KINETICS OF BIOLUBRICANT SYNTHESIS FROM *JATROPHA CURCAS* OIL USING *Paphia undulata* AS A SOLID CATALYST

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Thesis submitted in fulfillment of the requirements
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Dedication

To my beloved parents, Misebah bin Sanjan and Lilnajipa bt Asngari,

To my beloved husband, Amir Asri bin Al-Kharid

To my beloved son, Umar Adlan bin Amir Asri

families, and friends,

who gave me everlasting inspiration, never ending encouragements

and priceless support towards the success of this research

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In the name of God, the most gracious and the most merciful.

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ABSTRAK

Pada masa kini, pertambahan permintaan untuk kegunaan industri menyebabkan kesedaran bagi mendapatkan sumber yang boleh diperbaharui untuk minyak pelincir semakin berkembang disamping penurunan bekalan petroleum dunia dan ketidaktentuan bekalan petroleum telah meransang bagi mendapatkan sumber minyak pelincir yang mesra alam sebagai bahan alternative. Sehubungan itu, penyelidikan telah dilakukan mengunakan minyak *Jatropha curcas* untuk menghasikan minyak pelincir bio sebagai bahan gantian baru dengan menggunakan kalsium oksida yang diperolehi dari kulit *Papia undulata* sebagai bahan pemangkin. Tambahan lagi, penyelidikan ini telah bermatlamat untuk mengkaji tindakbalas kinetik untuk transesterifikasi minyak *Jatropha curcas* untuk penghasilan minyak pelincir bio. Langkah pertama dalam kaedah kajian ini ialah proses pengesteran asid lemak bebas (FFA) dalam minyak *Jatropha curcas* dan menghasilkan minyak Jatropha curcas metil ester (JCOME). Ini diikuti dengan sintesis minyak pelincir bio daripada pengolahan JCOME dengan TMP dan menilai proses optimum. Produk akhir telah di analisis menggunakan gas chromatography mass spectorophotometer (GCMS) untuk JCOME dan gas chromatography with Flame Ionization Detector (GC-FID) untuk minyak pelincir bio. Tindakbalas optimum untuk penghasilan JCOME telah ditemui pada ratio 6 mol metanol kepada 1 mol minyak, 4 wt% jumlah pemangkin, suhu 60°C dan 3 jam tindakblas dengan jumlah produk tertinggi iaitu 93.33%. Sementara itu, keadaan optimum bagi penghasilan minyak pelincir *Jatropha* ditemui pada suhu 110^0C,3 jam, ratio 4:1 JCOME:TMP dan 3wt% jumlah pemangkin dengan 96.66% penukaran TMP dan 78.67wt% triester (TE) composition. Tindak balas ini telah dikenalpati sesuai dengan kinetik model peringkat dua dengan keseluruhan kadar malar 0.0427 (%w/w min °C)$^{-1}$ dan 2.2kJ/mol tenaga pengatifan.

ABSTRACT

Nowadays, there is growing concern in looking for a renewable source of lubricant due to increasing demand for industrial applications besides depletion of world petroleum resource with uncertainty in petroleum supply has stimulated the search for biolubricants as an environmental friendly alternative source. Therefore, the research has been done using *Jatropha curcas* oil for biolubricant as new source over derived calcium oxide from *Papia undulata* shell as a solid catalyst. In addition, the research aims to determine the kinetic reaction for transesterification of *Jatropha curcas* oil on biolubricant yield. The first step in the research method was esterification process of free fatty acid (FFA) in *Jatropha curcas* oil, for reduction of the free fatty acid value and production of *Jatropha curcas* oil metyl ester (JCOME). This was followed by the synthesis of lubricant from blending JCOME with TMP by evaluating the process conditions. The final products were analyzed using gas chromatography mass spectorophotometer (GCMS) for JCOME production and gas chromatography with Flame Ionization Detector (GC-FID) for *Jatropha* biolubricant production. The optimum reaction for JCOME production was found to be at methanol/oil ratio of 6:1, catalyst amount of 4 wt.%, temperature of 60 ^{o}C and reaction time of 3 hours with the highest yield being 93.33%. Meanwhile *Jatropha* biolubricant optimum conditions were at 110 ^{0}C, 3 h, 4:1 of JME: TMP and 3% w/w of catalyst with 96.66% of TMP conversion and 78.67% of TE composition. The reaction was determined to fit the second order kinetics model with overall rate constant of 0.0427 (%w/w min °C)$^{-1}$ and activation energy of 2.2 kJ/mol.

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LIST OF SYMBOLS

%	Percent
cm	Centimeter
Cst	Centistokes
^{o}C	Degree Celsius
Ea	Activation Energy
g/L	Gram per Litre
g	Gram
hr	Hour
k	Rate of reaction
K	Kelvin
kJ/mol	Kilo joule per mol
L	Liter
M	Methanol
ml	Mililiter
min	Minute
mg/L	Milligram per Litre
ml	Mililitre
m	Meter
nm	Nanometer
sec	Second
R	Gas constant
rpm	Revolutions per minute
T	Temperature
wt %	Weight percent

LIST OF ABBREVIATIONS

ASTM	American Standard Testing Materials
BET	Brunauer-Emmett-Teller
Conc	Concentration
DE	Diester
DTA-TGA	Differential Thermal and thermo-gravimetric
EN	European Standard
FESEM	Field Emission Scanning Electron Microscopy (FESEM)
FFA	Free Fatty Acid
FTIR	Fourier Transformed Infra Red
IR	Infrared
JCOME	*Jatropha curcas* oil methyl ester
JCO	*Jatropha curcas* oil
ME	Monoester
RSM	Response surface methodology
SEM	Scanning Electron Microscopy
TE	Triester
TMP	Trimethylolpropane
VI	Viscosity Index
XRF	X-Ray Fluorescence spectrometry
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

Background of study

The most commonly used raw material for lubricant production is petroleum oil, as it is readily accessible for fulfilling the global demand for lubricants. Besides that, petroleum-based lubricant has the longest operating life of the different types of lubricant, and is able to lower the downtime of the machine (Akerman *et al.*, 2011). Most modern lubricants are complex formulated products consisting of 70–90% base oils mixed with functional additives to modify their natural properties such as cold stability, oxidation stability, hydrolytic stability, viscosity and viscosity index to suit a specific application (Derawi and Salimon, 2013). Unfortunately, due to the increased demand for lubricants, there is a growing concern in looking for a renewable source of lubricants (Bokade and Yadav, 2007).

Biofuels and biolubricants have gained interest due to both coming from renewable resources which help in reducing dependency on petroleum based oil in existing vehicles and their low greenhouse gas emission that help reduction of carbon dioxide (CO_2) emission to the environment. In this scenario, vegetables oils have gained popularity as lubricants over the last couple of decades, and are more efficient due their excellent properties and being environmentally friendly (Salih *et al*., 2010; Chang *et al.*, 2012; Li *et al.*, 2012).

Biobased lubricant has been shown to be an attractive alternative source because of its superior tribiological properties compared to mineral oils based lubricant (Salih *et al*., 2013; Yunus *et al.*, 2004). Vegetables oil that can be used for production lubricant has a high lubricity far superior to mineral oil lubricant, which has been shown to have a much lower coefficient of friction when used. Besides that, vegetables oil has a high flash point at about 326 °C compared to 200 °C for mineral oil, thus allowing it to operate in a high temperature environment, in addition to having a very high viscosity index (VI) at about 223, compared to mineral oil based lubricant at 90 to 100 (Chauhan, 2015). This shows that biobased lubricant can be used over a large range of temperatures (Josh, 2012). Last but not least, biobased lubricant is generally derived from natural resources, resulting in clean processing and being easy disposal, as they are non-toxic and biodegradable (Salimon *et al.*, 2010). Biobased lubricant also displayed superior performance compared to mineral oils in terms of anti-wear and fatigue resistance (Salimon and Ishak, 2012).

In Malaysia, development of renewable energy resources has become favorable due to fulfill domestic demand and instability in worldwide petroleum prices (Chong *et al.*, 2015). Furthermore, negative impact to the environment generated by the worldwide utilization of fossil fuels has grabbed attention from researchers for further study. This makes a strong reason for research on biobased lubricant as a renewable product that is friendly to the environment. In recent years, research on *Jatropha curcas* oil, a non-edible oil available in Malaysia, has become favorable as the most suitable raw material for biolubricant production (Arbain and Salimon, 2010).

Problem statement

Nowadays, millions of tons of lubricant are dumped into the environment through leakage from machines or vehicles, as well as careless disposal methods of wastes, some of which are not biodegradable. Besides the contribution of petroleum based lubricant usage to environmental pollution, there is also a depletion of supply within a few more decades. Thus, there is a pressing need to find lubricants from renewable resources that are biodegradable and clean in the environment with useful physical properties.

Besides that, several factors have been identified that contribute to the economical usage of biobased lubricant in the industry, among them is the high cost of raw materials. Previous study has reported that production of biobased lubricant from food based crops is widely used by researchers such as soybean seed, canola oil, rape seed and sunflower. This scenario has led to an issue in the global food supply due to the usage of raw materials that could disturb the human food chain. Thus, there is a pressing need to solve the problem by producing biolubricant at a low cost. *Jatropha curcas* oil is a source of non-edible oil that is available in Malaysia, and has the potential to be widely used in numerous industries such as the production of biofuels, surface coatings (resins) and low-cost soap. Nowadays, *Jatropha curcas* oil is seen as having great potential for the production of biolubricant.

Catalyst applied during processing biolubricant also becomes another challenge that need to overcome by researcher in biobased lubricant production. Previously, homogeneous acids or bases catalysts for biolubricant production required product neutralization and washing step that yields toxic wastewater (Margaretha et al., 2012). This processing step required proper disposal method to avoid any bad effect to environment. Therefore, solid catalysts get attention to be applied in biolubricant production. Previous study shows that snails shell has potential to be used as heterogeneous catalyst for transesterification process (Birla *et al*., 2011). Thus, *Paphia undulata* shell waste that contribute problem to seafood industry in manage their waste has potential to be utilized into valuable solid catalyst .

1.3 Objectives of Research

1. To develop and characterize the catalyst derived from *Paphia undulta* shell for *Jatropha curcas* oil methyl ester (JCOME) and biolubricant production.
2. To investigate of *Jatropha curcas* oil methyl ester (JCOME) production via two processing step (acid pretreatment and transesterification).
3. To study of biolubricant synthesis from *Jatropha curcas* oil methyl ester (JCOME).
4. To determine the kinetics of transesterification of *Jatropha curcas* oil to biolubricant.

1.4 Scope of Research

1. To synthesize and characterize *Paphia undulata* shell as a solid catalyst for production of *Jatropha curcas* oil methyl ester (JCOME) and biolubricant.
2. To evaluate the effect of catalyst concentration (0 to 2 w/w%), methanol to oil molar ratio (3:1 to 7:1 mol:mol), time (0 to 60 minutes) on free fatty acid (FFA) yield.
3. To investigate the effect of reaction time (1 to 5 hours), reaction temperature (30 to 70^0C), amount of catalyst (1 to 5 w/w%), (1:2 to 1:6 mol:mol) on *Jatropha curcas* oil methyl ester (JCOME) yield.
4. To evaluate the effect of reaction time (1 to 5 hours), reaction temperature (90 to 130^0C), amount of catalyst (0 to 4 w/w%) and TMP to JCOME molar ratio (1:1 to 1: 6 mol:mol) on the biolubricant yield.
5. To determine catalyst reuseability on the biolubricant synthesis.
6. To investigate kinetic model of the transestrification reaction in biolubricant production derived from rate law (first and second order) and activation energ using Arrheneius equation.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The purpose of this chapter is to review the previous work and research that has been carried out in relation to biolubricant production. The development and prospects of lubricants and biolubricants are discussed in this chapter. Furthermore, the key components of this research, such as trimethylolpropane (TMP), fatty acid methy ester (FAME) and feedstock avaiablity in Malaysia, are also discussed briefly. Lastly, previous kinetics approaches and physico-chemical properties of biolubricant production are presented in this chapter.

2.2 Lubricant

In 1760, during a period of industrial revolution when heavy industrial iron and steel machinery was widely introduced, there was an increased use of lubricants derived from mineral oil, animal fat such as sperm whale oil and vegetable oil such as palm and groundnut oil (Nie, 2012). Lubricant oil was used due to its ability to decrease the friction between two contacting surfaces by separating the surfaces with a film that resulted in decreasing the efforts and energies of working machines or engines (Force and Salas, 2011). Besides that, lubricant was also used to avoid corrosion on the steel surface component that usually becomes the main problem in machine maintenance (Mobarak *et al.,* 2014). In hydraulic machinery systems, lubricant functions as a power transmitter, like a chain in a mechanical driver (Jain and Suhane, 2013). In addition, lubricant oil also plays a role in controlling the temperature of automotive systems, where it is able to absorb heat produced during interaction between components and send that heat to the cooling system (Wright, 2011).

With the wide applications of lubricant, there was seen an increased demand for it in the industry. Figure 2.1 shows world lubricant market in application area where highest usage of lubricant as engine oils that is 47% compared than process oil and hydraulic oil. Meanwhile Figure 2.2, shows the world lubricant market that the highest world lubricant usage recorded was in the Asia/Pasific, also well known as an engine for global growth, which is by the industrial sector in developed and developing countries such as China, India, Indonesia, Malaysia and Singapore. This high usage of lubricant was followed by North America, Western Europe and the rest of world.

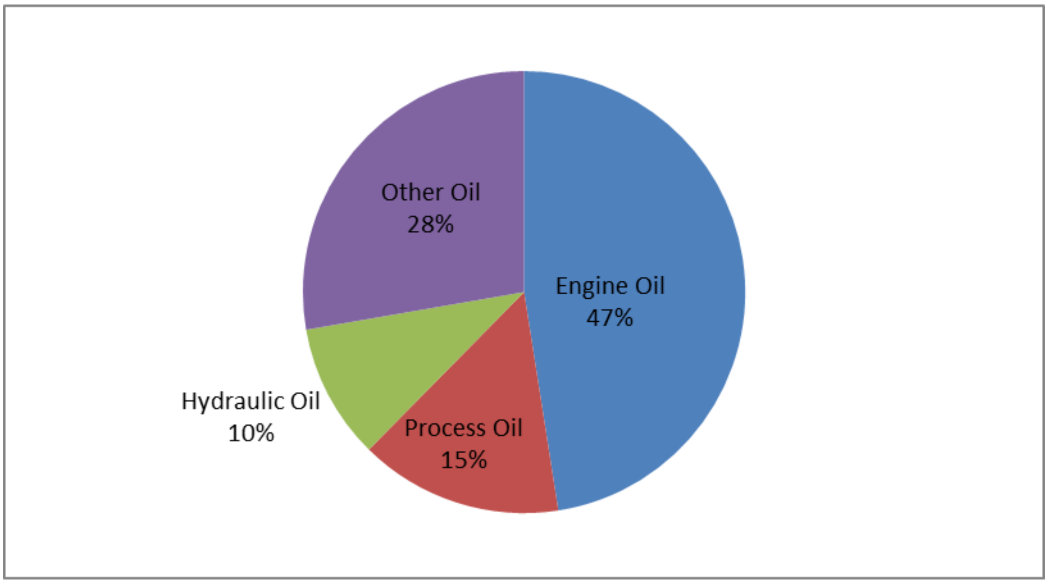


Figure 2.1. Application of lubricant.

Source: Mobarak *et al.*, 2014

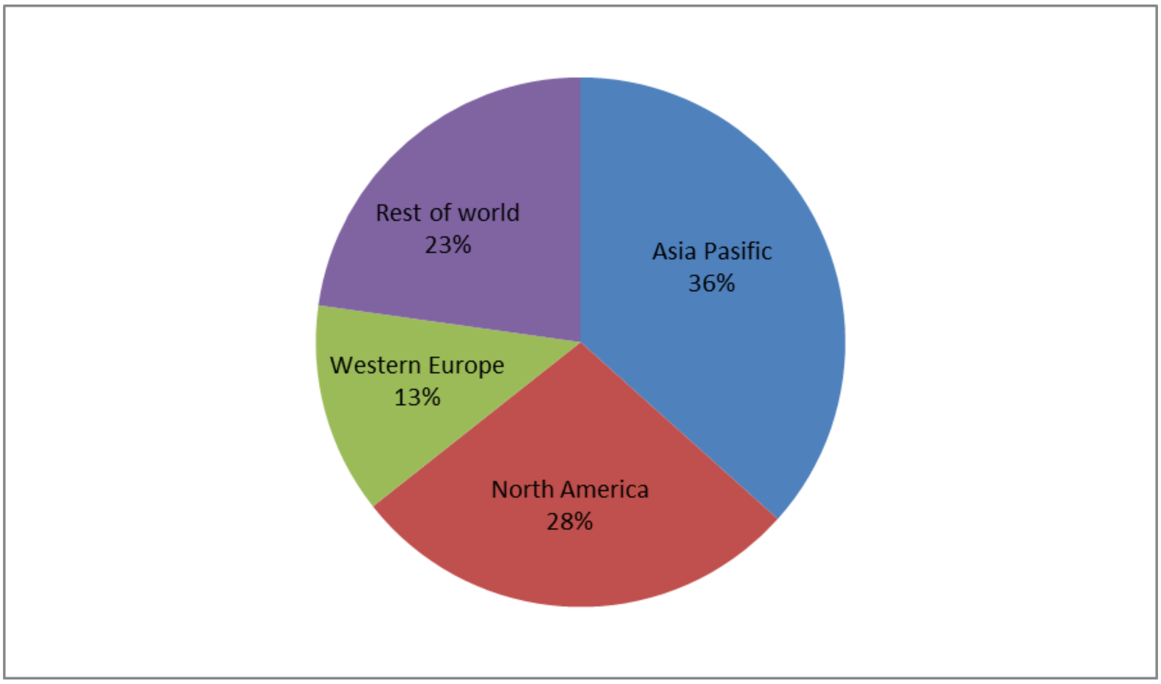


Figure 2.2. World lubricant market.

Source: Mobarak *et al.*, 2014

The increase in demand was aided by the expansion of Motor Vehicle Park and also development of manufacturing and industrial activities (Nagendramma and Kaul, 2012). In addition, it was also expected that global transportation energy consumption would increase by 1.8% per year from 2005 to 2025, and this would contribute to the demand for lubricant (Bilal *et al.*, 2013).

Lubricants can be classified according to their sources, either mineral oil lubricant or plant oil lubricant. Lubricant oil is refined from mineral oil through the process of fractional distillation at high temperature. Meanwhile, plant oil based lubricant originates from blending vegetable oil that contains high fatty acid through the process of esterification or transesterification processs to produce lubricant ester.

2.3 Biolubricant

During the early 19th century, the world was facing the problem of decreasing supply in fossil fuel, leading to the development of renewable and more efficient energy resources (Kulachate and Prachasanti, 2009). Thus, biolubricant production studies were carried out to help the world find another renewable resource for lubricant production to fulfill market demands. Biolubricant is an alternative lubricant that is derived from other than mineral oil resources, such as fatty acid from fats and oil or other natural resources that are biodegradable and renewable (Bremmer and Plonsker, 2008). Adopting biolubricants will overcome the dependency on petroleum for biolubricant production.

On the other hand, lubricant derived from petroleum has contributed to serious environmental problems due to its toxic and non-biodegradable properties. Biodegradable characteristics relate to clean ecological process in which a substance can broken down by enzymatic processes produced by living organisms (Arbain and Salimon, 2010). The fact remains that about 60% of lubricants used in the United States spill out to the environment, leading to water and air pollution (Erhan *et al.*, 2006). Thus, plant-based lubricants have gained a lot of interest from developers of environmentally friendly energy. Moreover, biolubricant tends to reduce contributions to global warming because biolubricant is known as a green energy product in which its usage does not release carbon dioxide and has only a minimum of soot and ash formation (Karzan and Vizintin, 2004). Biolubricant is well known as the perfect biodegradable lubricant that is non-toxic, biodegrades quickly and has non-damaging components (Jean, 2011).

