varies between countries and the requirements of different markets. Next-generation bio fuel production processes are also being tested in relatively small trial quantities.

The *International Energy Agency (IEA)* predicts that bio fuels usage in Asian countries will remain modest. But as a major producer of palm oil, the Malaysian government is encouraging the production of bio fuel feedstock and the building of palm oil biodiesel plants. Domestically, Malaysia is preparing to change from diesel to bio-fuels by 2008, including drafting legislation that will make the switch mandatory.

First generation biodiesel production from palm oil is in demand globally. Palm oil is also a primary substitute for rapeseed oil in Europe, which too is experiencing new demand for biodiesel purposes. Palm oil producers are investing heavily in the refineries needed for biodiesel. In Malaysia companies have been merging, buying others out and forming alliances to obtain the economies of scale needed to handle the high costs caused by increased feedstock prices. New refineries are being built across Asia and Europe.

According to Hamburg-based Oil World trade journal, in 2008, global production of oils and fats stood at 160 million tonnes. Palm oil and palm kernel oil were jointly the largest contributor, accounting for 48 million tonnes or 30% of the total output. Soybean oil came in second with 37 million tonnes (23%). About 38% of the

oils and fats produced in the world were shipped across oceans. Of the 60.3 million tonnes of oils and fats exported around the world, palm oil and palm kernel oil make up close to 60%; Malaysia, with 45% of the market share, dominates the palm oil trade. Palm oil stands out as the least expensive oil to be produced per tonne compared with other major vegetable oils.

2.4 CATALYST

A broad definition of catalysis also allows for materials that slow the rate of a reaction. Whereas catalysts can greatly affect the rate of a reaction, the equilibrium composition of reactants and products is still determined solely by thermodynamics. Heterogeneous catalysts are distinguished from homogeneous catalysts by the different phases present during reaction. Homogeneous catalysts are present in the same phase as reactants and products, usually liquid, while heterogeneous catalysts are present in a different phase, usually solid. The main advantage of using a heterogeneous catalyst is the relative ease of catalyst separation from the product stream that aids in the creation of continuous chemical processes. Additionally, heterogeneous catalysts are typically more tolerant of extreme operating conditions than their homogeneous analogues.

2.4.1 HOMOGENEOUS CATALYST

In general, homogeneous processes are characterised by both high chemical and high energy utilisation efficiencies but a major deterrent in the further exploitation of this methodology has been the perceived inability to readily separate the products from the catalysts. Attempts to overcome this difficulty have included ligand modification, biphasic catalysis and efforts to support homogeneous catalysts on polymeric and inorganic supports. The use of supports for the catalysts has in the past been only partially successful as most of these systems have lost catalytic metal species into solution during the reactions. Encinar et al (2002) say, the process is usually carried out in the presence of a homogeneous base or acid catalyst to reduce the reaction temperature and to control the product selectivity. Sodium or potassium hydroxides, carbonates or alkoxides are the common base catalysts.

From previous studies by Abiney et al (2008), the fact that homogeneous acids such as sulfuric acid need long reaction times, more than the alkaline catalysts, becomes a serious problem. These problems can be minimized by use of high catalyst concentrations. A further complication of working with high amounts of acid catalyst becomes apparent during the catalyst neutralization process, which precedes product separation. Since CaO addition during neutralization is proportional to the concentration of acid needed in the reactor, high acid concentrations lead to increased CaO costs, greater waste formation and higher production costs. According to Zullaikah et al (2005), we can be concluding that the main drawback of the pre-esterification method consists in the necessity to remove and to neutralize the homogeneous acid catalyst from the oil after pre-esterification.

2.4.2 HETEROGENEOUS CATALYST

In the field of heterogeneous catalysis, numerous carbon materials have been used to disperse and stabilize metallic particle. Catalytic properties of these solids are known to be dependent upon the interaction between the carbon support and the metal particles. Solid-state chemistry of fullerene-based materials is of much interest due to the novel electronic properties both of the intercalation compounds of solid C_{60} and of C_{60} monolayer's deposited on no alkali metals Furthermore, strong interaction was found to exist between nickel clusters and multilayer films of C_{60} . For carbon 'nanotubes, theoretical calculations show that, depending upon the fiber geometry and the curvature of graphitic planes, the nanotubes have metallic or semiconducting properties. The aim of the present study is to show the potential of carbon "nanotubes" as a support for metal catalysts. More recently, there has been an increasing development of heterogeneous catalysts, such as NaOH and a series of potassium catalysts supported on alumina say by Arzamendi et al (2007).

According to Gryglewicz (1999), there are many advantages of using heterogeneous catalyst such as non-corrosive, environmental friendly present fewer disposal problems, easier in separation from liquid product and they can be design to give higher activity, selectivity and longer catalyst lifetime.

 Table 2.1: Major Difference between Homogeneous and Heterogeneous catalyst.