Recently, the trend of using biodegradable and non-toxic hydraulic oil in machinery has grown in certain countries. For example, on June 2005, the United Kingdom Environment Agency made it a policy that all tracked excavators used in work must apply environmentally acceptable hydraulic fluid. In Germany, Europe, Sweden and Netherland, environmentally acceptable lubricants have been successfully applied, including grease, chain saw lubricant, mould releasing agent and other products (Eastwood *et al.*, 2005). Previously, several oils were widely used as raw materials in production of biolubricant such as palm oil, rubber seed oils, canola oils and other plant oils (Yunus *et al.*, 2004; Salimon and Ishak, 2012).

The renewability characteristic of plant oil where it can be produced locally is an advantage over mineral oil (Garces *et al*., 2011). Soybean oil biolubricant is currently available in the market, with wide applications including tractor hydraulic fluid, machinary hyraulic fluid, gear lubes and others (Nagendramma and Kaul, 2012). According to Karzan and Vizintin (2004), the interest in plant sources for lubricant production is not only due to the renewable and sustainable characteristics of biolubricant, but also due to its performance characteristics that are the same or better than mineral oil based lubricant. Commercial lubricants on the market are taken seriously in terms of stability, viscosity, lubrication and temperature range, as all of these lubricant oil characteristics will affect the lifespan of the lubricant oil when applied to machines (Force and Salas, 2011).

Unfortunately, lubricants derived from plants have limitations that have been investigated, and they are lower oxidative stability and poor cold flow behavior (Erhan *et al.*, 2006). Triglycerides from plants oils are limited by containing unsaturated double bonds that promote the oxidation process. Some plant oils contain a high degree of monosaturated fatty acid which tends to cause autoxidation to occur at high temperature and others contain a high amount of polysaturated fatty acid that can cause autooxidation at room temperature (Fox and Stachowiak, 2007).

On the other hand, the limitation of lubricant derived from plant oil due to glycerol, a component of the triglyceride molecule, was easily overcome when exposed to high temperature (Arbain and Salimon, 2011). The presence of hydrogen atoms in β relative in the glycerol molecule results in polymerization, which leads to increased viscosity and precipitation. Thus, there are some solutions to overcome this limitation such as hydrogenation, epoxidation and transesterification of oil. In this case, transesterification of vegetables oil with polyhydric alcohol or polyols will help to minimize the limitations of biolubricant characteristics by the elimination of hydrogen atom from β-carbon of vegetable oil structure (Chang *et al*., 2012).

2.4 Fatty Acid Methyl Ester (FAME)

Nowadays, demand for petroleum products in the industrial and motor sectors has significantly increased. Unfortunately, there will be diminishing fossil fuel supplies within a few years from now. Thus, there is pressing need to find renewable and economical raw materials that are able to fulfill the industrial demands. Biodiesel is known as an alternative and renewable energy for diesel engines that is more biodegradable, non-toxic and has low CO_2 emissions compared to petroleum diesel (Watcharathamrongkul *et al*., 2010). Chemically, it consists of long chains of fatty acid methyl ester that is produced from various vegetable oils (Rashid *et al.*, 2010). Meanwhile, Sharma et al (2010) state that biodiesel is the result of reaction between triglyceride and alcohol in the process of transesterification.

In the transesterification process, vegetable oils react with alcohol in the presence of either acidic or basic catalyst and produce ester that is called fatty acid methyl ester (FAME). The reaction is also known as *methanolysis* when the reaction uses methanol and *ethanolysis* if using ethanol (Roces *et al.,* 2011).

According to Krishnan and Dass (2012), the fluctuating price of biodiesel in the market is due to the raw material used. In a recent study, it was found that vegetables oils such as soybean, rapeseed and sunflower have been used for biodiesel production (Thiruvengadaravi *et al*., 2009). These kinds of oils have raised the issue in which consuming their raw material disturbs the human food chain. Thus, there is pressing need to find other sources for biodiesel production.

Basically, vegetables oil is divided into two types: edible oil, which can be eaten as food such as coconut oil, soyabean, sunflower and peanut, and non-edible oil, which is oil that cannot used as a food source such as Jatropha, castor, karanja oil and others (Jain and Suhane, 2013). Non-edible oil cannot be consumed by humans due to its toxic compounds that can be harmful to humans. Researchers have started to switch their focus from edible oil to non-edible oil as raw material in biodiesel production. Mofijur et al., (2012) state that, *Jatropha curcas* oil produce more than 60% oil rather than other seed such as palm kernel, soybean and other. Abdullah et al., (2013) also reported that Malaysia one of the country that see the potential on *Jatropha curcas* oil as another source that play important role as palm oil but at different industries. Thus, this shows the potential of *Jatropha curcas* oil to be used as raw material in biodiesel and biolubricant production.

Recently, Omotoso et al. (2011) prepared biodiesel from *Jatropha curcas* oil via two processing step with percentage yield 75.3% of biodiesel was obtained. First step was involved acid esterification reaction, in which methanol and 2% w/w sulfuric acid (catalyst) react in 65°C for 5 hours. Acid esterification was required to reduced free fatty acid level of oil for next transesterification process that used an alkali catalyst (Charoenchaitrakool and Thienmethangkoon, 2011). Then second step, involved a base transestericaton reaction where potassium hydroxide (catalyst) react with treated reaction mixture from first step in 65°C for 3 hours. Meanwhile Roces et al. (2011), obtained 92.7% yield of biodiesel from *Jatropha* curcas oil where first step carried out with 1%w/w hydrochloric acid in 70^0C for 2 hours. The second step carried out in 4:1 methanol to oil molar ratio, 1.5% w/w potassium hydroxide, 60^0C temperature for 2 hours reaction time. Thus, this shows that *Jatropha curcas* oil has high potential to be used for biodiesel production with desirable reaction condition.

2.5 *Jatropha* Curcas Oil

Vegetable oils become favorable alternative resources for producing biolubricant because they are renewable and environmentally friendly, as well as have excellent properties as feedstock (Ramadhas *et al.*, 2004). Vegetable oils used as feedstock for biolubricant production are able to alleviate carbon dioxide emission in the atmosphere, which nowadays has become a serious environmental problem. Besides that, lubricant derived from vegetable oils exhibits excellent lubricant properties such as excellent viscosity index and lower volatility compared to petroleum-based or synthetic lubricants (Yunus *et al.*, 2004). Fox and Stachowiak (2007) state that the triglyceride structure of vegetable oils has long, polar fatty acid chains that provide strong interaction between lubricant film with metallic surface, in addition to reducing friction and wear.

Jatropha curcas belongs to the *Euphorbiaceae* family, and is known as *Jarak Pagar* in Malaysia and *Jatropha curcas* fruit was shown in Figure 2.3.

Figure 2.3. *Jatropha curcas* fruit.

It is commonly found in tropical countries and sub-tropical countries in the world such as Malaysia, Indonesia, Hong Kong and India (Singh and Pandi, 2009). *Jatropha curcas* can usually be propagated either by direct seeding, seed planting in a nursery or by cutting. The height of the *Jatropha* tree is about 3.0 m, and it is able to growth in a wide range of soils such as gravel, sandy and clay soil, as well as in low fertility and alkaline soil (Rao and Rao, 2013). Besides that, it is able to tolerate extreme temperature conditions, with an average temperature range of 20 to 28 ^{0}C. In addition, *Jatropha* not only produces useful crude oil but also has valuable by-products such as a nutrient-rich press cake and seed husk that can be used as composting and crop fertilizer as well as feedstock for biogas plants (Wahl *et al*., 2012).

In 2014, the market price of *Jatropha curcas* oil was RM0.50/kg. This price shows its potential for use as raw material in biolubricant production. It was targeted for it to fulfill about 30% the Malaysian lubricant demand of 238 kilo tons of lubricant in the future. It has the potential ability to improve environmental quality performance as well as quality of rural economy (Rao and Rao, 2013). Thus, the availability of *Jatropha curcas* oil as a raw material and the ease of obtaining it without disturbing the human food chain can help to reduce the price of lubricant in the international market.

Jatropha curcas oil has gained interest from researchers for biolubricant production due to its valuable characteristics which are low acidity, high oxidative stability compared with soy bean oil, low viscosity compared with castor oil and better cooling characteristics compared with palm oil (Arbain and Salimon, 2010). *Jatropha curcas* oil has the potential to be used as feedstock in biodiesel and biolubricant production due to its high unsaturated fatty acid contents (Arbain and Salimon, 2010). The composition of fatty acid contained in crude *Jatropha curcas* oil is shown in Table 2.1.

Table 2.1 Fatty acid composition of *Jatropha curcas* oil

Fatty Acid	**Percentage**
Myristic acid (14:0)	0-0.1
Palmitic acid (16:0)	14.1-15.3
Stearic acid (18:0)	3.7-9.8
Arachidic acid (20:0)	0-0.3
Behenic acid (22:0)	0-0.2
Palmitoleic acid (16:1)	0-1.3
Oleic acid (18:1)	34.3-45.8
Linoleic acid (18:2)	29.0-44.2
Linolenic acid (18:3)	0-0.3

Source: Biofuel Bionas Sdn Bhd (2012)

2.6 Trimethylolpropane (TMP)

When manufacturing a product, the raw material becomes the main concern, and this is also true for biolubricant production. The solution to overcoming the disadvantages of plant oils was discovered by replacing the presence of glycerol with another polyhydric alcohol such as neopentyl glycol (NPG) and Trimethylolpropane (TMP) (Akerman *et al*, 2011). Synthesis of polyol ester was done by esterification or transesterification process of polyhydric alcohol with fatty acid methyl ester (FAME). Even though polyhydric alcohol tends to decompose at high temperature, its thermal decomposition proceeds slowly. The properties of lubricant ester depend on the length of the aliphatic chain and relative position of unsaturated fatty acid bonds. There have been studies using TMP in biolubricant production that show that its higher viscosity is due to the three acid group structure in TMP ester (Sulaiman *et al.*, 2007). In addition, trimethylolpropane was widely used in biolubricant synthesis due to its lower cost and more sensitive to temperature that able to react at lower temperature.

Trimethylolpropane (TMP), 2-ethyl-2-hydroxymethyl-1,3-propanediol with chemical formula $C_6H_{14}O_3$ is a colorless crystalline alcohol that is highly soluble in water and polar organic solvent. TMP has three hydroxyl group attachments that are able to undergo normal OH group reaction. TMP is widely used in synthesis of alkyls for paint, acrylic acid ester for radiation curing and also esters for synthetic lubricant. TMP ester is favorable for biolubricant production due to its excellent thermal properties (Salimon and Ishak, 2012). Thus, trimethylolpropane (TMP) is seen as having potential for use as biolubricant ester.

The transesterification process for lubricant production with TMP involves three phases with the presence of catalyst that started with trimethylolpropane (TMP) react with methyl ester (ME) and form Trimetylolpropane monoester (TMPME) and methanol (CH_3OH). The continue reaction will produce Trimetylolpropane monoester (TMPME) and trimethylolpropane diester (TMPDE) become intermediate products towards the completion reaction to form trimetylolpropane trimester (TMPTE) that becomes the main product to produce. The methanol produce was removed directly from reaction to avoid backward reaction. The reaction is shown below, where the overall reaction requires 3 mol of methyl ester (ME) and 1 mol of trimetylolpropane (TMP) (Chang *et al*., 2012).

$$\begin{array}{cccccc} C_6H_{14}O_3 & + RCOOCH_3 & \longleftrightarrow & C_7H_{12}O_4R & + CH_3OH & \\ \text{TMP} & \text{ME} & & \text{TMPME} & \text{METHANOL} & \end{array} \tag{2.1}$$

$$\begin{array}{cccccc} C_7H_{12}O_4R & + RCOOCH_3 & \longleftrightarrow & C_8H_{12}O_5R_2 & + CH_3OH & \\ \text{TMPME} & \text{ME} & & \text{TMPDE} & \text{METHANOL} & \end{array} \tag{2.2}$$

$$\begin{array}{cccccc} C_8H_{12}O_5R_2 & + RCOOCH_3 & \longleftrightarrow & C_9H_{12}O_6R_3 & + CH_3OH & \\ \text{TMPDE} & \text{ME} & & \text{TMPTE} & \text{METHANOL} & \end{array} \tag{2.3}$$

The overall reaction

$$\begin{array}{cccccc} C_6H_{14}O_3 & + 3\ RCOOCH_3 & \longleftrightarrow & C_9H_{12}O_6R_3 & + CH_3OH & \\ \text{TMP} & \text{3ME} & & \text{TMPTE} & \text{3METHANOL} & \end{array} \tag{2.4}$$

Transesterification of trimethylolpropane (TMP) in production biolubricant was achieve high conversion with optimized variable condition such as variables of temperature, time of reaction, TMP to oil molar ratio, catalyst amount and others (Chang *et al*., 2012; Salimon *et al*., 2012). High temperature shows insignificant improvement in biolubricant production that influence by evaporating of volatile substance in raw material besides tend to promote the oxidation of raw material (Resul et al., 2012). Despite the temperature of reaction, catalyst that applied in reaction also influnce the yield of biolubricant production with specific TMP to oil ratio with particular temperature.

From previous study, shows that Sulaiman et al., (2007) were successfully synthesized 83 to 87 w/w% triesters (TE) for transesterification of TMP with palm oil methyl ester (POME) with optimum reaction temperature 120°C , 3.8:1 TMP to POME molar ratio, catalyst sodium methoxide amount 0.9 w/w% and 2 hour of reaction. Meanwhile, Resul et al., (2012) determine 47% conversion transesterification of TMP with Jatropha curcas oil methyl ester (JCOME) with reaction temperature 200°C,amount

JCOME 3.9:1 to TMP molar ratio using 1 w/w% sodium methoxide as catalyst. Thus, from previous research transesterification of TMP was successfully convert in production biolubricant.

2.7 Transesterification of Vegetables Oil Using Solid Catalyst

The transesterification of vegetable oils into biolubricant has been conducted by various researchers with excellent production results. The reaction converts the fatty acid methyl ester into monoesters (ME), diesters (DE) and triesters (TE), which react with TMP, and this involves cleavage of the ester group, RCOO- from methyl ester and hydroxyl group, -OH from TMP (Yunus *et al.*, 2004). Catalyst plays an important role in the production of biolubricant for obtaining better yield in less time (Chang *et al.*, 2012). The catalyst in the biolubricant production process was used to reduce the reaction time. Besides that, the catalyst also needs to be easy to handle and be cost effective (Nagendramma and Kaul, 2012).

Different kinds of catalyst have been used in the production of biolubricant from different kinds of vegetable oils as feedstock. There are two categories of catalysts used to produce biolubricants: homogeneous and heterogenous catalysts. Homogenoeus catalysts, such as inorganic acids and alkali, have been applied widely in transesterification process either in biodiesel or biolubricant production (Li *et al*., 2012).

Previous researchers have achieved 98% conversion of TMP triester in 8 hour reaction time while using calcium methoxide as a catalyst (Chang *et al*., 2004; Yunus *et al.*, 2004). Meanwhile, Salimon and Ishak (2012) successfully converted TMP ester into 78% of TE using using sulfuric acid at 5 hour reaction time.

However, there was been a decrease in applying this kind of catalyst among researchers due to a few problems, such as not being able to regenerate or recover the catalyst after the reaction and also the tendency to produce toxic wastewater (Margaretha *et al*., 2012). In addition, free fatty acid and water contained in vegetable oil feedstocks tend to form unwanted soap as a by-product, thus deactivating homogenoeus catalyst activity. Meanwhile, inorganic acid will cause the reaction end product to become a dark color (Li *et al*., 2012).

In order to overcome these obstacles, the developement of heterogeneous catalyst as an alternative choice has been started. Heterogeneous catalysts such as metallic or metal oxide have wide potential for use, as these catalyst can be recycled easily (Li *et al.*, 2012). Besides that, it is much cheaper than enzyme-based or other biochemical catalysts (Boey *et al*., 2011). Heterogenoeous catalyst is also noncorrosive to the environment, therefore producing less disposal problems (Sanjay, 2013). The important reason a new solid base heterogeneous should be developed is because of their ablity to increase yield at lower temperature, shorter time and more ease in the separation process (Guo and Fang, 2011). Table 2.2 shows a list of heterogenous catalysts that are used in transesterification process.

Table 2.2 Heterogenous catalysts used for tranesterification process

Catalyst	**Feedstock**	**References**
Calcium Oxide	Soybean Oil	Kouzu *et al*., 2008
Silica Sulphuric Acid	Oleic Acid	Akerman *et al.*, 2011
Pomeca sp. shell	Palm Oil	Margaretha *et al*., 2012

Among the heterogeneous catalysts listed, calcium oxide (CaO) gains attention due to its ability to remain active under mild reaction condition, having long recycleability and low solubility in methanol, as well as being abundantly available in the enviroment as limestone (Kazuo *et al*., 2012).

Nowadays, waste from the seafood industry is characterized as product-specific waste, where the product is generated constantly from the raw material and thus unavoidable. Solid wastes that are produced from these operations, for example shells from clam waste, and skin or heads from fish waste tend to contaminate the processing environment if not disposed of in the right manner. Thus, there is increasing pressure for industries to manage their solid waste while at the same time maintaining their high profit level.

New possibilities for the utilization of seafood industry waste have been discovered, whereby these kinds of solid waste such as shell waste can be reduced in quantity by turning them into something valuable, such as utilizing them as catalysts.

Currently, studies on transesterification process using solid base heterogeneous calayst such as calcium oxide derived from snail shell shows potential among researchers (Margaretha *et al.,* 2012; Birla *et al.,* 2012).

Unfortunately, transesterification of vegetables oil using solid catalyst should not be more than 1% of free fatty acid (FFA) content. If the FFA level is over this threshold, saponification will take place, leading to reduction in production (Viele *et al.*, 2013). Thus, an alternative that has been suggested is applying a two-step process of esterification and transesterification for methyl ester production from high fatty acid oil such as *Jatropha curcas* oil. The pre-treatment of non-edible oil is to reduce the FFA level in oil (Jayasighe *et al.,* 2014). The first step is by esterification of the FFA with methanol in the presence of acid catalyst. The process continues for 1 to 2 hours until the presence of free fatty acid is less than 1%. The acid-esterification step is applied nowadays even in industrial and laboratory processes where the methanol can be recovered at the end of the process (Chai *et al.*, 2014). Then, transesterification is continued by applying alkaline catalyst. This two-step process has shown a high yield of production (Arbain and Salimon, 2010).

2.8 *Papia Undulata a*s Solid Catalyst

The surf clam (*Paphia undulata*) is commonly found in muddy areas in Malaysia and Thailand. The surf clam is supported offshore of Thailand and Malaysia bordering the Andaman sea, in the intertidal zone up to a deph of 25 m, since the 1970s (Dunrong *et al.*, 2011). There was estimated to be an annual *Paphia undulata* production of 20,000 MT in the fishery industry, and this has steadily increased since the 1990's (Nurdin *et al*., 2014).

Usually, the shell waste of *Paphia undulata* in Malaysia was commonly thrown away from restaurants, as well as food and cannaries industries without any utilization of it as a valuable product. This scenario tends to lead to unpleasent odours occurring in the environment (Tsai *et al.,* 2009). Thus, using wastes for catalyst synthesis will reduce the quantity of unutilized waste. Besides that, it helps to produce catalyst at a cost effective rate.

The waste shell of mollusk contains calcium carbonate that can be converted to calcium oxide by calcination process. Calcium oxide is an environmentally friendly material which can be derived from several natural sources of waste such as mollusk shell, egg shell and bone (Viriya-empikul *et al.,* 2010). The facts show that *Paphia undulata* shell waste has great potential to be utilized as a catalyst due to containing 95% of calcium carbonate ($CaCO_3$) (Tantra *et al.*, 2014).

2.9 Kinetic Model of Transesterification Process for Biolubricant Synthesis

The derivation of this kinetic reaction is based on a few generally accepted principles of kinetic reactions which are usually applied in esterification of oil either in production of biodiesel or biolubricant (Turner, 2005). The kinetic reaction was developed to determine the effectiveness of the process. The kinetic model of the decomposition of mineral oil lubricant has been widely studied by reaserchers to determine the stability of lubricants in response to thermal effects (Santos *et al*., 2006; Mohoric *et al.,* 2009). Unfortunately, there has not been much research carried out on the kinetic reaction of transesterification for lubricant ester synthesis. Thus, a kinetic model for transesterification of *Jatropha* seed oil for lubricant synthesis was adapted from the kinetic model for biodiesel production. The experimental data was analyzed in order to understand the reaction rate of the process by determining the rate constant of the process.

An earlier kinetic study on transestrification of biolubricant stated that the rate constant was directly proportional with temperature (Resul *et al.*, 2012). Apart from this, the analysis data was fit to first-order and second-order kinetics to determine the reaction rate of the process. Curve fitting was used to determine the suitable reaction order of the process (Slinn and Kendal, 2009). Resul et al.(2012) state that the transesterification of *Jatropha* biolubricant follows second-order kinetics.

In addition, the influence of temperature on the rate constants was determined by fitting the results to the Arrhenius equation (Thiruvengadaravi *et al.*, 2009). Since the activation energy, ΔE, is dependent on the rate constant, K, therefore the temperature should fit in the following equation:

$$\ln K = [(-Ea/RT)] + \ln A \tag{2.5}$$

where R is gas constant, T is temperature in Kelvin, and Ea is Activation energy.

Activation energy was determined from the slope plot ln K versus 1/T in this kinetic study. Krishnan and Dass (2012) state that the activation energy is the minimum energy that is required to start a reaction. Thus, determination of the activation energy is important to determine the energy required to promote the reaction effectively.

2.10 Physico-Chemical Properties

The physico-chemical properties of a lubricant is important to determine its performance as a commercial application by using standard American society for testing and material (ASTM) test methods. In order to increase the commercial viability of biolubricant in the industry, the standard for biolubricant properties must be fulfilled. Akerman *et al*. (2011) state that the basic requirement of a lubricant is to maintain in liquid form over a wide range of temperature. Thus, temperature limit is determined based on pour point for low temperature and flash point for high temperature (Arbain and Salimon, 2010). A reduced pour point has negative effect on oxidative stability (Bakar *et al*., 2007). Meanwhile, a high flash point that influence by carbon contains in the structure is important for carrying out a safe operation at high operating temperature (Arbain and Salimon *et al.,* 2010).

Besides that, viscosity refers to the thickness of the lubricant oil that can be measured by time taken to pass through an orifice of a specific size at a given temperature. Fox and Stachowiak (2007) state that strong intermolecular interaction provides the stable viscosity that characterizes the biolubricant produced using vegetable oils. Meanwhile, Singh and Chhibber (2013) state that the polar ester group contained in biolubricant produced from vegetable oil allows it to adhere to metal surfaces, which results in the good lubricant properties.

In addition, biolubricant is suitable for a wide range of applications due to having a much lower pour point (Nagendramma and Kaul, 2012). Besides that, previous researchers have shown that *Jatropha curcas* oil has high potential for use as a raw material, both in production of biodiesel and biolubricant due to its effective anti-wear and anti-friction capabilities (Golshokouh *et al.,* 2013). Thus, non-edible oil is seen as having great potential as a raw material in biolubricant production due to its excellent psycho-chemical properties.

2.11 Conclusion

Demand of lubricant oil increased due to its ability to decrease the friction between two contacting surfaces by separating the surfaces and avoid corrosion on the steel surface component. Thus, biolubricant is an alternative lubricant that is derived from vegetables oil has potential to fulfill market demand. *Jatropha curcas* that can be found in Malaysia has gained interest for synthesis biolubricant production. Meanwhile, Trimethylolpropane (TMP), a colorless crystalline alcohol was applied for synthetic lubricant due to its excellent thermal properties tends to be applied. In this research, *Paphia undulata* shell waste was review has great potential to be utilized as a catalyst due to containing 95% of calcium carbonate ($CaCO_3$). On the other hands, kinetic reaction was developed to determine the effectiveness of the lubricant ester synthesis. Thus, a simple kinetic model (first-order and second-order kinetics) for transesterification of *Jatropha curcas* oil methyl ester (JCOME) for biolubricant synthesis was adapted. In addition, the influence of temperature on the rate constants was determined by fitting the results to the Arrhenius equation.

CHAPTER 3

RESEARCH DESIGN AND METHODOLOGY

3.1 Introduction

This chapter explains in detail the experiments that were conducted in this research. This includes materials used, experimental procedures, schematic diagrams and product analysis. In this research, *Jatropha curcas* oil (JCO) was used as a raw material in synthesis of biolubricant by applying solid catalyst from *Papia undulata* waste shell. The optimum conditions for acid esterification of *Jatropha curcas* oil (JCO), *Jatropha curcas* Oil Methyl Ester (JCOME) and *Jatropha* biolubricant production were determined, as well as the kinetics of the transesterification reaction in synthesis biolubricant. This research was carried out following the research process flow diagram as shown in Figure 3.1.

3.2 Research Methodology Process Flow Diagram

The research methodology process flow diagram is shown in Figure 3.1 started with the synthesis and analysis of solid catalyst from *Paphia undulata* shell waste. Then, research was proceed with production and analysis of Jatropha curcas oil methyl ester (JCOME) by applying solid catalyst prepared before via two steps processing (acid esterification of Jatropha curcas oil and transesterification process). This was followed by synthesis of biolubricant and analysis of the final product. Finally, catalyst recycleability and transesterification kinetics also were accomplished in this research.

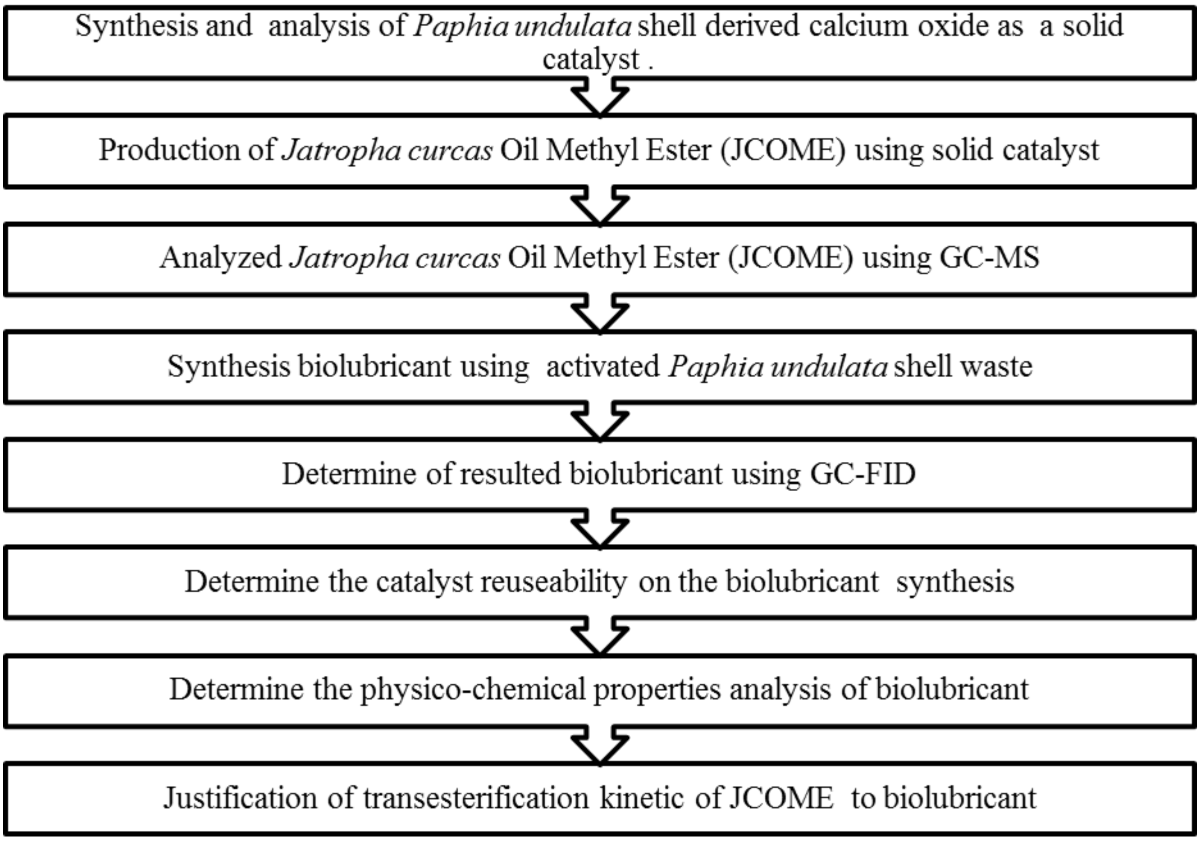


Figure 3.1. Research methodology process flow diagram.

3.3 Materials

The *Paphia undulata* waste shell was collected from a seafood restaurant in Tanjung Lumpur, Kuantan. *Jatropha curcas* oil was procured from Bionas Sdn Bhd. Trimethylolpropane, ACS grade, 99% purity, was procured from Sigma Aldrich, Malaysia. The methanol (synthesis grade), hydrocloric acid (95% pure) and hexane (GC grade) which were used in this research were purchased from Chemmart Asia, Malaysia.

3.4 Preparation and Characterization Paphia Undulata Shell Waste as Solid Catalyst

3.4.1 Preparation of Solid Catalyst

The waste shells that had been collected were repeatedly washed using clean water and dried at 100°C overnight. Then, the solid catalysts were crushed and calcinated in a furnace at 680°C for 2 hours. Figure 3.2 shows *Paphia undulate* shell during crushing process. After calcinations in the furnace, the catalyst was removed from the furnace and kept in desiccators to prevent air contact.

Figure 3.2. *Paphia Undulata shell* chrushing process.

3.4.2 Characterization of Solid Catalyst

The raw material (*Paphia undulata* shell) before and after activated were characterized using several methods such as Field Emission Scanning Electron Microscopy (FESEM), X-Ray Florescence (XRF), Fourier Transformed Infra Red (FTIR) Spectroscopy, Brunauer-Emmett-Teller (BET) and Differential Thermal and thermo-gravimetric (DTA-TGA).

3.4.2.1 Scanning Electron Microscopy (SEM)

The Scanning Electron Microscopy (SEM) (Carl Zeiss, EVO50) was used to investigate molecular surface structure of the catalyst by operating in the 15-20 kV voltage. The sample was placed in a stub that using platinum coater to cover the sample during analysis.

In this research, SEM analysis provided a topographical display of the catalyst structure at magnification of 5,000x before activation and after activation of catalyst sample, and both were analyzed for comparison. This analysis was also important to know the effect of calcination process on the solid catalyst.

3.4.2.2 X-Ray Fluorescence (XRF) spectrometry

XRF analysis was used to determine the major and trace elements of a catalyst. For this purpose, S8 Tiger, Bruker X-ray fluorescence with Pd X-ray tube operating at 40 kV and 1.2 mA, was employed.

3.4.2.3 X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) (Rigaku Miniflex II) was used to analyse the crystal structure of solid catalyst at 2ϴ range 0° to 80° with a step size 0.1˚ using Kα- Co source at 40 kV and 40 mA. Sample solid catalyst send for XRD analysis in Faculty of Science and Technology, University Malaysia Pahang laboratory**.**

3.4.2.4 Fourier Transform Infrared Spectrophotometer (FTIR)

Fourier Transformed Infrared Spectrophotometer (FTIR) (Perkin-Elmer Spectrum 100) was carried out to determine functional groups attached to the catalyst surface using the potassium bromide technique with a wave number range of 4,000 to 400 cm^{-1}. Sample solid catalyst send for FTIR analysis in Faculty of Science and Technology, University Malaysia Pahang laboratory**.**

3.4.2.5 Physisorption of Nitrogen

Nitrogen adsorption and desorption isotherms at 77K were measured using Micrometric ASAP 2020 surface analyzer. The surface area of solid catalyst was determined using Brunauer-Emmet-Teller (BET) method and pore size distribution was determined by using Barrett-Joyner-Halenda (BJH) method.

3.4.2.6 Thermo-gravimetric analysis (TGA)

Thermo-gravimetric analysis (TGA) (TAQ-500) analysis was carried out from room temperature to 850^0C with a heating rate at 20^0C/min under nitrogen flow of 20 ml/min. This analysis was important to determine the optimum calcination temperature of the solid catalyst.

3.5 Development of Optimum Synthesis Conditions for Esterification of Jatropha Curcas Oil Methyl Ester (JCOME)

3.5.1 Experimental Setup

The bench scale set-up for synthesis of *Jathropha curcas* oil methyl ester (JCOME) is illustrated in Figure 3.3. It consists of a round bottom flask reactor placed in an adjusted temperature water bath using a thermometer and hot plate. Meanwhile, a condenser was fitted to the flask as a cooling system to avoid reactant from vaporizing into the atmosphere.

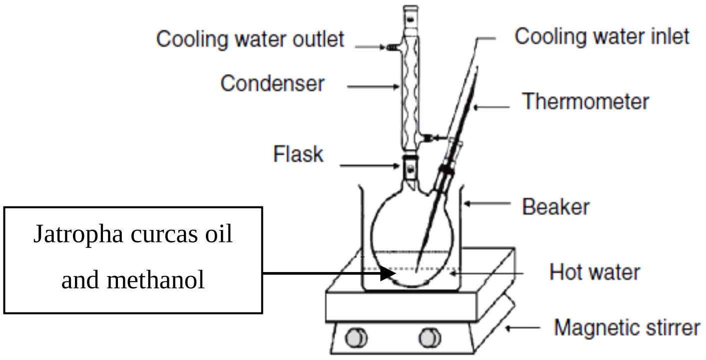


Figure 3.3. Experimental setup for JCOME production.

3.5.2 Fatty Acid Reduction

Jatropha curcas oil contains a high amount of fatty acids which need to be reduced by acid esterification process with methanol. This method was important step to avoid the production of soap that would occur if the acid value of oil was higher than 2. The oil was placed in two neck flasks equipped with magnetic stirrer and condenser that were used as a cooling system to prevent alcohol loss as Figure 3.4.

Then, the catalyst solution (a specified amount of HCl with oil dissolved in methanol) was poured into each flask. The mixture was heated up to 60°C with constant stirring for 1 hour. After that, the mixture was placed in a separating funnel for 24 hours to separate excess methanol. The excess methanol with hydrochloric acid (HCl) and impurities moved to the top surface and were removed. Meanwhile, the lower layer was collected and the process was continued with transesterification using solid catalyst. Figure 3.5 shows separation process for acid esterification stage.

Figure 3.4. Esterification of *Jatropha crucas* oil.

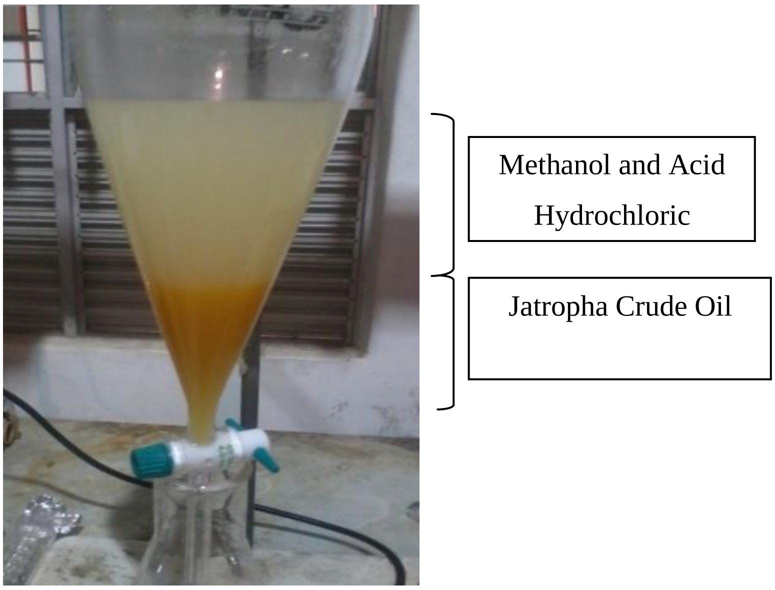


Figure 3.5. Separation Process.

In order to optimize the reaction of acid esterification of *Jatropha curcas* oil, research was conducted in various levels of conditions. Table 3.1 shows the independent variables that involved in acid esterification process.

Table 3.1 Independent variables of acid esterification reaction

Independent Variables	**Value**
Catalyst concentration (wt/wt%)	0,0.5,1.0,1.5,2.0
Methanol to oil (mol:mol)	3:1, 4:1, 5:1, 6:1, 7:1
Time (min)	20,30,40,50,60

3.5.3 JCOME Transesterification

After the fatty acid pre-treatment process, *Jatropha curcas* oil transesterification was continued in order to produce *Jathropha curcas* oil methyl ester (JCOME) using the heterogeneous catalyst from *Papia undulata* shell waste. The experimental setup for JCOME transesterification process followed as Figure 3.4.

In order to optimize the reaction of JCOME synthesis, research was conducted at various temperature levels, amounts of catalyst and times of reaction. Table 3.2 shows the independent variables that involve different reaction times (h), different reaction temperatures ($^{\circ}$C), different percentages of catalyst (% wt/wt) and different methanol to oil ratios (mol:mol). The experiment was performed in triplicate and the JCOME yield result was presented as average value.

Table 3.2 Independent variables of JCOME transesterification reaction

Independent variables	**Value**
Time (h)	1, 2, 3, 4, 5
Temperature (^{0}C)	30, 40, 50, 60, 70
Amount of Catalyst (wt%)	1, 2, 3, 4, 5
Oil : Methanol (mol: mol)	1:2, 1:3, 1:4, 1:5, 1:6

After final separation as Figure 3.6, the catalyst with other debris remained at the bottom layer was removed, while the upper layer was collect. The upper layer products were purified by washed using warm water (50°C) as Figure 3.7. The purification process was repeated until the water became clear and the product was analyzed using gas chromatography.

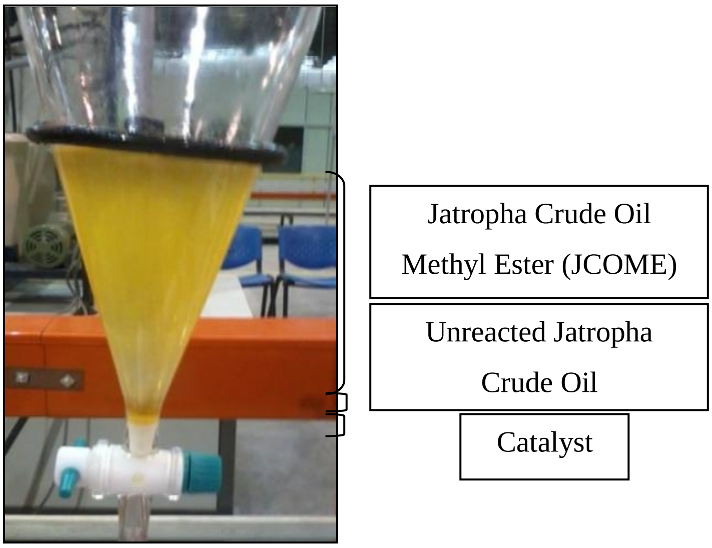
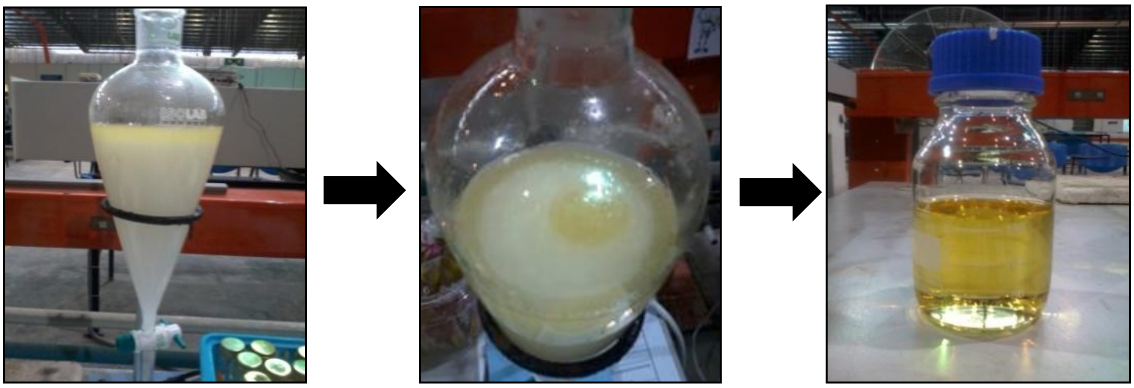


Figure 3.6. Separation Process.