	Homogeneous	Heterogeneous
Form	Soluble metal complexes,	Metals, usually supported,
	usually mononuclear	or metal oxides
Active site	well-defined, discrete molecules	poorly defined
Phase	Liquid	Gas/solid
Temperature	Low (<250°C)	High (250 - 500°C)
Activity	Moderate	High
Selectivity	High	Low
Diffusion	Facile	Can be very important
Heat transfer	Facile	Can be problematic
Product separation	Generally problematic	Facile
Catalyst recycle	Expensive	Simple
Catalyst modification	Easy	Difficult
Reaction mechanisms	Reasonably well understood	Poorly understood

Reaction	Catalyst	Finding	Arthor
Transesterification of palm oil	Aluminum Oxide	The catalyst is catalytically active, giving a high	Ebiru et al. (2005)
	(Al ₂ O ₃)	triglyceride conversion.	Xie et al. (2006)
			Xie and Li (2006)
Transesterification of palm crude oil	Potassium and	The catalysis over these supported alkali metal	
	Aluminum Oxide	oxides has been considered to occur through the	Alonso et al. (2007)
		homogeneous route to a significant extent	
Transesterification of vegetable oil		Base catalyst to the transesterification of soybean	
	Base catalyst	oil, showing a comparable performance to the	Kim et al. (2004)
		conventional homogeneous NaOH catalyst.	
Transesterification of rapeseed oil	Heteropolyacids (HPA)	Higher transesterification rates were obtained with	
with ethanol	with Keggin structure	ethanol than methanol in presence of HPA.	Morin <i>et al.</i> (2007)
		Homogeneous catalyst even with presence of HPA	
		would lead to serious contamination problems as	
		used acids neutralization and equipments corrosion.	

Table 2.2: Summary of transesterification process for previous studies

Simultaneous transesterification of	Series of heterogeneous	The zinc and lanthanum mixed oxides catalysts		
unrefined or waste oils	zinc and lanthanum mixed oxides	allows the direct use of unrefined and waste oils for biodiesel production	Yan <i>et al. (2009)</i>	
Transesterification of soybean oil	Metal Hydroxides	Basic catalysts are usually preferred to acid catalysts because of the higher activity and the lower process temperatures required as compared to acid-catalyzed transesterification	Freedman et al. (1986)	
Biodiesel production by methanol sis of soybean oil	Calcium Supported On Mesoporous Silica	Heterogeneous catalysts that show excellent catalytic activity and these catalysts are expensive and complicated to prepare, which limits their potential application in industrial scale operation.	Samart et al. (2010)	
Transesterification of crude palm kernel oil and crude coconut oil	Sulfated zirconia	Display high activity and selectivity for transesterification of several vegetable oils and fatty acids under ambient pressure at temperatures up to 100°C	Jitputti et al. (2006)	
Transesterification of palm kernel oil	Ca and Zn mixed oxide catalyst	The most attractive catalyst among the alkali earth metal oxides because of its high transesterification	Ngamcharussrivichai et al. (2008)	

CHAPTER THREE

METHODOLOGY

3.1 INTRODUCTION

The experimental detail such as raw material and chemical substances, apparatus and equipment used in the experiment, experimental procedure, sample preparation, and analysis with gas chromatography will be discussed in this chapter.

3.2 RAW MATERIAL and CHEMICAL SUBSTANCE

Raw materials and chemical substances are shown in Table 3.1:

Table 3.1: List Raw material and Chemical Substances

NO	Raw Materials/ Chemical	
	Substances	Functions
1	Palm oil	Reactants
2	Methanol	
3	Lithium Nitrate	Catalyst

4	Aluminium Oxide	
5	Methyl Palmitate	
6	Methyl Oleate	Working standards for calibration curve
7	Methyl Linoleate	
8	Hexane	Gas Chromatography analysis

3.3 EQUIPMENT AND APPARATUS

Equipment and Apparatus are shown in table 3.2:

Table 3.2:	List Equipment	and Apparatus
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No	Equipment and Apparatus	Function	
1	3-neck round bottom flask	Place where the reaction occur	
2	Overhead stirring motor	Mixing the raw materials	
3	Condenser	Condense the sample from being release to the atmosphere	
4	Water bath	Heat the reaction mixture to its desired temperature	
5	Rotary evaporator	Remove excess methanol	
6	Furnace	Catalyst calcined at 550°C	
7	Oven	Dry catalyst at 120°C overnight	
8	Gas chromatography	Used to analyse the purity organic compound	

3.4 CATALYST PREPARATION

Supported metal oxide catalysts were prepared according to the conventional incipient-wetness impregnation of aqueous solutions of the corresponding metal salt precursors on an aluminium oxide support. The metal precursors applied to the study were analytical grade nitrate salts of alkali metals, including LiNO₃. A series of LiNO₃/Al2O3 catalysts with varying LiNO₃ loadings (5, 10 and 15 wt %) were prepared. The support was then added into the solution followed by overhead stirring motor. After equilibrating, the mixture for 2 h, the paste will be dried in an oven at 120 °C overnight. Prior to use in the transesterification, the dried solid will be calcined at 550 °C for 4 h.

3.5 CATALYST CHARACTERIZATION

Crystalline of supports and metal oxide catalysts will be confirmed by technique of Fourier Transform Infra Red (FT-IR), that can identify unknown materials, can determine the quality or consistency of a sample and can determine the amount of components in a mixture using method the KBr technique. FTIR analysis was carried out on a Shimadzu 8400 S FTIR instrument in wave number range of 4000–500 cm⁻¹. The X-ray diffraction (XRD) method is ideally suited for characterization and identification of the internal structure, bulk phase, and composition in crystalline phases using a Rigaku D/MAX 2200/Ultima + diffractometer using Cu K α radiation at a step size of 0.01°. Thermo Gravimetric Analysis (TGA) is an analytical method used to measure mass change of a sample as a function of temperature or time.