Washing Process

Final Product (JCOME)

Figure 3.7. Purification of JCOME

3.6 Synthesis of Biolubricant

3.6.1 Transesterification of Biolubricantusing Solid Catalyst

Blending process was prepared for transesterification process in biolubricant production, which was carried out by adding JCOME with TMP in a 250 ml three necks round bottom flask equipped with thermometer and reflux condenser. After the reactor was set up as illustrated in Figure 3.8, TMP was added and melted with constant stirring in the flask at temperature 60°C. After that, a calculated amount of JCOME with TMP molar ratio of 1:4 was introduced to the reactor and after the catalyst was added, the temperature of the reaction mixture was raised to the desired temperature. Then, vacuum (50 mmHg) was applied to remove methanol produced from the reaction mixture. The final products of transesterification were TMP ester and methanol. After reaction termination, the final liquid product went through vacuum filtration to remove the solid catalyst and soap product. Filter that used in this step are grade 1 quantitative filter paper with pore size 11µm (Whatman). After filtration, the product was cooled at room temperature and analyzed.

Figure 3.8. Experimental setup for biolubricant synthesis.

The research was conducted at various temperature levels, amounts of catalyst and times of reaction. Table 3.3 shows the different reaction times (h), different reaction temperatures (°C), different percentages of catalyst (% wt/wt) and different JCOME to TMP molar ratios (mol/mol). JCOME was prepared by applying the optimum parameter that had been studied before in section 3.4. The experiment was performed in triplicate and the result was presented as average value.

Table 3.3 Independent variables of the biolubricant transesterification reaction.

Independent Variables	Value
Time (h)	1, 2, 3, 4, 5
Temperature (^{0}C)	90, 100, 110, 120, 130
Amount of Catalyst (wt%)	0, 1, 2, 3, 4
JCOME : TMP (mol: mol)	1:1, 1:3, 1:4, 1:5, 1:6

3.7 Analysis of Product

The *Jatropha curcas* oil methyl ester (JCOME) that was obtained from transesterification of crude oil with methanol was measured using Gas Chromatography Mass Spectrometer (GC-MS) to determine the composition of methyl ester and measure the product yield. Then, characterization of its properties, such as kinematic viscosities at 40 °C and 100°C as well as pour point, was carried out. Meanwhile, TMP ester biolubricant derived from JCOME was evaluated using Gas Chromatography equipped with Flame Ionization Detector (GC-FID) to get the conversion and percentage composition of the product. Finally, characterization of its properties, such as kinematic viscosities at 40 °C and 100°C as well as pour point, was carried out.

3.7.1 Jatropha Curcas Oil Methyl Ester (JCOME)

The analysis of JCOME was performed using Gas Chromatography Mass Spectrometer (GC-MS) to determine the percentage composition of methyl ester in the product. The sample was prepared in a 2 ml vial with 0.02 ml of the sample mixed with 1.980 ml of hexane (GC Grade). For this purpose, GC-MS was conducted with gas chromatography (Agilent 7890A GC system equipped with Agilent 7683B series Injector, 5975C Inert MSD) and equipped with DB-1 column (30 m X 0.25m X 0.25 µm film) and parameter as described in subsection 3. 7.1.2.

3.7.1.1 JCOME Yield

According to Leung and Guo,(2006), the biodiesel percentage yield was evaluated using Eq.(3.1).

$$\text{Yield (\%)} = \frac{(\text{Weight of } JCOME)}{(\text{Weight of Jatropha Oil})} \text{ x } 100 \qquad (3.1)$$

3.7.1.2 GC-MS Parameter

The parameter for JCOME analysis using GC-MS as shown in Table 3.4.

Table 3.4 GC-MS parameters for JCOME composition

GAS CHROMATOGRAPH	**FAME Analysis**
Injector temperature	200^0C
Column Flow	1 ml/min
Split flow	30 ml/min
Injection volume	1µl
Oven Temperature	
Initial temperature	70^0C
Hold temperature	3 mins
Ramp	7 ^{0}C/min
Final Temperature	230 ^{0}C
Hold time	2 mins

3.7.2 Physicochemical Characterization of JCOME

3.7.2.1 Viscosity at 40 °C and 100 °C

The viscosity of JCOME was measured at the temperatures of 40 and 100 ºC. Measurements were made using a DV-II+ Pro Viscometer (Brookfield, USA) equipped with a constant-temperature bath. Viscosity was calculated in accordance with ASTM standard method D445 and followed the required limit set for (ASTMD6751) biodiesel standard.

3.7.2.2 Pour point

Cloud point is denoted as the highest temperature at which haziness is observed, while pour point is the lowest temperature at which movement of the oil is observed. Cloud point and pour point were determined in accordance with ASTM standard methods D2500 and D97.

3.7.3 Biolubricant

The biolubricant sample was analyzed using Gas Chromatography equipped with flame ion detector (GC-FID) (Agilent G 890N) to determine the TMP ester composition in the product. The equation of biolubricant yield is shown in sub section 3.6.2.1. Equation 3.2. was used for determine conversion of TMP and Equation 3.3 for determine percentage composition of biolubricant.

The sample was prepared by taking 30 µl of the sample and mixing it in a 5 ml vial, diluted with 1 ml of ethyl acetate (GC grade) and swirled for a few minutes to dissolve the mixture. Next, 0.5 ml of *N,O*-Bis(trimethylsilyl)tri-fluoroacetamide (BSTFA) was added and the vial was then transferred to a water bath at 40^0C for 10 minutes. Finally, the sample was transferred to a 2 ml vial for GC analysis.

The analysis used GC equipped with DB-5HT column, 30 m x 0.25 mm, i.d. 0.10 µm (DB, United States). Injector and detector temperature were set at 380^0C and 400^0C, respectively. Initial oven temperature was set at 100^0C with 1 minute of initial holding time increased at a rate of 5^0C/min until it reached 380^0C, and was maintained at that temperature for 25 minutes. Standard solutions for product analysis were taken from partial glyceride standards. The 3 partial glyceride standards that were chosen were palmitate, linoleate and oleate, with each standard consisting of mono-, di- and tri-glyceride, respectively. The calibration curve was prepared for quantitative measurement to represent the top 3 highest fatty acid content in feedstock, as shown in Appendix B.2. Identification of peaks of all TMP ester produced was performed by comparing the retention times with the library standards under the same conditions. Meanwhile, the TMP standard curve for kinetic study is shown in Appendix B.3.

3.7.3.1 Biolubricant Yield

The conversion of Trimethylolpropane (TMP) as limiting reactant and percentage composition of biolubricant were calculated using the Eq. (3.2) and Eq.(3.3):

$$\text{Conversion TMP (\%)} = \left[1 - \frac{C_{TMP,P}}{C_{TMP,S}}\right] X\ 100 \qquad (3.2)$$

where TMP_P = final Trimethylolrpopane (TMP) concentration in the product, TMP_S = initial concentration trimetylolpropane (TMP).Refer Appendix B.2.1 for TMP standard curve.

$$\text{Percentage Composition (w/w\%)} = \frac{(Weight\ of\ ME)}{(Weight\ of\ ME + DE + TE)} \text{X100} \qquad (3.3)$$

where ME = mono-ester, DE = di-ester, TE = tri-ester. Refer Appendix B.2.2 for biolubricant percentage composition standard curve.

3.8 Evaluation of Produced Biolubricant

3.8.1 Produced Biolubricant Analysis

Final product was analyzed to reconfirm the result by determined molecular structure for the TMP ester has been produced in this research. Thus, Fourier Transform Infrared Spectrometry (FTIR) and Proton and Carbon Nuclear Magnetic Resonance (1H-NMR and 13C-NMR) Spectra analysis were carried out.

3.8.1.1 Fourier Transform Infrared Spectrometry (FTIR)

The functional group of biolubricant ester was confirmed using FTIR (Perkin Elmer Spectrum 100) in the range 700-4000 m^{-1}. FTIR analysis was done by placing a very thin film of biolubricant ester sample and sodium chloride (NaCl) cell (25mm id x 4mm thickness) for analysis. The spectra were obtained directly at room temperature.

3.8.1.2 Proton and Carbon Nuclear Magnetic Resonance (1H-NMR and 13C-NMR) Spectra

The final product was collected for analysis by NMR spectrometry (Bruker Ultrashield 500 Plus) to reconfirm the signal display of ester carbonyl functional group in biolubricant ester produced. The reaction sample was pipetted into NMR tube and then deutered chloroform ($CDCl_3$) was added to dissolved the low polarity reaction mixture with operating frequency for ^{1}H-NMR and ^{13}C-NMR were at 400 and 100 MHz.

3.8.2 Physicochemical Characterization of Biolubricant

3.8.2.1 Viscosities at 40°C and 100°C

Viscosity is an important characteristic of lubricant, where it is defined as the measure of fluid resistance to flow at the corresponding temperature. The viscosity of TMP ester was measured at the temperatures of 40 and 100ºC according to ASTM D 445 and viscosity index according to ASTM D 2270-93.

3.8.2.2 Pour point

The pour point, the lowest point at which a sample (lubricant) continues to flow when cooled under specific standard conditions, was measured according to ASTM D 97-02. The pour point was determined by placing the test jar filled with the process oil into a cooling media and measured at 3^0C increments until it stopped pouring. The pour point was taken as the temperature where the oil was still able to pour.

3.9 Reaction Kinetics of Transterification for Biolubricant Synthesis

Kinetic model for transesterification of JCOME for lubricant synthesis was developed using experimental data for understanding the reaction rate of process by determining the rate constant of the process. The effects of temperature and time were measured for reaction kinetics. The reaction follows the scheme as shown below. in

Eq.(3.4). By ignoring the intermediate products, such as monoester in Eq.(3.5) and diester reaction in Eq.(3.6), the three steps can be combined into one overall step in Eq.(3.7).

$$\mathrm{JCOME} + \mathrm{TMP} \longleftrightarrow \mathrm{ME} + \mathrm{M} \qquad (3.4)$$

$$\mathrm{JCOME} + \mathrm{ME} \longleftrightarrow \mathrm{DE} + \mathrm{M} \qquad (3.5)$$

$$\mathrm{JCOME} + \mathrm{DE} \longleftrightarrow \mathrm{TE} + \mathrm{M} \qquad (3.6)$$

Overall reaction

$$3\mathrm{JCOME} + \mathrm{TMP} \longleftrightarrow \mathrm{TE} + 3\mathrm{M} \qquad (3.7)$$

Then, a simple kinetic approach was taken in this research by applying first and secon kinetic models.

3.9.1 First Order Reaction

Firstly, consider that the reaction was conversion of TMP to TMP ester (TE), the rate law of transesterification reaction for first order reaction can be expressed in Eq.(3.8) as:

$$\text{TMP} \longrightarrow \text{TE} \tag{3.8}$$

When TMP was converted to TE, the reaction is as Eq.(3.9).

$$r_{TMP} = -\frac{d[TMP]}{dt} = +\frac{d[TE]}{dt} = k\,.\,[\text{TMP}] \tag{3.9}$$

where [TMP] is concentration of TMP[, TE] is concentration of TE and k is rate constant. Eliminating the term –d[TMP]/dt by integration will form Eq.(3.10).

$$r_{TMP} = -\frac{d(TMP)}{dt} = -\int_{[TMP]_0}^{[TMP]} \frac{d[TMP]}{[TMP]} = k\int_{t_0}^{t} dt \tag{3.10}$$

Solving the equation gives the following result as Eq.(3.11).

$$-\ln[\text{TMP}] + \ln[\text{TMP}_0] = kt \tag{3.11}$$

Eq.(3.11) can be rewritten as Eq.(3.12).

$$\ln\frac{[TMP]_0}{[TMP]} = kt \tag{3.12}$$

Taking antilog gives Eq.(3.12).

$$[\text{TMP}] = [\text{TMP}]_0\, e^{-kt} \tag{3.13}$$

Plotting the log(ln) of the concentration TMP versus time (t) for first order reaction, will get the slope as –k.

3.9.2 Second Order Reaction

Consider the reaction that involved two reactants that were converted to the product as Eq.(3.14).

$$3JCOME + TMP \longleftrightarrow TE + 3M \qquad (3.14)$$

This kinetics study assumes that the solid catalyst was used at sufficent amount with respect to the oil ratio to shift the equilbrium towards TMP ester. Thus, catalyst reaction can be ignored and the concentration of catalyst during reaction was constant, therefore they can be assumed to be negligeble. Secondly, reaction was also assumed to be forward step tranesesterification reaction where concentration of JME was used in excess and methanol product was constantly drawn out by vacuum suction. Thus, for second order kinetics the reaction can be expressed as Eq.(3.15).

$$-r_{TMP} = -\frac{d(TMP)}{dt} = k_{TMP} . [TMP]^2 \qquad (3.15)$$

Then, Eq.(3.15) was integrated (Eq. 3.16) to obtain Eq.(3.17), which was rearranged to get Eq.(3.18).

$$-\int_{TMP_0}^{TMP} \frac{d[TMP]}{[TMP]^2} = k_{TMP} \int_0^t dt \qquad (3.16)$$

$$[\frac{1}{TMP} - \frac{1}{TMP_0}] = k_{TMP} [t-0] \qquad 3.17)$$

$$\frac{1}{[TMP]} - \frac{1}{[TMP]_0} = k_{TMP} t \qquad (3.18)$$

Lastly, 1/[TMP] versus time (t) for second order reaction was plotted to get the slope as k.

3.9.3 Activation Energy

The influence of temperature on the rate constants were determined by fitting the results to the Arrhenius equation. Since the activation energy, ΔE, is dependent on rate constant, k, the temperature should be fit in Eq.(3.19):

$$\log_{10} k = \left[\frac{-\Delta E}{2.303 R.T}\right] + \log_{10} A \qquad (3.19)$$

where R is gas constant, T is temperature in Kelvin and ΔE is an Activation energy, which was determined from plotting the slope of $\log_{10}$ k versus 1/T.

3.10 Catalyst Reusability

Reusability of a catalyst is important to know the stability of the catalyst for the reaction. For biolubricant, the reusability of the catalyst was conducted with the solid catalyst directly used after drying process. The process was started by collecting the catalyst from the final product using centrifugation after termination of the reaction. Then, the catalyst was dried in an oven at 60 ^{0}C and directly applied for the next experiment. These procedures were repeated three times for one of four cycles experiment.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Introduction

This chapter presents the experimental results and discussion of this research work. Section 4.1 deals with the characterization of catalyst using Scanning Electron Microscopy (SEM), X-Ray Fluorescence (XRF), Fourier Transformed Infra-Red (FTIR) Spectroscopy, Physisorption of nitrogen analysis as well as Differential Thermal and thermo-gravimetric Analysis (DTA-TGA). Section 4.2 discusses the synthesis of methyl ester from Jatropha curcas oil to produce Jatropha Curcas Oil Methyl Ester (JCOME) that was the used as raw material for synthesis of biolubricant. Meanwhile, section 4.3 discusses the development One factor at one time (OFAT) for synthesis of biolubricant from JCOME and section 4.4 discusses the kinetics of biolubricant transesterification using first order and second order reaction kinetics. Finally, the physicochemical properties of biolubricant and reusability of catalyst are discussed in sections 4.5 and 4.6.

4.2 Synthesis and Characterization of Solid Catalyst

The characterization of solid catalyst fom *Papia Undulata* shell are discussed in this section. This section is important for understanding the characteristics of solid catalyst that will contribute to a better yield of methyl ester from *Jatropha curcas* oil.

4.2.1 Differential Thermal and thermo-gravimetric (DTA-TGA)

Paphia undulata shell waste was analyzed using TGA-DTA to determine the suitable calcination temperature for preparing the catalyst for esterification. From Figure 4.1, the TGA curve shown that 41.76% weight loss was observed in the samples at temperature range of 610 to 760 °C. Above 760 °C, the weight loss remained almost constant until the sample became ash. Previously, uncalcined eggshell had shown weight loss from 400°C until 480°C (Sharma *et al*., 2010).

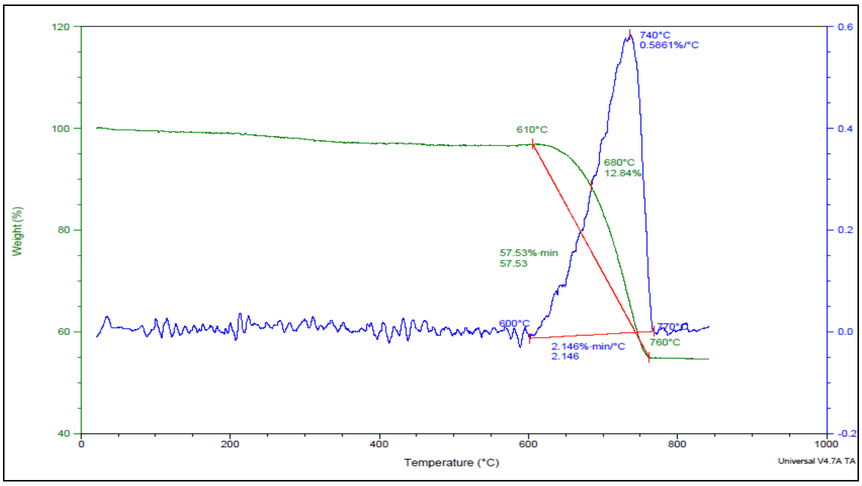


Figure 4.1. DTA/TGA graph of *Paphia undulata* shell.

Meanwhile, on the DTA curve, maximum temperature was found to be around 600 to 770 °C. The clam shell from *Paphia undulata* required a temperature above 610 °C, as clam shells are generally known to mainly contain $CaCO_3$, and thus need a high temperature to transform $CaCO_3$ into CaO, which can be determined by DTA curve. This result shows temperatures much lower than for cockle and egg shell, where the maximum temperature for DTA curve was 810 to 860°C (Viriya-empikul *et al.*, 2010). This is due to the size of the catalyst that was used in the reaction, which is one of the crucial factors that directly influences the reaction rate (Rashidi *et al.*, 2011).

From this analysis, also taking into account preparation time and energy consumption, the temperature that was selected to produce CaO from *Paphia undulata* shell was 680°C. In this research, moderate temperature was seen to be enough to convert $CaCO_3$ into CaO within 2 hours. Above this temperature, the catalyst has a tendency for shrinkage, closure of the pores and decreased volume of the particles (Rashidi *et al.*, 2011)..

4.2.2 X-Ray Fluorescence (XRF)

The detailed chemical composition of the solid catalyst from *Papia undulata* shell waste obtained from X-ray fluorescence (XRF) is shown in Table 4.1 and it indicates a significant amount of CaO content (86.25%) with small amounts of other compounds.