3.6 EXPERIMENTAL PROCEDURE

In order to perform experimental studies for the biodiesel production, several steps are involved. These steps are shown in Figure 3.1.

Firstly, mixed all together the Palm oil and methanol with LiNO₃/Al₂O₃ in a 250-mL three-neck round bottom flask equipped with a condenser and an overhead stirring motor. The methanol/oil molar ratios 6.5.







Figure 3.2: Schematic diagram of a batch reactor system using water bath.

3.7 EXPERIMENTAL STUDIES ON THE EFFECT OF DIFFERENCE OPERATING PARAMETERS.

For this research, the experiment plan involves two independent variables which are loading LiNO₃ supported Al_2O_3 and reaction temperature. The loading LiNO₃ supported Al_2O_3 used in the experiment was directed 5 wt% - 15 wt%. For reaction temperature, it was varied from 40°C to 60°C. There are two parameters that will be studied in order to obtain the optimum condition for the biodiesel production. The parameters are:

a) Effect loading of LiNO3 wt% supported Al2O3

The operating condition data for the study of 1st parameter is shown in Table 3.3:

Experimental	Temperature	LiNO ₃ loading	Molar Ration
run	(°C)	(wt %)	Methanol to Palm Oil
1	60	5 wt%	6.5:1
2	60	10 wt%	6.5:1
3	60	15 wt%	6.5:1

 Table 3.3: Operating condition for first parameter

b) Effect of temperature (°C).

For the third parameter, the optimized value of molar ratio oil/ alcohol and LiNO₃ loading (wt %) from previous studies is used to determine which temperature could give the best performance.

The operating condition data for the study of 2^{nd} parameter is shown in Table 3.4:

 Table 3.4:
 Operating condition for second parameter

Experimental	Temperature	Catalyst	Molar Ratio Methanol to
run	(°C)	Concentration	Palm Oil
1	40	10 wt%	6.5:1
2	50	10 wt%	6.5:1
3	60	10 wt%	6.5:1

PROCEDURE:

The reaction was carried out in a 250-mL three-neck round bottom flask equipped with a condenser and a magnetic stirrer. Typically, 1 g of calcined catalyst
was suspended in a required volume of methanol (99.5%, commercial grade) and heated to a controlled temperature of 60 °C by a water bath. Subsequently, the oil was added into the mixture under vigorous stirring.

The methanol/oil molar ratios were varied between 10 and 65. After the course of reaction (1–3 h), the products collected were kept in a refrigerator at $T = 4^{\circ}C$ overnight. After been kept overnight the samples are settled into two layers. The samples then are diluted with hexane GC standard. Finally, the GC analysis were performed to obtain the area peaks and then converted into conversion.

3.8 ANALYTICAL METHOD

Analytical method is one of the major fields of analytical chemistry. Analytical Chemistry involved with analyzing compound in samples or substances. In this study, Gas Chromatography was used.

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

The final product was analyzed by using gas chromatography because of its efficiency in separating the compound. The analysis of biodiesel for each reaction mixture was carried out using gas chromatography and the component of the product was showed in term of chromatogram.

The condition of the gas chromatography is as shown in Table 3.5:

Temperature column	Initially held at 40°C for 3 min, then ramped to 180°C		
	with 40°C/min (held for 3 min), and finally ramped up at		
	10°C/min to 270°C and maintained for 5 min.		
Injector temperature	250°C		
Detector temperature	250°C		
Injection size	1.0µL (10:1 split)		
Hydrogen flow	35mL/min		
Air flow	450mL/min		
Nitrogen make up	35mL/min		
Carrier gas	Hydrogen, compressed air, H2, N2		
Type of Column	DB-WAX 122-7032		
	Size = 30 m x 30 um		

Table 3.5: Gas Chromatography Flame Ionization Detector (FID)

3.8.1 PROCEDURE FOR STOCK STANDARD

 $300 \ \mu$ l for each ester are measured out the appropriate amount of standard required in a 10ml volumetric flask for a concentration of 25mg/ml. Then, it was diluted in 10ml volumetric flask with n-Hexane; reagent grade.

Component	Concentratio mg/ml	Volumetric Flask (ml)
Methyl Palmitate	25	10ml
Methyl Linoleate	25	10ml
Methyl Oleate	25	10ml

Table 3.6: The concentrations of stock standard:

3.8.2 PROCEDURE FOR WORKING STANDARD

Appropriate volumes of stock solution of methyl palmitate, methyl oleate and methyl linoleate are pipetted into a 1.5 ml vial for different concentration. Then it is diluted to the mark with n-Hexane. After that it is cap and mix in the vials.

Component	S1 (µg/ml)	S2 (µg/ml)	S3 (µg/ml)	S4 (µg/ml)	S5 (µg/ml)
Methyl Palmitate	500	1000	1500	2000	2500
Methyl Linoleate	500	1000	1500	2000	2500
Methyl Oleate	500	1000	1500	2000	2500

 Table 3.7: The concentrations of working standard:

3.8.3 CALIBRATION CURVE

A calibration curve is a general method for determining the concentration of a substance in an unknown sample by comparing the unknown to a set of standard samples of known concentration. The calibration curve is a plot of how the instrumental response, the so-called analytical signal, changes with the concentration of the analyzed. The operator prepares a series of standards across a range of concentrations near the expected concentration of analyzed in the unknown. 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, we can calculate the quantity of that compound and its relative proportions in the sample. Standard curve biodiesel for this experiment is methyl linoleate, methyl palmitate and methyl oleate. Figure 3.3, 3.4 and 3.5 shows the curve.



Figure 3.2: Standard calibration curve for methyl linoleate.



Figure 3.3: Standard calibration curve for methyl oleate.



Figure 3.4: Standard calibration curve for methyl palmitat

CHAPTER FOUR

RESULTS AND DISCUSSION

This chapter to explain the catalyst characterization using three instruments and the affect on transesterification process by the mode of reaction condition, molar ratio of alcohol to oil, type of alcohol, type and amount of catalysts, reaction time and temperature of reactants. In this reaction studies, two types of variables affecting the transesterification reaction are studied. They are the effect of loading LiNO₃ (wt %), and effect of the temperature on the reaction.

4.1 THE CATALYST CHARACTERIZATION

4.1.1 THERMAL GRAVIMETRIC ANALYSIS (TGA)

TGA/DTA curves of LiNO₃/Al₂O₃ sample calcined at 450°C are shown in figure 4.1. In figure 4.1, an endothermic peak is observed at 50°C with 8.256% weight loss, attributed to dehydration of the sample. The slight endothermic peak at 200 to 400°Cbecause to melting point of LiNO₃ is observed at 250°C. When the material is calcined at 450°C, it is amorphous and absorbs large quantity of water before thermal analysis. The endothermic peak at 410°C with 33.82% weight loss is attributed to thermal decomposition of LiNO₃. At 640°C, the last endothermic peak, with 31% weight loss, it is related to oxide formation.

When the temperature of 40 to 100° C is the sufficient to run any process because weight loss happen. In this research, temperature for transesterification process of 40 to 60° C and the catalyst can use for this process.



Figure 4.1: TGA/DTA curves of powder by LiNO₃/Al₂O₃ sample.

DTA analysis reveals the evolution of an exothermic peak at 600°C, indicating the rapid decomposition of LiNO₃ and formation oxide. The remaining compounds transform in the temperature range 600-700°C by chemical reactions. The observed exothermic peak is thus representing the possible reaction between LiNO₃ and Al₂O₃ forming the final compound α -LiAlO₂.

4.1.2 FTIR ANALYSIS

FTIR spectroscopy is a powerful tool for identifying the nature bonding and different functional groups present in a sample by monitoring the vibration energy levels of molecules, which are essentially the fingerprint of different molecules. The FTIR spectra of pure Lithium Nitrate (LiNO₃), Aluminium Oxide (Al₂O₃) and sample are shown in figure 4.2, 4.3a, b and c, and 4.4 respectively.

From FTIR spectra in figure 4.2, the spectra showed nitrate group peaks stretching vibration Li-O bond at 1255.70 -1266.02 cm⁻¹ and Li-H bond at 853.13-998.05 cm⁻¹. Only one group peaks bonding vibration at 2444.35- 3154.78 cm⁻¹. This may be due to the improper vibration of the nitrate anion as a result of the change in lattice parameters and point lattice of unit-cell of LiNO₃ as mentioned earlier.



Figure 4.2: FTIR spectra pure Lithium Nitrate (LiNO₃)

Figure 4.3a, b and c show sample loading $LiNO_3$ support Al_2O_3 was observed that the band of the nitrate group was follow in range from those of pure $LiNO_3$. All sample show more group peak $LiNO_3$ from Al_2O_3 . Table 4.1 show group peaks in three samples.

Table 4.1: Group and Vibration Peaks sample Loading LiNO3: (a) 5 wt%, (b) 10 wt%,(c) 15 wt%

Sample	Group Peak (cm ⁻¹)	Bond	Vibration Peak
a	690.32- 851.83	Li-H	Bending
	1265.16	Li-O	Bending
	2989.91	Al-H	Stretching
	2407.83-3067.08	Li-H	Bending
	3268.57-3449.52	Al-H	Stretching
b	667.12-880.33	Li-H	Bending
	1034.41-1081.43	Al-N	Bending
	1266.67-1278	Li-O	Stretching
	2401.89-3010.87	Li-H	Bending
	2946.54-2997.36	Al-H	Stretching
С	677.22-869.44	Li-H	Bending
	1263.48	Li-O	Stretching
	2556.53-2950.01	Al-H	Bending
	2401.72-3275.08	Li-H	Stretching
	3484.39	Al-H	Stretching



Figure 4.3: FTIR spectra sample loading LiNO₃, a) 15%, b) 10%, c) 15%



Figure 4.4: FTIR spectra pure Al₂O₃

From figure 4.4, the spectra showed stretching vibration on Al-H bond at 2913.17 cm⁻¹, 3409.41-3468.85 cm⁻¹ and 975.61-992.20 cm⁻¹. These medium bonds at 1013.41-1183.57 cm⁻¹ were assigned to Al-O bending vibrations (Chatterjee et. al, 2003) in the crystalline α -LiAlO₂ formed in this sample.