Table 4.1 The chemical composition of the solid catalyst from *Paphia undulata* shell waste

No	Chemical Composition	Percentage (%)
1	Calcium Oxide (CaO)	86.25
2	Sodium Oxide (Na2O)	12.54
3	Strontium Oxide (SrO)	0.29
4	Magnesium Oxide (MgO)	0.47
5	Sulphur Trioxide (SO3)	0.15
6	Chlorine (Cl)	0.07
7	Iron Oxide (Fe2O3)	0.06
8	Phosphorus Pentoxide (P_2O_5)	0.06
9	Silicon Dioxide (SiO_2)	0.05
10	Potassium Oxide (K_2O)	0.03
11	Aluminium Oxide (Al_2O_3)	0.02
12	Chromium Oxide	0.01

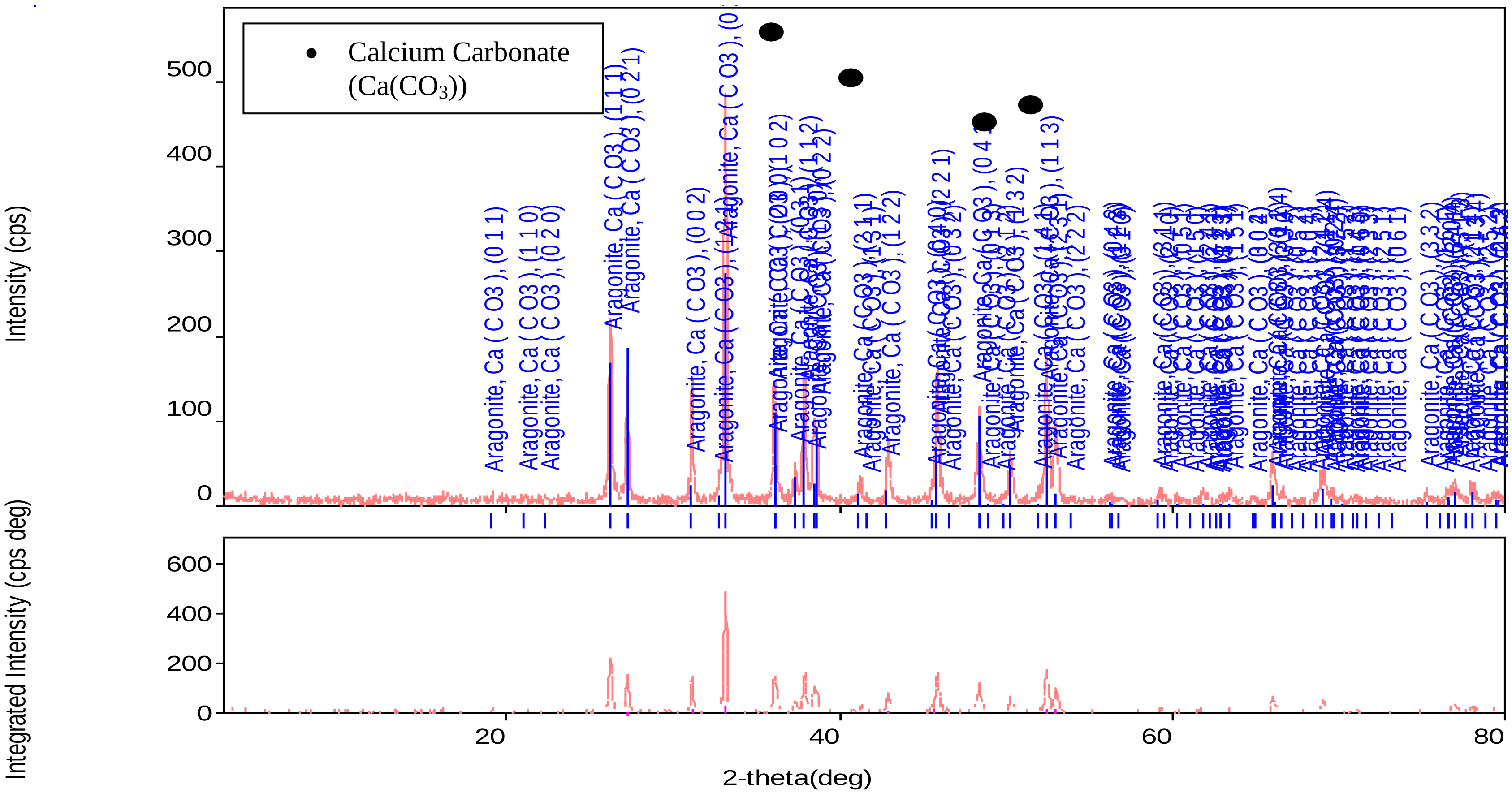
This CaO content is much higher than in other solid catalysts, for example cement clinker (66.61%) (Gimbun *et al*., 2013). According to Margaretha *et al*. (2012), CaO produced from calcination of waste shell is useful for the transesterification process. The CaO has high potential for use as base catalyst for transesterification due to its cheap and non-toxic properties (Endalew *et al*., 2011). Thus, the XRF analysis showed that the solid catalyst from *Papia undulata* shell waste has high potential to be used for biodiesel and biolubricant production.

4.2.3 X-Ray Diffraction (XRD)

XRD analysis was important to determine the cystalline structure of CaO compound in the catalyst. Figure 4.2 (a) reveals that the composition of uncalcined *Paphia undulata* shell waste mainly consists of orthorhombic aragonite calcium carbonate ($CaCO_3$), with peaks at 26.38°, 33.26°, 46.00° and 52.55°, and an absence of CaO. This is similar to a study by Birla *et al.*, (2012), which obtained the main $CaCO_3$ peaks in uncalcined snail shell catalyst analysis at peaks 26.24°, 33.17° and 45.89°, in the form of weak orthorhombic structure. Research related to crab shells also determined the absence of CaO peak in uncalcined catalyst (Boey *et al.*, 2009).

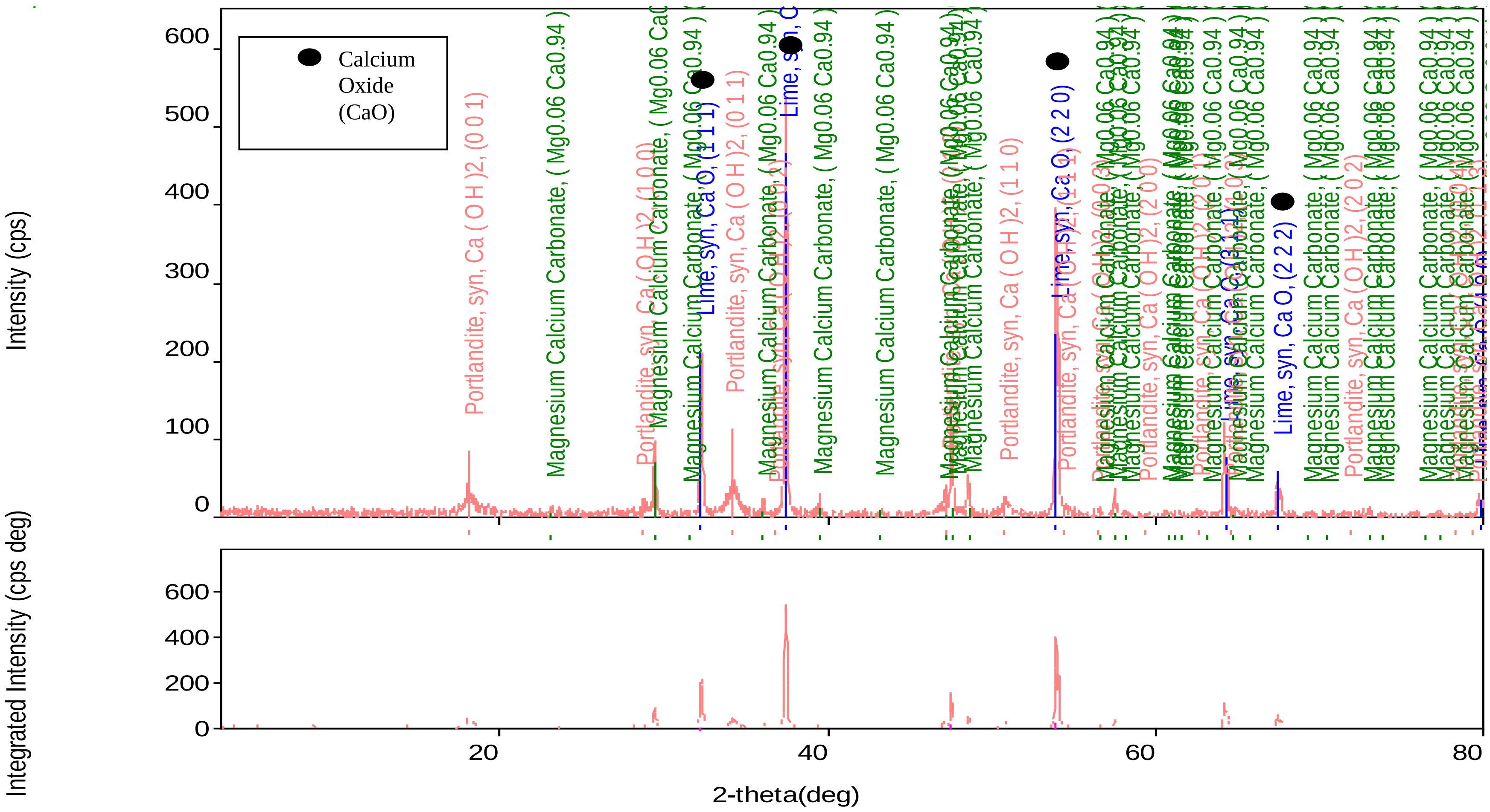
Meanwhile, Figure 4.1 (b) shows that identical CaO peaks appeared after calcination of *Paphia undulata* shell waste at 32.29°, 37.44°, 53.95°, and 64.22°. After calcination, the $CaCO_3$ was completely converted to activated CaO (Buasri *et al*., 2013). Therefore, the high and intense peaks mainly consisted of CaO. The same results were obtained by Birla *et al.*, (2011), where the intense sharp peaks of CaO appeared after calcination process at 32.2°, 37.3° and 53.8°. The single crystalline phase of CaO was also seen in another research by applying mollusk and egg shell waste after calcination (Viriya-empikul *et al.*, 2010). According to Boey *et al.*, (2009), the narrow and high intense peak represents the well crystallized structure of the CaO catalyst.

Theoretically, the $CaCO_3$ is seen as less applicable in transesterification process due to taking too much time to synthesise the product compared to CaO. Thus, the XRD analysis shows that the CaO clearly formed after thermal activation of the *Paphia undulata* shell, showing its potential as a catalyst in biolubricant production.



● Calcium Carbonate
(Ca(CO₃))
Intensity (cps)
500
400
300
200
100
0
Integrated Intensity (cps deg)
600
400
200
0
20
40
60
80
2-theta(deg)
Aragonite, Ca (C O3) , (0 1 1)
Aragonite, Ca (C O3) , (1 1 0)
Aragonite, Ca (C O3) , (0 2 0)
Aragonite, Ca (C O3) , (1 1 1)
Aragonite, Ca (C O3) , (0 2 1)
Aragonite, Ca (C O3) , (0 0 2)
Aragonite, Ca (C O3) , (1 2 2)
Aragonite, Ca (C O3) , (1 3 2)
Aragonite, Ca (C O3) , (1 1 3)
Aragonite, Ca (C O3) , (2 2 2)
Aragonite, Ca (C O3) , (3 3 2)

(a)



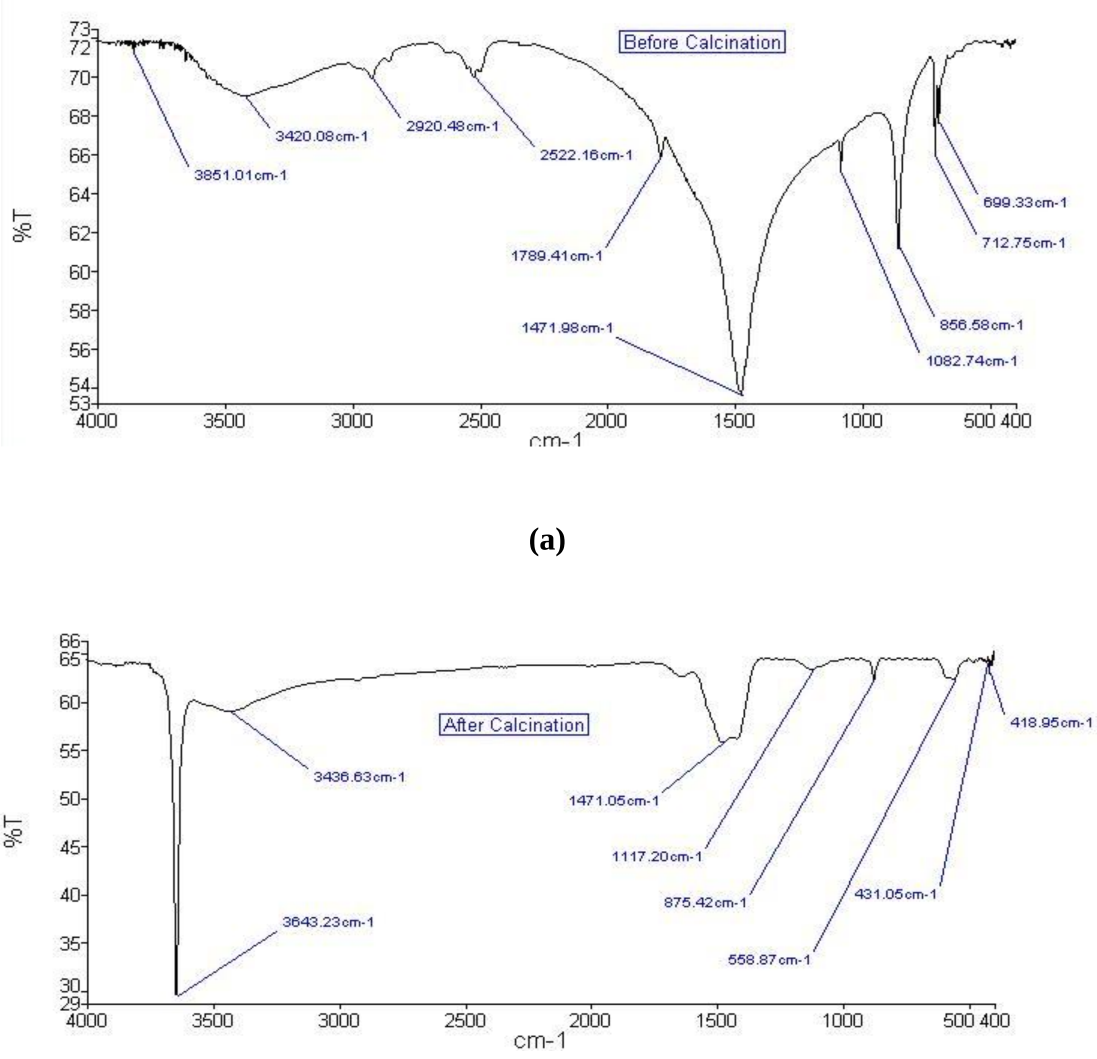
(b)

Figure 4.2. *Paphia undulata* shell (a) before calcinations, (b) after calcination

4.2.4 Fourier Transformed Infra Red (FTIR) Spectroscopy

The FTIR spectra of *Papia undulata* shell both before and after calcination are given in Figures 4.3. According to Sharma *et al* (2010), the major bands displayed for the uncalcined catalyst represent carbonate (CO_3^{2-}) molecules that have in-plane bending with modes in vibration. In this research, Figure 4.3 (a) shows that the major peaks of carbonate ion in uncalcined catalyst occur at 1471.96, 856.58 and 712.75 cm^{-1}. This is similar to raw snail shell that was implemented as catalyst, in which the peak of carbonate occurred at bands 3448.84, 1479.45 and 864.14 cm^{-1} (Birla *et al.*, 2011). Similar peaks were also observed by Margaretha *et al*., (2012) for the $CaCO_3$ molecule from *Pomacea* sp. shell, where bands occurred at 2513, 1420, 867 and 3117cm^{-1}.

Meanwhile, after calcination there were decreases in major bands of the IR spectra, occurring at 1471.05, 876.42 and 558.07 cm^{-1}, as displayed in Figure 4.3 (b). The changes to the IR spectra in the analysis is due to the complete conversion of $CaCO_3$ to CaO (Ngamcharussrivichai *et al.,* 2010). Since the catalyst surface was reduced in mass due to loss of carbonate (CO_3^{2-}) ion, the the molecules were shifted to higher energy, resulted in hydroxide (-OH) band occurring sharply (Birla *et al*., 2012). In this research, a new weak peak occurred after calcination, representing hydroxide (-OH) band which was observed at 3643.23cm^{-1}. The findings in this research on calcined catalyst are supported by research that was done by Margaretha *et al*., (2012) where the hyroxide (-OH) band was obtained at band 3620 cm^{-1}.



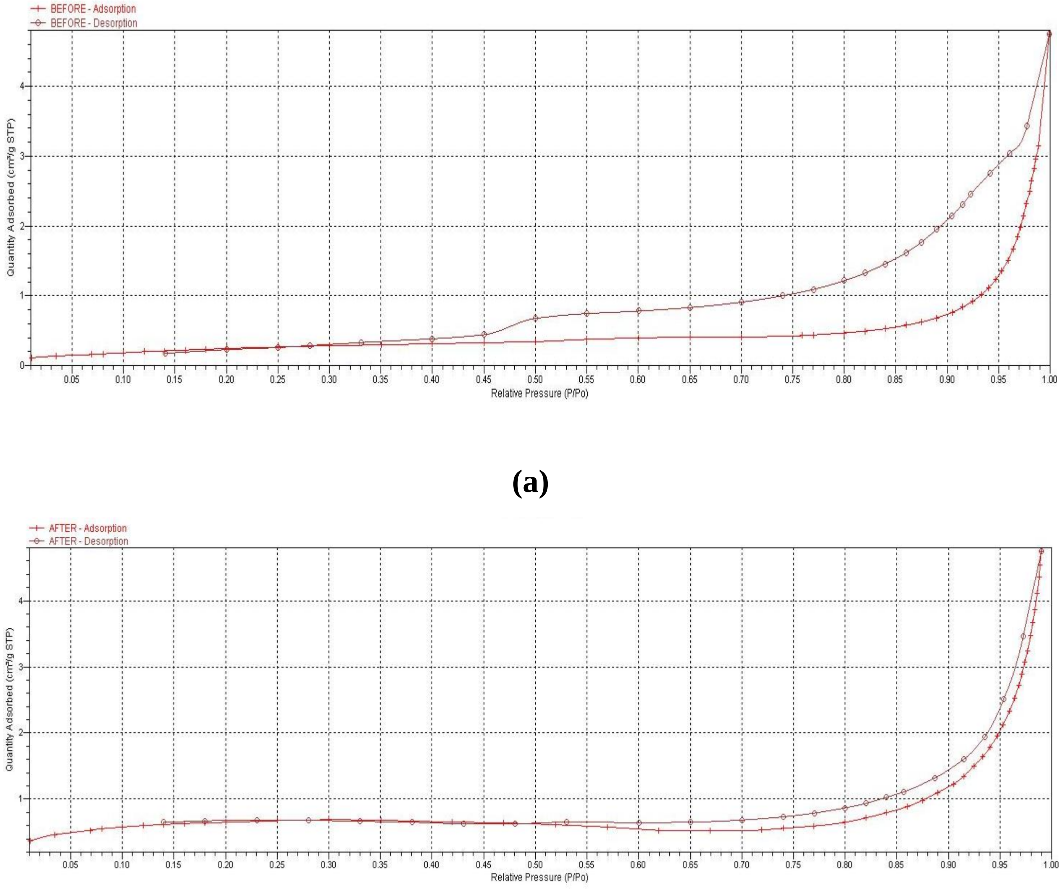
(a)

(b)

Figure 4.3. FTIR spectra of *Paphia undulata* shell (a) before calcinations , (b) after calcinations.