4.1.3 X-Ray Diffraction (XRD) Analysis

Figure 4.5 shows XRD spectra of prepared composite samples. Pure LiNO₃ peaks at 2-theta of 25°, 35°, and 43°. The broadening of peaks and disappearance of LiNO₃ peaks at 2-theta of 60.5° and 67° indicated the formation of the amorphous phase in sample 15 wt% LiNO₃. A similar observation has been reported by Uvarov et al. (1996). This phase was expected to form at the LiNO₃-Al₂O₃ crystalline phases. For the sample 15 wt% LiNO₃, appearance of new LiNO₃ peaks were observed at 2-theta of 26°, 30° and 69°. This peak intensity is too low for sample 5 wt% LiNO₃. This corresponded to the formation of this new type of point lattice of LiNO₃ unit cell. The intensity of these peaks increased from the samples with all samples (25°, 35° and 43°). The crystal structure for pure LiNO₃ peaks is hexagonal in shape. The hexagonal unit-cell has parameters of a=b=3.921675 and c= 6.661892, and its cell angel are 90°, 90° and 120° for α , β and γ , respectively as in table 4.2. It was observed that for samples 15 wt% LiNO₃, the unit-cell parameters have changed to a=b=4.147000 and c= 5.283000 with a base centred on opposite cells and to the corners of the unit cell (Jayaraman and Thompson, 2010).

In this new type of point lattice, a large number of lithium atoms were arranged on the surface of the crystal. This led to a greater possibility of free Li⁺ ions formation when Al₂O₃ particles were dispersed in these samples. The spectrum all sample exhibited crystalline Al₂O₃ peaks indicating the presence of totally amorphous LiNO₃ in the samples. Trace of crystalline α -LiAlO₂ were also formed in the sample prepared as indicated by weak peaks at 2-theta of 15°, 21°, 41°, 52° and 65° as shown figure 4.5. The peaks were detected in the spectrum of sample 15 wt% LiNO₃ but some peaks were also observed in those of samples with 5 and 10 wt% LiNO3. The transformation of the interaction in the samples can be represented by the following route (Kwon et al, 1997):

Lithium nitrate + alumina \longrightarrow amorphous + α -LiAlO₂

Sample	a(ang)	b(ang)	c(ang)	α	β	γ	Point lattices
5 wt%	3.921675	3.921675	6.66189	90°	90°	120°	Body centred cell
10 wt%	3.921675	3.921675	6.66189	90°	90°	120°	Body centred cell
15 wt%	4.147000	4.147000	5.28300	90°	90°	120°	Base centred cell

Table 4.2: Lattice parameters of the hexagonal phase of LiNO₃



Figure 4.5: XRD patterns of LiNO₃/Al₂O₃ catalyst at loading LiNO₃: 5 wt %(a), 10 wt%(b), and 15 wt%(c). (Symbols: () LiNO₃, () Al₂O₃ and () α -LiAlO₂.

4.2.1 EFFECT OF REACTION TIME

As shown in Figure 4.6, trend of reaction time on oil conversion. The operating conditions for effect of reaction time; molar ratio methanol/oil: 6.5, reaction temperature: 60°C, LiNO₃ loading amount: 10 wt%.

From Figure 4.6 show there are upward trend with the increasing time. The conversion could achieve at amount of 58 % in first hours. In 3rd hours, the conversion increased to 93 %, it is the higher conversion in the effect of reaction time. After 3rd hours the conversion remained nearly constant as a result of near-equilibrium conversion. It can be concluded that the conversion slightly increases as the effect reaction time increases. According to Ma and Hanna (1999), conversion increases with reaction time. It can be concluded that reaction time is also a controlling factor of product yield and extending the reaction time has a positive effect on the product yield in term of heterogeneous catalytic transesterification.



Figure 4.6: Effect of reaction for optimum time on Transesterification of palm oil. Reaction condition: methanol/oil molar ratio=6.5, reaction temperature= 65°C, LiNO₃ loading amount= 10 wt%.

Ma (1998) studied the effect of reaction time on the transesterification of beef tallow with methanol. His reported that the reaction is very slow during first minute due to the mixing and dispersion of methanol into beef tallow but from one to five minutes, the reaction proceeded very fast.

In conclusion the optimum suitable reaction time in 3 hours for transesterification process at optimum condition; methanol/oil molar ratio 6.5, reaction temperature at 60° C and LiNO₃ loading amount; 10 wt% in conversion 93 %.

4.2.2 EFFECT OF LITHIUM NITRATE (LiNO₃) LOADING ON ALUMINIUM OXIDE (Al₂O₃)

The effect of wt% LiNO₃ loading on the conversion of biodiesel was studied. The LiNO₃/Al₂O₃ catalysts were prepared by varying the loading amount of LiNO₃ from 5 to 15 wt % and were used to catalyze the transesterification reaction. Three experimental run done in this study by using three different LiNO₃ loading on Al₂O₃ and the conversions had been determined. The operating condition; methanol/oil molar ratio 6.5, reaction temperature= 60° C, and reaction time= 5 hours.



Figure 4.7: Effect of different amount of LiNO₃ loading amount on transesterification process. Reaction condition; methanol/oil molar ratio 6.5:1, reaction temperature= 60°C, reaction time= 5 hours.

Figure 4.7 show three different loading LiNO₃ amount and three different result conversion of biodiesel. Loading LiNO₃ at 10 wt% provides the highest content of conversion to 93%. In comparison with 5 wt% and 15 wt% of LiNO₃ loading, the loading give the lower conversion content. The conversion of 83 % was obtained if 15 wt% and 54% was obtained if 5 wt% of loading LiNO₃ amount supported on Al₂O₃. The potential performance occurs may be due to the good formation of strong basic sites on the catalyst therefore soap formation did not occur in the product of biodiesel (Istadi et al, 2010).

After 3 hours, conversion decreases all samples because 3 hours of reaction time is sufficient to purity the biodiesel product. The parent of alumina is slight acidic and when the amount of LiNO₃ is loaded, the catalyst basically is increased. However, when the loaded LiNO₃ is over 10 wt%, the conversion is decreased which may be due to the LiNO₃ cannot be well dispersed on alumina support. The excess LiNO₃ loading could cover the basic sites on the surface of composite and cause a lowered catalytis activity. Therefore, it seems that the catalytis activity is proportional to the amount of decomposed LiNO₃ instead of the total loading amount of LiNO₃ (Chen et al, 2006).

In conclusion the optimum suitable loading LiNO₃ amount is 10 wt% for transesterification process at optimum condition; methanol/oil molar ratio 6.5, reaction temperature at 60° C and reaction time in 3 hours on conversion 93 %.

4.2.3 EFFECT OF REACTION TEMPERATURE (^OC)

The second parameter studied is the effect of reaction temperature. Three experimental run are done by using during three different temperatures in range 40-60°C and the conversions have been determined. The operating condition; methanol/oil molar ratio 6.5, reaction time 5 hours and LiNO₃ loading amount is 10 wt%.

Figure 4.8 shows three different effect of reaction temperature at 40°C, 50°C and 60°C. Temperature at 60°C provides the highest conversion of biodiesel to 92.53 % in 3 hours. Compare other temperature at 40 and 50°C, the highest conversion of biodiesel is 45.4% and 75.03% in 3 hours. After 3 hours, conversion decreases all sample as if purity of biodiesel in 3 hours.

The reaction studies are done in a water bath to have a uniform heat transfer with high temperature. A normal heating can only reach about 60° C of reaction temperature for this transesterification process. For temperature at40°C are the lowest conversion between three different temperatures. This is because the temperature is too low and not enough to make the oil miscible in methanol thus causes a slower rate of transesterification. From the effect of temperature variable, it shows that T= 60° C is the best temperature to perform transesterification process.



Figure 4.8: Effect of reaction temperature (^OC). Reaction conditions; methanol/oil molar ratio 6.5:1, LiNO₃ loading= 10 wt%, reaction time= 5 hours.

From previous studies by Shakhashiri (1989), the optimum reaction temperature was found to be 60°C. The reason being was 60°C is just slightly below the boiling point of methanol 64.7°C. Hence at temperature higher than 64.7°C, methanol evaporates and causes lower yield obtained at reaction temperature after 70°C.

Temperature higher than 50°C had a negative impact on the product yield for neat oil, but had a positive effect for waste oil with higher viscosities. While in this higher reaction temperature shows negative effect and show lower of crude biodiesel and conversion of FFA to FAME. However in order to reduce the energy consumed, lower temperature should applied (Leung and Guo, 2006).

In conclusion the optimum suitable reaction temperature at 60° C for transesterification process at optimum condition; methanol/oil molar ratio 6.5, reaction time in 3 hours and LiNO₃ loading amount; 10 wt% in conversion 92.53 %.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

The heterogeneously catalyzed transesterification of palm oil was studied using Aluminium Oxide support alkali earth metal oxides, prepared through the conventional impregnation method and the optimum operating condition has been determined.

Composite solid electrolytes with high conductivity values in the system $LiNO_3/Al_2O_3$ had been successfully synthesized. The thermal analysis showed that the weight loss the catalyst and sufficient the catalyst for transesterification process. The XRD pattern revealed that the composite consists of both crystalline and amorphous phases of LiNO₃, crystalline Al₂O₃ phase and traces crystalline α -LiAlO₂. The presence of these phases was further confirmed by the FTIR results. The results of XRD analyses indicated that a new type of point lattice of base centred cell was formed for composite sample 15 wt% loading LiNO₃ due to the presence of nanosized particles. The prepared composite samples posse's high ionic conductivities at room temperature and elevated temperatures on account of the formations of a new type of point lattice of hexagonal unit-cell of LiNO₃ and the formation of both amorphous and crystalline phases.

By transesterification process, it shows that 10 wt% loading lithium nitrate has the highest conversion of biodiesel. The potential performance occurs may be due to the good formation of strong basic sites on the catalyst therefore soap formation did not occur in the product of methyl ester. The conversion obtained is 93 %. From second parameter studied by temperature variable and temperature at 60°C produced highest conversion of 92.53%.

The suitable conditions for the transesterification of palm oil with methanol/oil ratio 6.5, temperature 60°C, and reaction time are 3 hours and loading lithium nitrate 10wt%, respectively in conversion of 93 %.