4.2.5 Physisorption of Nitrogen Analysis

The major roles in catalyst activity are specific surface area and active sites. Theoretically, the specific surface area of a catalyst is determined by physical adsorption of gas on the solid surface using Brunauer-Emmett-Teller (BET) equation. Figure 4.4 (a) shows the standard isotherm of nitrogen adsorption and desorption analysis for *Paphia* *undulata* shell waste before the calcination process. Meanwhile, Figure 4.4 (b) illustrates the same analysis, but for after the calcination process.



(a)

(b)

Figure 4.4. Nitrogen adsorption and desorption analysis of *Pahia undulata* shell (a) before calcinations, (b) after calcination.

The BET surface area of *Papia undulata* shell before calcination was determined to be 0.9482m²/g, and after calcinations it increased to 2.1290 m²/g. This comparison proves that the calcination process helps in increasing the active sites for catalyst activity. Furthermore, the hysteresis curve on adsorption and desorption plots from Figure 4.4(b) indicates the presence of macropores structure in the catalyst where pore diameter was 312.53 nm. According to Sharma *et al.*, (2010), better diffusion between reactant and product molecules can be attributed to a high pore size.

Table 4.2 summarizes the surface area of widely applied heterogeneous catalyst derived from various natural resources in the transesterification process. The surface area of calcined *Papia undulata* shell is much higher compared to that of activated cockle shell and egg shell. The differences in surface area value of different catalyst were due to their individual material source and treatment (Watcharathamrongkul *et al*., 2010).

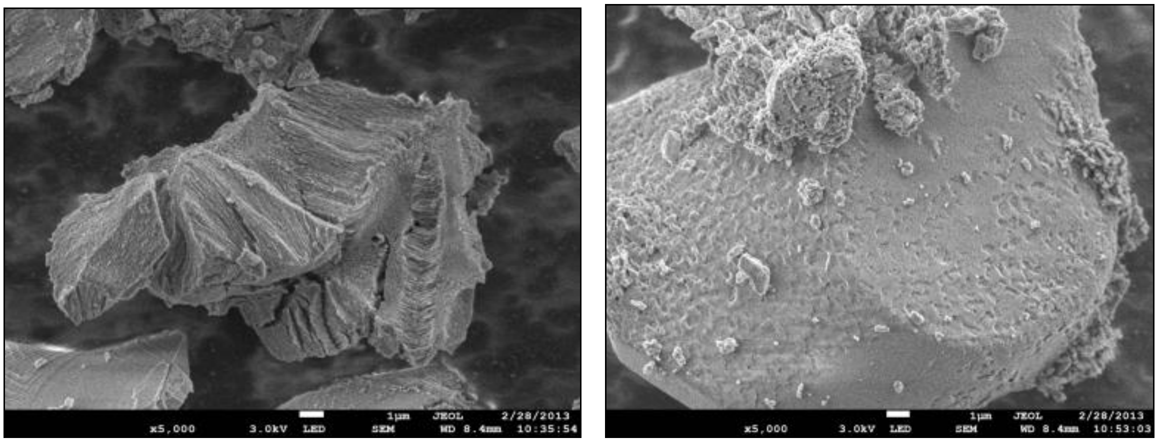
Meanwhile, for the pore volume of *Papia undulata* shell was 0.005986 cm^3/g that not much different when compared with Cockle shell and egg shell. The pore volume can determine the structure of non-porous material when the pore volume was less than 0.03 cm^3/g (Watcharathamrongkul *et al*.,2010).

Table 4.2 Summarized Texture Properties

Source of Catalyst	**Calcinations Temperature (°C) and time (h)**	**BET Surface Area (m^2/g)**	**Pore Volume (cm^3/g)**	**Reference**
Paphia undulata shell	680°C, 2h	2.1290	0.005986	This work
Cockle Shell	850°C, 40 min	1.56	0.00492	Rashidi *et al*., (2011)
Egg shell	800°C, 2h	1.1	0.005	Viriya-empikul *et al*., (2010)

4.2.6 Scanning Electron Microscopy (SEM)

The SEM analysis was done to determine the surface topology of catalyst from *Papia undulata* shell waste, and the result is shown in Figure 4.5. Figure 4.5(a) shows the image of the catalyst surface before calcination, where it was determined to have a rough and disordered surface with low porosity structure. After the catalyst was activated by heating with a furnace at 680°C for 2 hours, which is known as the calcination process, the surface structure of the catalyst showed changes. Figure 4.5 (b) illustrates a relatively smooth surface with spherical particles of porous structure after the catalyst was activated. The structure is also similar to another mollusk shell, cockle shell (Rashidi *et al*., 2011). Furthermore, the analysis shows a grain-neck growth on the surface of catalyst after activation due to thermal decomposition during the calcination process. In this case, the increased surface area of the catalyst that occured after calcination resulted in a larger active site area for interaction between reactants during the transesterification process.



(a) (b)

Figure 4.5. SEM micrograph of *Papia Undulata* shell at 5,000x, (a) before activating, (b) after activating.

4.3 Synthesis of *Jatropha Curcas* Oil Methyl Ester (JCOME)

4.3.1 Fatty Acid Reduction of *Jatropha curcas* Oil

In order to reduce free fatty acid (FFA) levels in *Jatropla* curcas oil (JCO), a preliminary esterification treatment with acid catalyst must be carried out. Then, FFA determination process involving dilution with neutralized solvent was conducted, followed by titration process (Azhari *et al*., 2008). The reaction of acid treatment is as follows in Eq. 4.1.

$$\underset{\text{FFA}}{RCOOH} + \underset{\text{Methanol}}{CH_3OH} \longleftrightarrow \underset{\text{Water}}{H_2O} + \underset{\text{Methyl Ester}}{RCOOCH_3} \tag{4.1}$$

On the other hand, Bouaid *et al.,* (2012) states that a high FFA level of more than 1% promotes the saponification process, making it difficult to separate the product at the end of the alkali-transesterification process, resulting in decreased yield of the product. Meanwhile, Kulachate and Prachasanti (2009) found that acid treatment for biodiesel production not only reduced FFA level but also removed phosphatides that are known for acid degumming. Phosphatides tend to accumulate water in ester products. As JCOME would be applied to biolubricant production, it is important to remove water from ester.

Moreover, the product will become gel-like at the end of the process if the FFA level is not reduced. Thus, this section was done to determine the optimum condition for acid esterification of JCO through various catalyst concentrations, methanol to oil ratios and times of reaction.

4.3.1.1 Effect of Catalyst Concentration on FFA Yield

Previously, sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) have been widely applied in acid pretreatment of crude oil in order to reduce FFA value (Berrios et al., 2007, Fadhil et al., 2012). The concentration of catalyst used was dependent on the FFA level in crude oil, thus the effect of HCl concentration used as catalyst in this research was studied under constant conditions of 60°C reaction temperature, 1:6 molar ratio of methanol to JCO and half an hour reaction time.

Figure 4.6 illustrates that there was a high reduction of FFA value when the acid catalyst was applied. Unfortunately, the small amount of catalyst still did not reach less than 1% of FFA level. By then, after 1% w/w catalyst concentration, there was seen to be less than 1% of FFA. Even though the catalyst concentration was 2 w/w% of the oil, which was determined as the lowest FFA level, 1% w/w of catalyst was selected as the optimum condition due to being able to achieve less than 1% of FFA level in JCO. This step has also been established by Roces *et al.*, (2011) who succeeded in reducing FFA level in JCO by applying 1 w/w% of HCl as an acid catalyst.

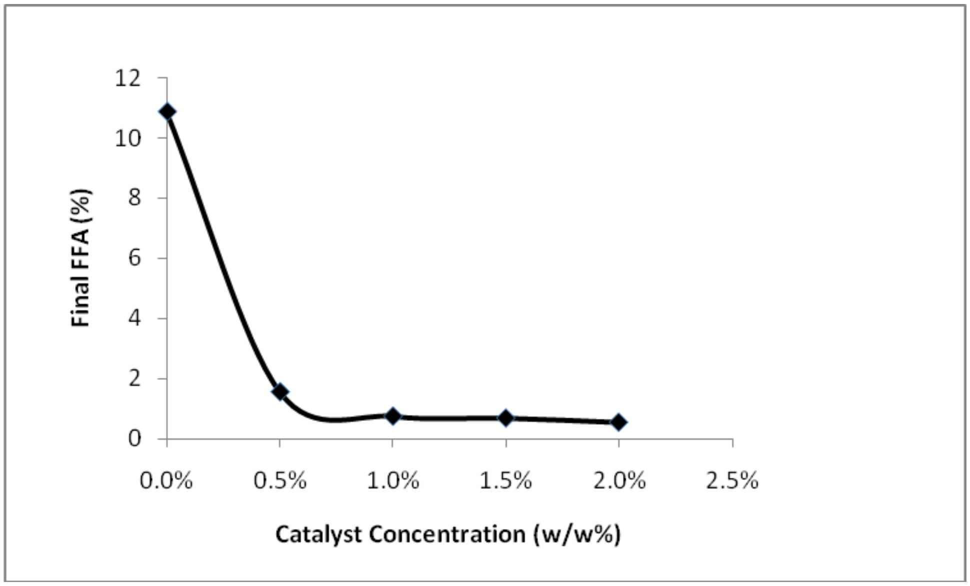


Figure 4.6. Effect of catalyst concentration on FFA yield.

4.3.1.2 Effect of Methanol to Oil Molar Ratio on FFA Yield

The effect of the molar ratio of methanol to oil on the FFA level of the mixture after half an hour reaction time at 1% w/w catalyst load and 60°C is shown in Figure 4.7. Based on the result, the FFA decreased sharply with increased molar ratio of methanol and oil. The lowest percentage of FFA was 0.63%, at 6:1 mol/mol of methanol to oil ratio.

Unfortunately, further increases after 6:1 mol/mol of methanol to oil ratio had insignificant effect on FFA level. Theoretically, excess methanol tends to accelerate forward reaction. However, the formation of water at the end of the reaction promoted the backward reaction in order to stabilize the process (Azhari *et al.*, 2008). This resulted in a slightly high FFA level after optimum methanol to oil molar ratio. Thus, 6:1 molar ratio of methanol to oil was selected for acid treatment process.

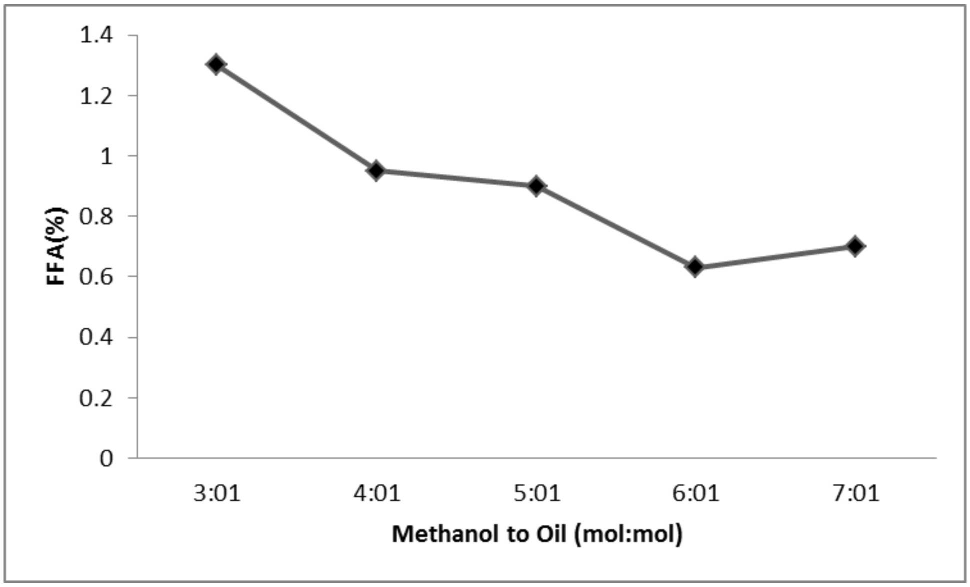


Figure 4.7. Effect of methanol to oil molar ratio on FFA yield.

4.3.1.3 Effect of Time on FFA Yield

The reaction time also plays a crucial role in the esterification of JCO to reduce FFA level. The parameters in this step remained constant with methanol to oil molar ratio of 6:1, HCl: oil ratio of 1% w/w, and reaction temperature of 60 ^{0}C. Figure 4.8 shows the effect of reaction time on acid pretreatment up to one hour of reaction. A sharp reduction of FFA was seen with increased time of reaction. This is due to a greater conversion of FFA to ester as time passes, thus reducing the FFA level (Azhari *et al.*, 2008). Then, when the reaction time had reached an hour, the FFA had reached maximum conversion and no more reduction was seen. Thus, an hour of reaction was enough to reduce the FFA level, after which it remained unchanged.

Based on the optimum conditions, three replications were done to confirm the optimum conditions before being applied to further processes. From experiment 1 to 3, it was determined that 60 ^{0}C, 6:1 methanol to oil molar ratio, 1% w/w of catalyst and 1 hour of reaction were the optimum conditions for successfully reducing the FFA level, and they were applied for further processes in JCOME production.

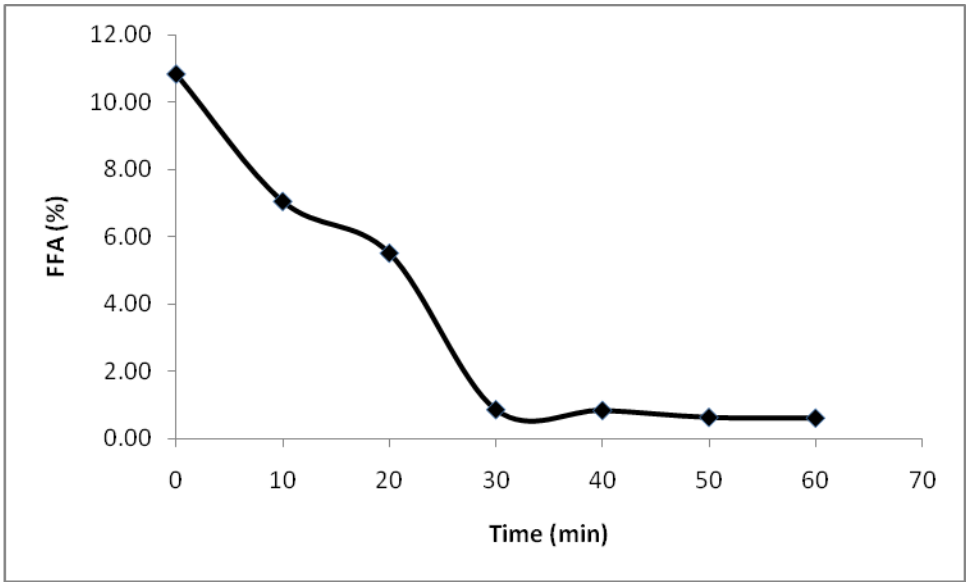


Figure 4.8. Effect of time on FFA yield.

4.3.2 Transesterification Process of Jatropha Curcas Oil (JCO) to Jatropha Curcas Oil Methyl Ester (JCOME) (Biodiesel)

4.3.2.1 Effect of Methanol to Oil Molar Ratio

After pretreatment, the purified JCO with lower FFA level was proceed to the second stage which is the transesterification process. Thus, the effect of oil to methanol molar ratio was investigated in this research to determine the optimum methanol to oil ratio for applying *Paphia undulata* shell waste as solid catalyst. Theoretically, the transesterification process would require 3:1 molar ratio of oil to methanol to produce 3:1 molar ratio of JCOME and glycerol (Krishnan and Dass, 2012). Thus, the effect of molar ratio, ranging from 3:1 to 12:1, was determined, while maintaining reaction temperature at 60°C, reaction time at 1 hour and solid catalyst loading at 3 w/w %.

From Figure 4.9, there was seen an increase in JCOME yield from 79.2% to 91.67%, corresponding to an increase in molar ratio from 3:1 mol/mol to 6:1 mol/mol. Unfortunately, the yield of JCOME became slightly decreased after the 6:1 molar ratio, until it reached 86.57%. This is similar to findings by Fadhil *et al*., (2012), in which applied *Silybum marianum* L. seed oil for biodiesel production obtained the highest yield of 94% at 6:1 methanol to oil molar ratio. This result is also comparable with the effect of methanol to oil ratio on transesterification of palm oil biodiesel by applying *Pomeca* sp shell as catalyst where the highest yield of up to 86.63% was obtained at 7:1 methanol to oil ratio (Margaretha *et al.,* 2012). Meanwhile, the optimum methanol to oil ratio for biodiesel production by applying waste cooking oil using snail shell as catalyst was at 8.45:1 with a yield of 87.59% (Birla *et al.,* 2012). The result was slightly lower than the yield for JCOME due to differences in catalyst and oil characteristics.

While the usage of high molar ratio of methanol to oil tends to promote a shift to the right in the chemical reaction equilibrium in producing the end product, the usage of excess methanol may on the other hand affected the cost of production without giving any increase in yield. This is due to the recovery of methanol step at the end of the process that increases the cost of production. In addition, the reduced yields with high molar ratio of methanol and oil is due to dilution of glycerol form and catalyst by methanol (Yingying *et al*., 2012, Fadhil *et al.*, 2012). Besides that, reduction of viscosity was also discovered with increased molar ratio, thus affecting the physical properties of the biodiesel. Hence, from this result, the optimum molar ratio of methanol and JCO in JCOME production was determined to be at 6:1, with the high yield of 91.67%.

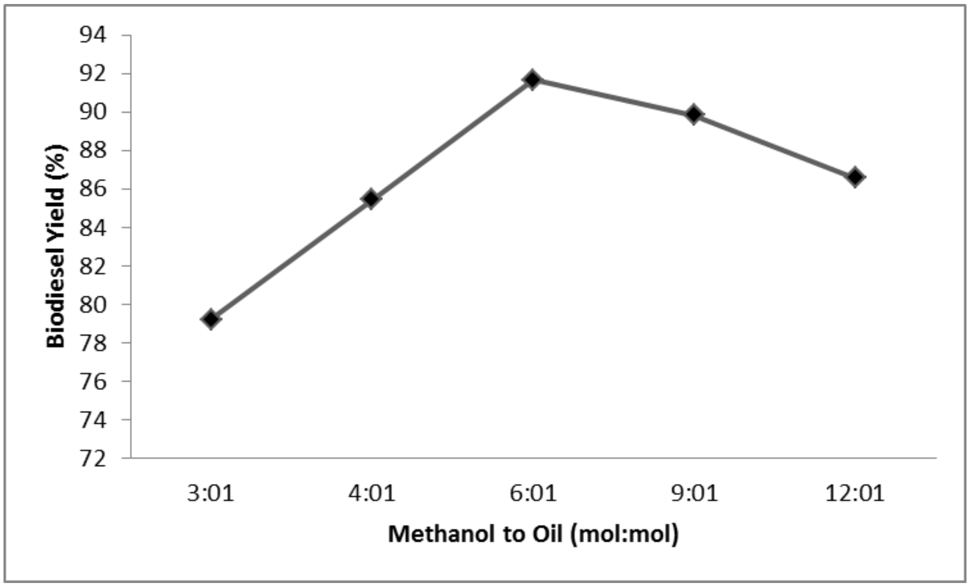


Figure 4.9. Effect of methanol to oil molar ratio on JCOME (biodiesel).