5.2 RECOMMENDATION

Using Aluminium oxide as the support catalyst is more benefit in transesterification process rather than using homogenous not supports catalyst such as lithium nitrate. However, these homogeneous catalysis systems have many drawbacks. Removal of the catalysts to purify the biodiesel fuel and glycerol by-product is difficult and requires a large amount ofwater. Consequently, a considerable amount of wastewater is inevitably produced. To overcome these problems, the transesterification over environmentally benign solid catalysts is a promising route. In order to determine the capabilities of heterogeneous acid catalyst, it is recommended researcher should consider the study of catalyst in transesterification process.

There are many types of variables parameters affecting the production of transesterification process such as catalyst amount, molar ratio alcohol/oil, mixing intensity and effect of using ultrasonic bath. It is recommended that these other parameter to be tested in the study of transesterification process.

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APPENDIX A

EXPERIMENTAL DIAGRAM



Figure A.1: Experimental setup for batch reactor system.



Figure A.2: Samples catalyst taken after the reaction study.



Figure A.3: Samples taken after the reaction study.

APPENDIX B

Calculation of Methyl Ester Conversion

From calibration curve,

For Methyl Palmitate	y = 0.061x
For Methyl Oleate	y = 0.182x
For Methyl Linoleate	y = 0.127x

Amount of methyl ester in palm oil:

Methyl Ester	Percentages in palm oil
Methyl Palmitate	44%
Methyl Oleate	39.2%
Methyl Linoleate	10.1%

Calculation for initial concentration, C_{FAo} :

Detail	
Concentration of oil	800 kg/m ³
Volume of oil at sample	150 ml
Volume of methanol at sample	60 ml

$\mathbf{W}_{\mathrm{oil}}$	$= 800 \text{ kg/m}^3 \text{ x } 100 \text{ x} 10^{-3} \text{ x } 10^{-3} \text{ m}^3$
	= 0.08 kg
Wmethyl palmitate	= 0.08 kg x 0.44
	= 0.0352 kg
W _{methyl oleate}	= 0.08 kg x 0.392
	= 0.03136
W _{methyl} linoleate	= 0.08 kg x 0.101
	= 0.00808 kg
C _{FAo}	$= W_{methyl \ palmitate} + W_{methyl \ oleate} + W_{methyl \ linoleate}$
	Volume of oil + Volume of methanol
	= 0.0352 kg + 0.03136 kg + 0.00808 kg
	128.6 ml
	$= 5.804 \text{x} 10^{-4} \text{ kg/ml}$

 $= 580.40 \ \mu g/\mu l$

Sample calculation for conversion:

Area and concentration obtained from GC analysis for effect of reaction time at 60 minutes:

Sample	Area	Concentration
Methyl palmitate	34.14	563.47
Methyl oleate	94.60	504.97
Methyl linoleate	10.99	150.28

W _{sample}	= Concentration of sample x Volume of vessel
Wmethyl palmitate	= 563.47µg/µl x 2µl
	= 1126.94µg
W _{methyl oleate}	= 504.97µg/µl x 2µl
	$= 1009.94 \mu g$
Wmethyl linoleate	= 150.28µg/µl x 2µl
	= 300.56µg

Final concentration, C_{FA}:

 C_{FA}

 $= \mathbf{W}_{methyl \ palmitate} + \mathbf{W}_{methyl \ oleate} + \mathbf{W}_{methyl \ linoleate}$

Volume of stock sample

 $= 1126.94 \mu g + 1009.\ 94 \mu g + 300.56 \mu g$

10 µl

 $= 243.768 \mu g/\mu l$

To calculate conversion:

 \mathbf{X}_{FA}

$$= C_{FAo} - C_{FA} \times 100$$

$$C_{FAo}$$

$$= (580.40 \mu g/\mu l - 243.77 \mu g/\mu l) \times 100\%$$

 $580.40~\mu\text{g/}\mu\text{l}$

= 58.00%

APPENDIX C

Data of Methyl Ester Conversion

Data for the effect of reaction time:

Table C.1: Effect at 60 minutes.

Sample	Area	Concentration
Methyl palmitate	34.14	563.47
Methyl oleate	94.60	504.97
Methyl linoleate	10.99	150.28

 Table C.2: Effect at 180 minutes.

Sample 2	Area	Concentration
Methyl palmitate	63.25	1033.03
Methyl oleate	170.34	925.77
Methyl linoleate	27.40	275.52

Table C.3: Effect at 300 minutes.

Sample 2	Area	Concentration
Methyl palmitate	63.66	1039.74
Methyl oleate	171.42	931.78
Methyl linoleate	27.63	277.31

 Table C.4: Final effect of reaction time.

Sample	Final concentration	Conversion	Time (minutes)
1	243.77	58	60
2	446.91	93	180
3	449.81	93.5	300

Data for the effect of loading LiNO₃

Table C.5: Effect of 5 wt%.

For methyl palmitate:

Sample	Area	Concentration	Time (minutes)
1	54.10	885.45	60
2	70.73	1153.77	180
3	65.74	1073.28	300

For methyl oleate:

Sample	Area	Concentration	Time (minutes)
1	146.53	793.52	60
2	189.82	1033.98	180
3	176.83	961.84	300

For methyl linoleate:

Sample	Area	Concentration	Time (minutes)
1	22.24	236.16	60
2	31.61	307.72	180
3	28.80	286.25	300
3	28.80	286.25	300

Final effect of 5 wt%:

Sample	Final concentration	Conversion	Time (minutes)
1	383.06	34.00	60
2	266.98	54.00	180
3	301,81	48.00	300

Table C.6: Effect of 10 wt%.

For methyl palmitate:

Sample	Area	Concentration	Time (minutes)
1	28.31	469.56	60
2	51.60	845.20	180
3	48.28	791.54	300

For methyl oleate:

Sample	Area	Concentration	Time (minutes)
1	79.44	420.80	60
2	140.04	757.45	180
3	131.38	709.36	300

For methyl linoleate:

Sample	Area	Concentration	Time (minutes)
1	7 71	125.24	60
1	/./1	123.24	
2	20.83	225.42	180
3	18.96	211.11	300

Final effect of 10 wt%:

Sample	Final concentration	Conversion	Time (minutes)
1	203.14	65.00	60
2	40.63	93.00	180
3	63.84	89.00	300

Table C.7: Effect of 15 wt%.

For methyl palmitate:

Sample	Area	Concentration	Time (minutes)
1	35.80	590.30	60
2	58.26	952.53	180
3	49.11	804.96	300

For methyl oleate:

Sample	Area	Concentration	Time (minutes)
1	98.92	529.01	60
2	157.35	853.63	180
3	133.55	721.38	300

For methyl linoleate:

Sample	Area	Concentration	Time (minutes)
1	11.92	157.44	60
2	24.58	254.05	180
3	19.42	214.69	300

Final effect of 15 wt%:

Sample	Final concentration	Conversion	Time (minutes)
1	255.34	56.00	60
2	98.67	83.00	180
3	162.51	72.00	300

Data for the effect of temperature

Table C.8: Effect at 40°C.

For methyl palmitate:

Sample	Area	Concentration	Time (minutes)
1	60.29	985.40	60
2	75.97	1238.30	180
3	74.30	1211.33	300

For methyl oleate:

Sample	Area	Concentration	Time (minutes)
1	162.66	883.09	60
2	203.45	1109.72	180
3	199.10	1085.56	300

For methyl linoleate:

Sample	Area	Concentration	Time (minutes)
1	25.73	262.82	60
2	34.56	330.26	180
3	33.62	323.07	300
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Final effect at 40°C:

Sample	Final concentration	Conversion	Time (minutes)
1	426.30	26.55	60
2	316.90	45.40	180
3	328.56	43.39	300

Table C.9: Effect at 50°C.

Final effect at 50°C:

Sample	Final concentration	Conversion	Time (minutes)
1	330.54	43.05	60
2	144.93	75.03	180
3	158.57	72.68	300

Table C.10: Effect at 60°C.

Sample	Final concentration	Conversion	Time (minutes)
1	201.81	65.23	60
2	43.36	92.53	180
3	59.96	89.67	300

Final effect at 60°C:

APPENDIX D

DATA FROM GAS CHROMATOGRAPHY ANALYSIS



Figure D.1: Data for sample 1 for standard curve 500 ug/ml



Figure D.2: Data for sample 2 for standard curve 1000 ug/ml



Figure D.3: Data for sample 3 for standard curve 1500 ug/ml



Figure D.4: Data for sample 4 for standard curve 2000 ug/ml



Figure D.5: Data for sample 5 for standard curve 2500 ug/ml



Figure D.6: Data for sample 6 for effect of 5 wt% loading LiNO₃



Figure D.7: Data for sample 7 for effect of 10 wt% loading LiNO₃



Figure D.8: Data for sample 8 for effect of 15 wt% loading LiNO₃



Figure D.9: Data for sample 9 for effect at 40°C.



Figure D.10: Data for sample 10 for effect at 50°C.



Figure D.11: Data for sample 11 for effect at 60°C.

APPENDIX E

Table E.1: Typical IR Absorption Frequencies for Common Functional Groups

Bond	Functional Group	Frequency in cm ⁻¹ (Intensity*)
С-Н	Alkane	3000-2850 (s)
	-CH ₃	1450 and 1375 (m)
	-CH ₂ .	1465 (m)
	Alkene	3100-3000 (m), 1000-650 (s)
	Aromatic	3100-3050 (s), 900-690 (s)
	Alkyne (terminal)	3300 (s)
	Aldehyde	2850 and 2750 (w)
C=C	Alkene	1630 (w-m)
	Aromatic	1600-1475 (w-m)
C-C	Alkyne	2150-2100 (w-m)
C=O	Aldehyde	1740-1720 (s)
	Ketone	1725-1705 (s)
	Carboxylic Acid	1730-1700 (s)
	Ester	1750-1730 (s)
	Amide	1670-1640 (s)
	Anhydride	1810 and 1760 (s)
	Acid Chloride	1800 (s)
C-0	Alcohol, Ether, Ester, Carboxylic Acid, Anhydride	1300-1000 (s)
О-Н	Alcohol, Phenol	

	Free	3650-3600 (m)
	Hydrogen-bonded	3500-3200 (m)
	Carboxylic Acids	3300-2400 (m)
N-H	Primary and Secondary Amine and Amide	3550-3060 (m-s); 1640-1550 (m-s)
C-N	Amine	1250-1000 (m-s)
C=N	Imine and Oxime	1690-1640 (w-s)
C=N	Nitrile	2260-2240 (m)
N=O	Nitro (R-NO ₂)	1550 and 1350 (s)
C-Cl	Chloride	800-600 (s)

s = strong; m = medium; w = weak