4.3.2.2 Effect of Catalyst Loading

Figure 4.10 represents the effects of catalyst loading from 1 to 5 w/w % on JCOME production at constant reaction conditions of 60°C temperature, 2 hours reaction time and methanol to oil ratio of 6:1. In order to achieve a desirable reaction, the catalyst plays a crucial role in creating an alternative reaction pathway, in addition to lowering the activation energy for molecule reaction. During the reaction, the transition state is the highest-energy state in the system. Thus, the catalyst is added to reduce the transition state energy and promote production. The result shows that with an increased catalyst amount, the biodiesel yield also increases until a maximum JCOME yield of 91.67%, at 4% w/w catalyst amount. Then, above the optimum catalyst loading level, the production yield decreased slightly to 90%.

This result is supported by Margaretha et al., (2012) which obtained optimum biodiesel production using 4% w/w calcium oxide with *Pomeca* sp. shell as catalyst, in which after reaching the optimum level there was a constant yield of production. According to Kozua and Hidaka (2012), CaO basic site from solid catalyst has the tendency to transform alcohol group into nucleophile molecule, which is more active, and attach carbonyl group to triglyceride, forming alkyl ester and glycerol. Thus, when there is an insufficient amount of catalyst, there is a high chance triglyceride will not react with methanol to form ester. This will result in an incomplete reaction between the reactants (Encinar *et al.,* 2010).

On the other hand, Pedavoah (2010) states that the decreased amount of ester yield with the increased amount of base catalyst is due to formation of high amounts of soap in the product. In addition, the reason for the slight decrease in JCOME yield with increased catalyst loading in the reaction is due to increased viscosity of the medium reaction, resulting in reduced interaction between catalyst and reactant (Zhang *et al.,* 2010). Despite an increased amount of catalyst in the reaction, there was seen a reduction in the product yield due to the limited amount of reactant used to control the reaction process. It was also seen that the increased catalyst loading caused the formation of bulky particles of catalyst which reduced the contact surface area of the catalyst. In conclusion, the results suggest that the optimum catalyst loading for transesterification of JCOME using *Papia undulata* shell as solid catalyst is at 4% w/w.

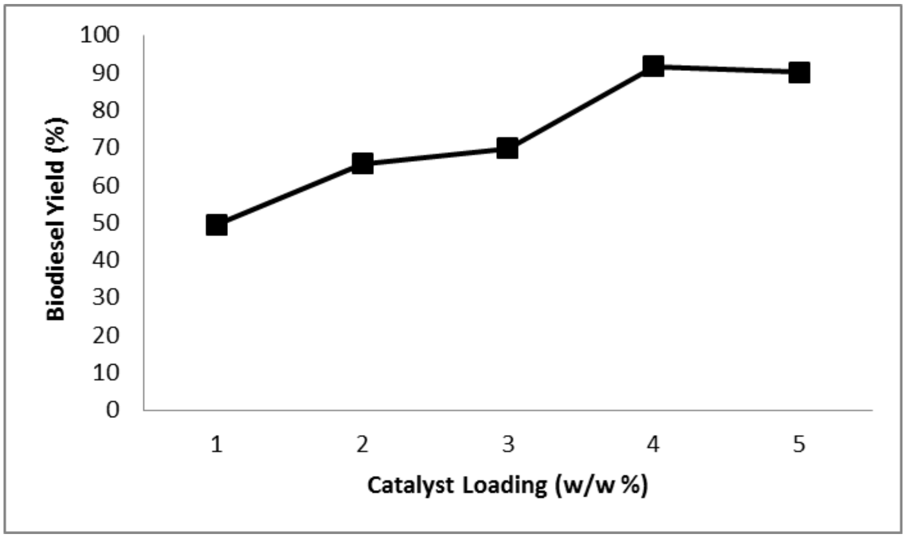


Figure 4.10. Effect of catalyst loading on JCOME (biodiesel).

4.3.2.3 Effect of Reaction Time

The influence of time taken by the reaction was studied in this research for better yield production of JCOME to use as raw material in biolubricant. To study the effect of reaction time on JCOME production, the optimum temperature from previous study, which is 60 °C, was applied with constant methanol to oil ratio (6:1) and 4% w/w catalyst loading, at different reaction times ranging from 1 to 5 hours.

Figure 4.11 demonstrates that the optimum transesterification time for production of JCOME was 3 hours, with a high production yield of 92.67%. This result is parallel with findings by Birla *et al*., (2011) that used catalyst derived from snail shell, which found that 8 hours of reaction was needed to achieve 87.28% yield of production. During the first few hours of reaction, the reaction rate was slow due to dispersion of interactions between molecules still in progress.

Meanwhile, Viriya-empikul *et al*., (2010) discovered that only 2 hours of reaction was needed to achieve more than 90% yield of production when using mollusk and egg shell as catalyst. This shows that the optimum reaction time is different for other catalysts, and in this case was due to the higher surface area of the catalyst used in that research. Besides that, another factor is that the acid catalyst esterification process is much slower than the base catalyst transesterification process (Omotoso *et al.,* 2011).

This research also discovered that above the optimum point, yield of JCOME was decreased slightly to 91.09%. Leung *et al.,* (2010) states that reduction in product yield is due to backward reaction, causing fatty acid to produce more soap. In addition, the reaction had reached the equilibrium state, which decreased the product yield (Watcharathamrongkul *et al.*, 2012). Thus, the optimum reaction time for JCOME production was determined to be at 3 hours.

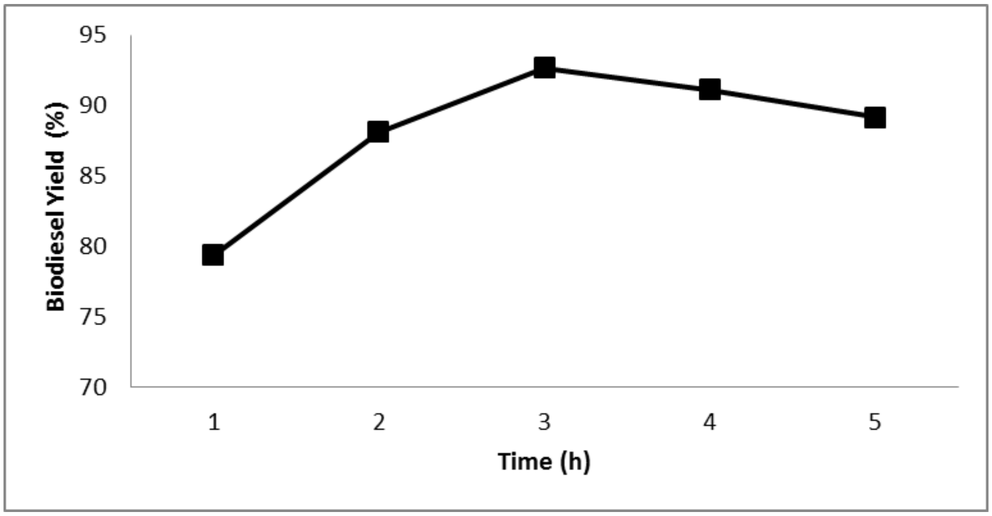


Figure 4.11. Effect of reaction time on JCOME (Biodiesel).

4.3.2.4 Effect of Temperature

The reaction temperature for JCOME production is important because the optimum reaction temperature is necessary for better collision and reaction kinetics. To determine the effect of temperature on JCOME production, research was carried out at variable temperatures with constant methanol to oil molar ratio (6 to 1), reaction time (3 hours) and *Papia undulata* solid catalyst loading (4% w/w). The maximum yield of JCOME was 93.33% at 60°C, and the rest of the results are shown in Figure 4.12. The yield of JCOME decreased slightly above the optimum temperature. The optimum reaction temperature of 60°C has also been obtained for synthesis of biodiesel from *Jatropha curcas* oil with 92.7% yield of ester (Roces *et al.*, 2011). Meanwhile, Fadhil *et al*., (2012) also succeeded in achieving 94% yield of biodiesel at 60°C.

This result can be compared with research by Gimbun *et al*., (2013), in which the optimum temperature for biodiesel production using lime stone base catalyst was 65°C. Theoretically, a high temperature is able to supply sufficient energy for collision between reactant molecules that promote towards maximum reaction (Pedavoah, 2010). Unfortunately, temperatures above 60°C tend to accelerate the saponification of triglyceride before completion of the transesterification process (Ramadhas *et al*., 2005). Besides that, methanol which has a boiling point of 64.7°C will vaporize at that temperature, resulting in decreased yield (Pedavoah, 2010). In addition, the product tends to be darkened at higher temperature reaction due to the occurrence of polymerization.

On the other hand, research by Otomoso *et al.,* (2011) that compared Jatropha oil with palm oil in production of biodiesel discovered that *Jatropha curcas* oil obtained the highest yield of 75.3% at 65°C. This is much lower than the yield obtained in this research when the temperature was increased from 60°C. According to Leung and Guo (2006), the optimum temperature for biodiesel production depends on the fat and the oil used. Moreover, temperature higher than the optimum condition promotes the occurrence of reverse reaction, where the equilibrium state becomes constrained from increasing yield (Yingying *et al*., 2012). Thus, this research found that the optimum temperature for JCOME production was at 60°C.

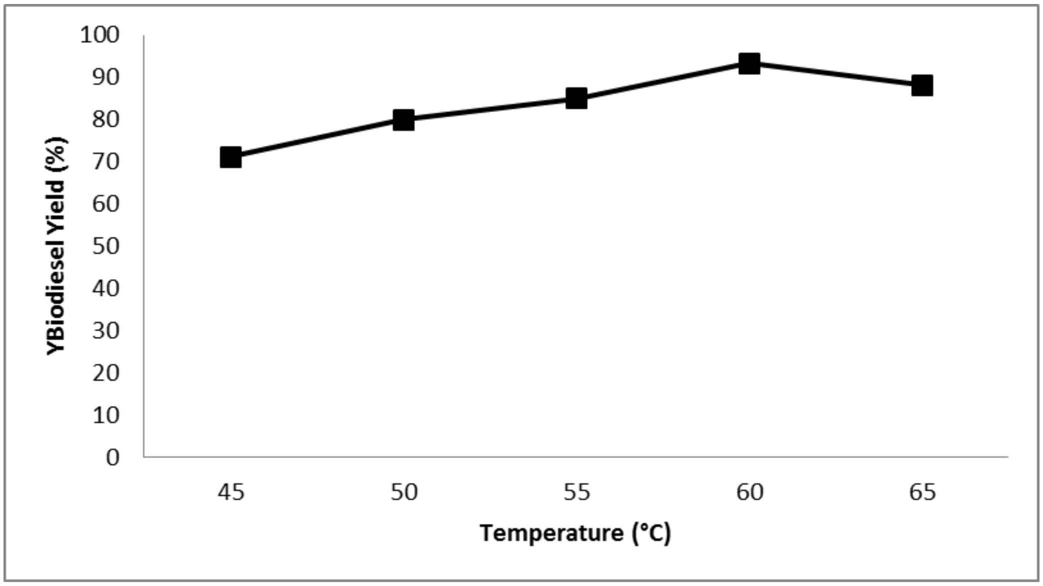


Figure 4.12. Effect of Temperature JCOME (Biodiesel).

4.3.3 Physico-chemical Properties of JCOME

The performance of biodiesel depends on the quality specifications of production that must follow the standard provided (Nakpong and Woothikanokkhan, 2010). The chemical properties of JCOME were determined following the American Standard for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels (ASTMD6751) and European Standard Biodiesel (EN14214:2003). In the previous section, the optimum conditions for JCOME production were as follows: methanol to oil ratio of 6:1, 1 wt/wt % of HCl and 1 hour reaction time for the first step. This was followed by the second step that used methanol to oil ratio 6:1, 4 w/w % *Paphia undulata* waste shell at 60^0C and 3 hours of reaction time. The biodiesel produced at these conditions were analyzed further to determine the physical properties of the product based on the ASTM standard and the results are shown in Table 4.3.

Table 4.3 Comparison between biodiesel produced with standard biodiesel

Properties	**Unit**	**Limit Biodiesel (ASTMD6751)**	**European Standard (EN14214:2003)**	**Crude JCO**	**JCOME from this work**
Density	g/m^3	-	860-900		900
Viscosity	c.s.t	1.9-6.0	3.5-5.0	52	3.9
Acid value	mg KOH/g	0.50max	0.50max	12.4	0.40
Pour Point	^{0}C	-15 to 10	-	-	-1

The results indicate that the JCOME viscosity decreased to 3.9 cst after the alkali-transesterification process of JCO (52 cst). The viscosity value of JCOME from this reseach was slightly lower than the viscosity value of biodiesel from waste frying oil, which was 4.61 cst (Charoenchaitrakool and Thienmethangkoon, 2011). The differences are because viscosity increases with molecular weight, but decreases with heating effect (Omotoso *et al.*, 2011). In this case, viscosity becomes the main concern where the increased viscosity tends to promote the occurrence of problems when applied as engine oil, such as deposition and jelliking due to contamination. From this research, the viscosity of JCOME fell within the standard limit range american standard (ASTMD6751) and European standard (EN14214:2003) of biodiesel.

Meanwhile, the acid value for this research was determined following ASTM D 974. Biodiesel with high acid value tends to increase deposition in the fueling system and corrosion of metal surfaces. In this research, the acid value was obtained as 0.40 mg KOH/g, and this is within the standard limit of ASTMD6751 and EN14214:2003. Thus, biodisel derived from *Jatropha curcas* oil has less tendency to cause wear and tear in fuel systems and storage tanks.

In addition, the pour point was determined following ASTM D5950-02. From the result, JCOME from this research was shown to follow the provided standard, making it suitable for application in tropical and moderate temperature regions.

4.4 Development of Biolubricant Synthesis Condition from Jatropha Curcas Oil Methyl Ester (JCOME)

4.4.1 Effect Of JCOME to TMP Molar Ratio on Biolubricant Production

The effect of JCOME to TMP molar ratio on biolubricant production is shown in Figure 4.13. During this study, the other conditions were kept constant at 100^0C reaction temperature, 50 mbar pressure, 2% w/w solid catalyst and 2 hours reaction time. Prior to this experiment, the product consisted of monoester (ME), diester (DE) and triester (TE), whereby ME and DE were formed first before the desired product, which is TE (Ghazi et al., 2009).

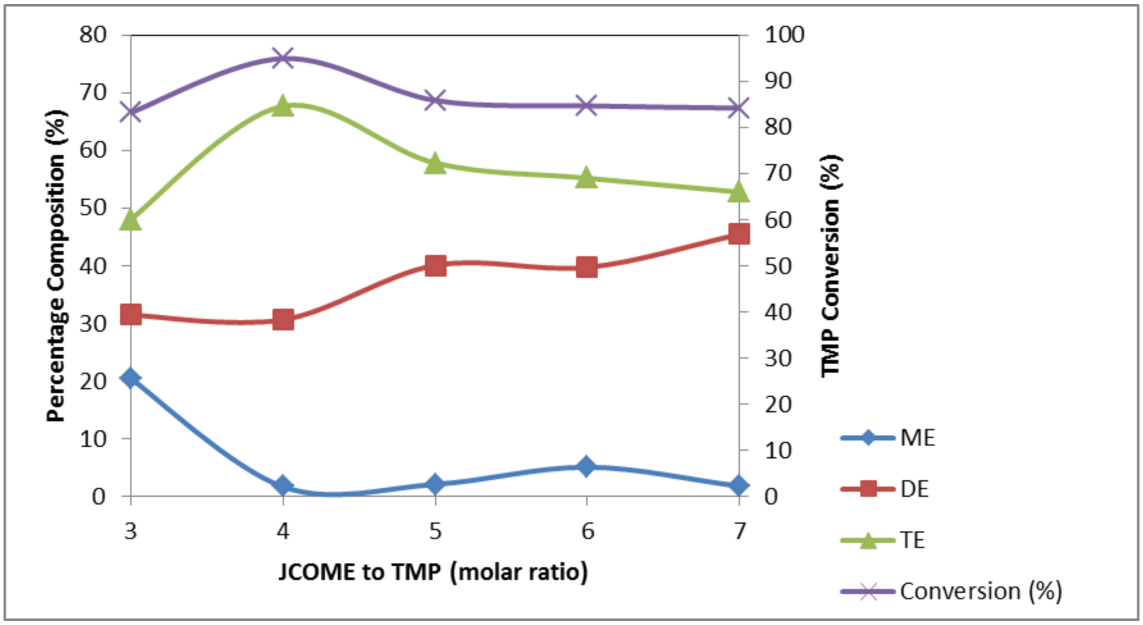


Figure 4.13. Effect of JCOME to TMP ratio on biolubricant production.

As expected, Figure 4.13 indicates that the yield of TE composition increased until it reached the optimum value of 4:1 JCOME to TMP molar ratio, where the highest TE composition was obtained (67.66%), with conversion of 94.92%. ME composition was also produced at the lowest percentage when using the optimum value. This shows that all the

JCOME used was converted to DE in order to produce TE. Increased JCOME molar ratio promoted accelaration of the equilbrium reaction to produce TE.

Unfortunately, TE composition became slightly decreased when the JCOME to TMP molar ratio was at 5:1, which was above the optimum value, with 57.81% composition and 85.83% conversion. The decrease is due to limited surface area of the heterogeneous catalyst used. Chang *et al.*, (2012) also found that this hindrance caused a reduction of mass transfer rate, which was constrained by the surface area of the catalyst.

From this pattern, it was shown that increasing the JME to TMP molar ratio higher than 4:1 molar ratio had no significant effect due to the TMP amount limiting the reaction. Conversion of the limiting reactant also showed insignificant changes at JCOME to TMP molar ratio higher than 4:1. Previous reports have also stated that increased methyl ester molar ratio had negligible effect on TMP ester production (Sulaiman *et al.*, 2007; Widayati *et al.*, 2014). Thus, from this study, it was shown that 4:1 JCOME to TMP molar ratio was enough to produce a high yield of TMP ester.

4.4.2 Effect of Catalyst Loading

To determine the effect of catalyst loading, an experiment was carried out with 0, 1, 2, 3 and 4% catalyst loading based on the total weights of JCOME and TMP. The other condition were kept constant at 2 hours reaction time, temperature 100°C and 4:1 JCOME to TMP molar ratio.

Results from Figure 4.14 show that at 0% catalyst loading, there was no conversion of product. This is because the catalyst was used to fasten the reaction. Without a catalyst, more than 2 hours of reaction was needed to produce the product. This point is important for determining catalyst reactivity with the reactant.

From this experiment, conversion of reaction was increased from 84.92% at 1 w/w % of catalyst until reaching the highest amount of conversion when applying 3 w/w%

catalyst (90.66%), with 69.21% TE composition. However, further increases of catalyst loading above 3 w/w% resulted in slightly decreased TE composition of 68.947% and conversion of 89.17%. This was caused by increased solid content in the medium reaction when the catalyst amount was higher than the optimum level. The medium that contains reactant and catalyst can become too viscous, leading to a mixing problem occurring, resulting in decreased yield of product. Thus, the optimum catalyst amount of 3 w/w% must be employed to avoid these problems.

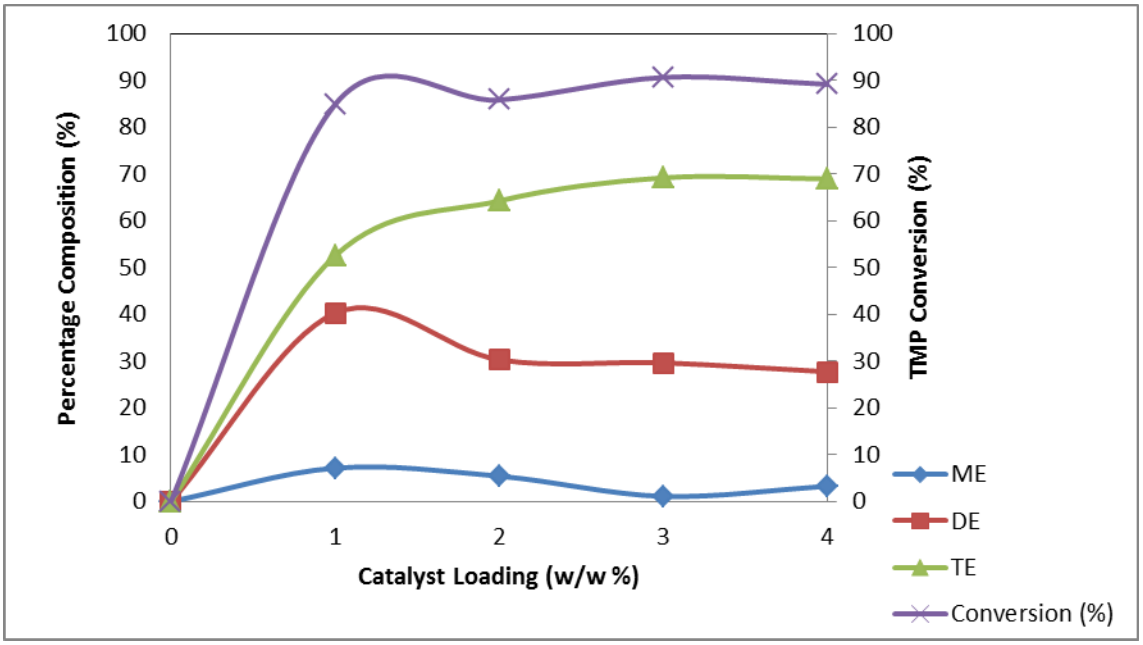


Figure 4.14. Effect of catalyst loading on biolubricant production.

4.4.3 Effect of Time

The effect of reaction time (1 to 5 hours) on the product yield of biolubricant production with *Paphia undulata* shell waste catalyst was investigated as shown in Figure 4.15. Meanwhile, other parameter conditions were kept constant at 4:1 JCOME to TMP molar ratio, 3 w/w % catalyst loading, 50 mbar pressure and 110 ^{0}C temperature. It can be seen that as the reaction time was raised from 1 hour to 3 hours, the TE composition increased until it reached 72.3% with conversion of 95.6 %. Above 3 hours, the conversion amount also became higher at more than 90%. Unfortunately, the TE composition decreased slightly to 65.7%, with the ME composition lower than 5%. This shows that reversible process has occurred to achieve equilbrium state of reaction during the conversion of DE to TE. Besides that, hydrolized phenomenon has occurred, which promoted the final product TE to reconvert to ME and DE.

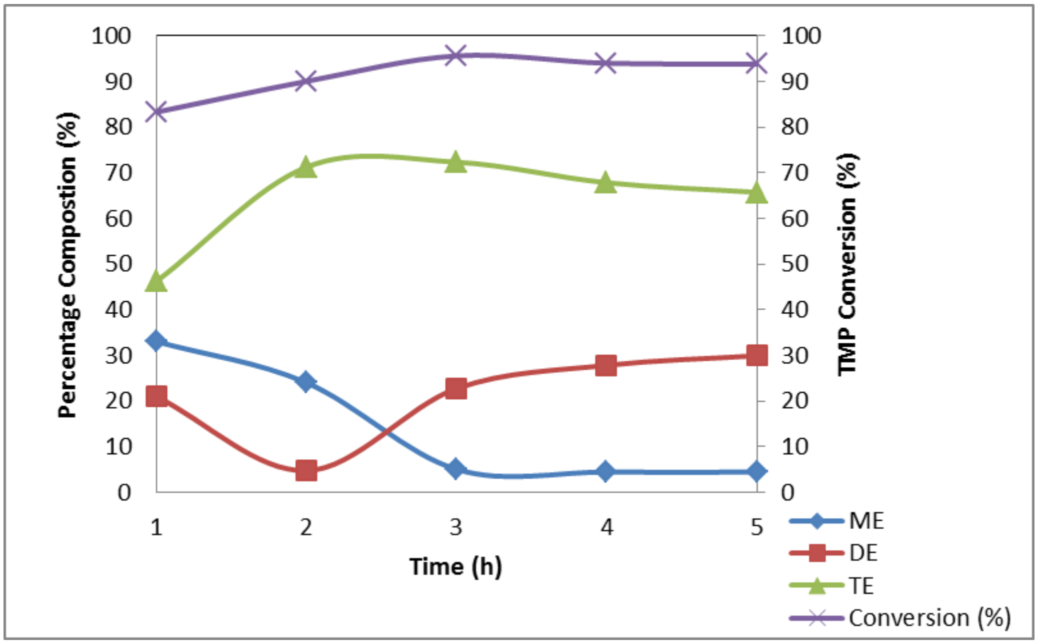


Figure 4.15. Effect of time reaction on biolubricant production.

Furthermore, after longer than 3 hours of reaction, the reaction mixture was also seen turned to dark colour. According to Chang et al., (2012), polymerization occurs when reaction time is extended longer than the optimum time. From this result, it can be determined that the most suitable reaction time is at 3 hours.

4.4.4 Effect of Temperature

The reaction temperature plays a crucial role in biolubricant production. Thus, a preliminary experiment was done to see the effect of temperature at 90 to 130 ^{0}C, with other conditions kept constant at 4:1 JCOME to TMP molar ratio, 3 w/w % catalyst loading, 50 mbar pressure and 3 hours reaction time. The curve from Figure 4.16 indicates that the conversion of TMP and TMP ester composition occurred simultaneously.

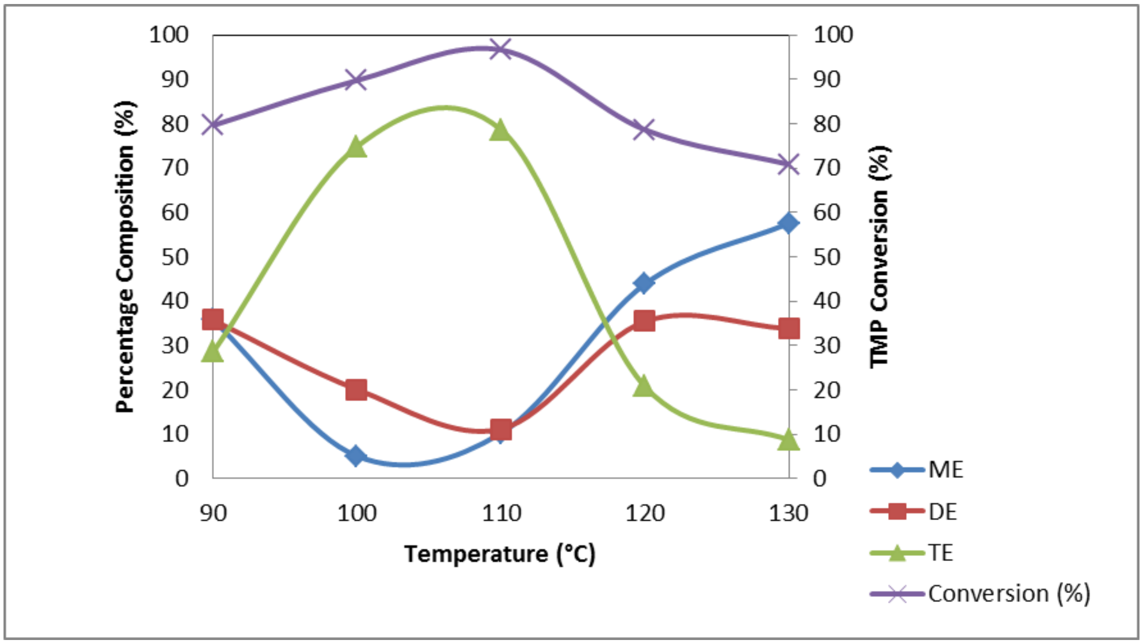


Figure 4.16. Effect of temperature reaction on biolubricant production.

Initially, the conversion of TMP ester with increased reaction temperature until reaching 110 ^{0}C, in which the highest conversion was determined to be 96.66% and TE composition was 78.67%. Rapid depletion of ME and DE composition also occurred, with less than 10% composition, in contrast to the very high composition of TE which became the main product.

Above that point, the conversion was decreased as well as TE composition. The same trend was also obtained in a previous study using sodium methoxide as solid catalyst, where the yield started to decrease after further increases in temperature above the optimum level (Chang *et al.,* 2012). This is due to the evaporation of volatile components that lead to the supression of forward reaction from DE to TE.

On the other hand, Sulaiman *et al.,* (2007) determined that the optimum temperature condition for biolubricant production from palm oil methyl ester (POME) was at 120 ^{0}C. This is slightly higher than the optimal temperatures in this research which used *Jatropha curcas* oil methyl ester (JCOME), due to differences in the catalytic activation energy of the catalysts used. The catalysts also have different capabilities at avoiding sintering, which can occur at high temperature. The sintering process is when the catalyst fuses together and forms 'cake' that decreases catalytic activity.

Even though a high temperature is required for better diffusion between reactant and solid catalyst, if the temperature is too high it tends to promote saponification in the mixture which reduces the catalytic reactivity. This results in decreased conversion of TMP as well as product composition. Besides that, increasing the temperature higher than the optimum level does not play a crucial role in diffusion, due to molecules already being at the optimum energy state for collision when the optimum temperature has been reached.

In addition, changes in end product colour were observed when temperature was increased higher than 120°C. According to Abu Bakar *et al*., (2007), oxidation of palm oil methyl ester (POME) caused the colour to change from yellowish to dark orange. Thus, from this observation, high temperature not only caused reduction in the product yield, but also disturbed the product appearance. Therefore, the optimum temperature was suggested to be at 110°C, which provided better yield.

4.5 Catalyst Reuseability

The *Paphia undulata* waste shell was investigated to determine whether the solid catalyst could be recycled after transesterification. The recyclability of the solid catalyst is a main concern in synthesized reaction of biolubricant due to the stability consideration for fast reactions demanded by industrial operations. From the result of the preliminary study as shown in Figure 4.17, the composition of TE was more than 50% after being recycled three times, before starting to decrease in the fourth cycle when the spent catalyst was used directly without treatment with any chemical apart from the drying process to collect white powder in the same condition before starting the experiment.

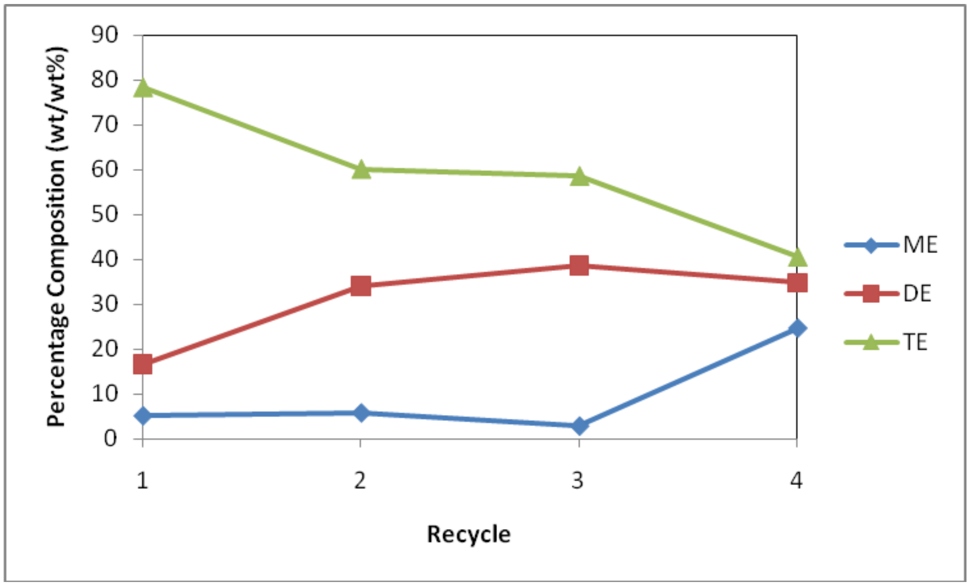


Figure 4.17. The composition of Jatropha biolubricant at various cycles.

The yield of TE composition was reduced from 78% to 40% due to catalyst deactivation. The deactivation of the catalyst cannot be avoided due to adsorption of H_2O from ambient atmosphere. The effect of deactivation of catalyst also can be seen from the forth cycle, DE much higher than TE due to catalyst unable to accelerate the reaction resulted incomplete reaction occur.

From Figure 4.18, which shows the results of XRD analysis of spent catalyst after the fourth cycle in biolubricant production. Calcium oxide that was contained in the catalyst was converted to calcium hydroxide $Ca(OH)_2$ after each cycle of reaction. Thus, from this experiment it was proven that the catalyst is stable and can be reused for three cycles of the biolubricant reaction by undergoing the drying process.

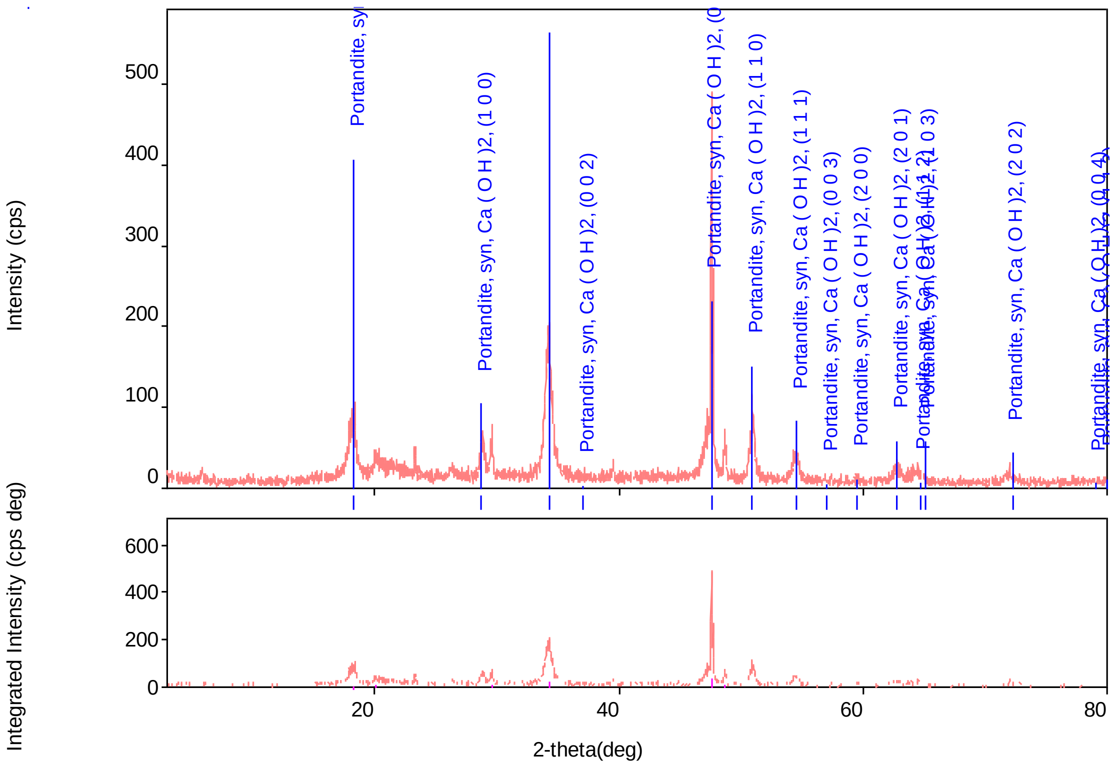


Figure 4.18. After the 4th Cycle.

4.6 Kinetics Model of Temperature Dependence

The experiment was carefully conducted to determine the reaction order and rate constant of *Jatropha* biolubricant transesterification. Theoretically, the rate of reaction can be determined by the decrease in the reactant concentration per unit of time or increase in the product concentration per unit of time (Pedavoah, 2010). Thus, from this research, the rate constant was determined from reduction of the concentration limiting reactant, which was trimethylolpropane (TMP). Figure 4.19 shows the percentage of TE composition by time from 0 to 180 minutes. A precautionary step was conducted by storing the sample at 0 ^{0}C in a cold room prior to analysis.

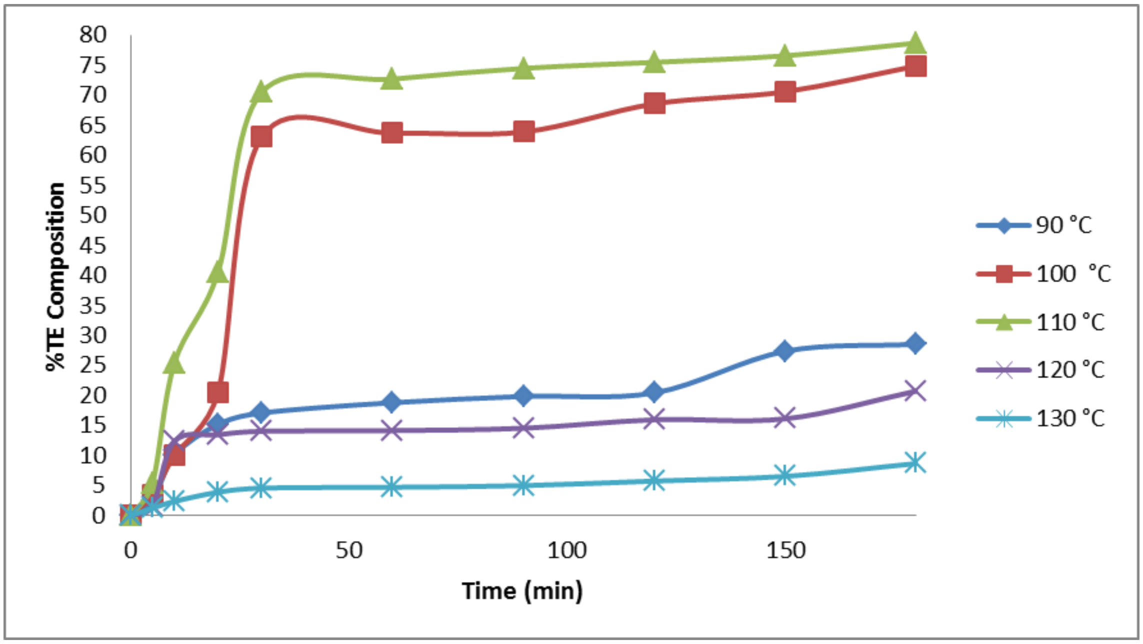


Figure 4.19. Percentage of TE composition with time.

From the curve, it was shown that various temperatures had significant effects on the reaction times of biolubricant synthesis. This phenomenon was determined from Figure 4.21 where the reaction at 130 ^{0}C was the slowest reaction compared to reactions at other temperatures. This observation was further supported by the fact that when using NaOH as catalyst, the rate of reaction became slower at 120 ^{0}C. This could be due to diffrences in catalyst amount and catalyst properties. It was also seen that the highest conversion rate was at 110 ^{0}C with 3 hours of reaction. On the other hand, the curve also indicates that the rapid reaction was seen in the first 30 minutes of reaction at various temperatures. Thus, it is appropriate to establish the reaction kinetics during this time period of the reaction.

In order to determine the order of reaction, a simple kinetic model was established by ignoring the intermediate products. There were a few assumptions that were made for this kinetics model. Firstly, the heterogeneous catalyst used was assumed to be in sufficient amount to shift the reaction toward equilibrium state while the concentration was constant, so it could be assumed to be insignificant. Secondly, in the single step transesterification process it is assumed that the excess amount of JCOME was constant and negligible. Meanwhile, the methanol product that was collected using vacuum pressure was found to favor single reaction step without any reversible process. Thus, the depletion concentration of limiting reactant (TMP) was analyzed to obtain reaction rate and kinetics order.

The collected result of TMP concentration was analyzed and fitted to the proposed rate law. The graph was plotted following first order (ln (Conc) against time) and second order (1/Conc against time) reaction rate. From Figure 4.20 and Figure 4.21, it is confirmed that the reaction followed second order of reaction, as a linear graph and high regression value were obtained.

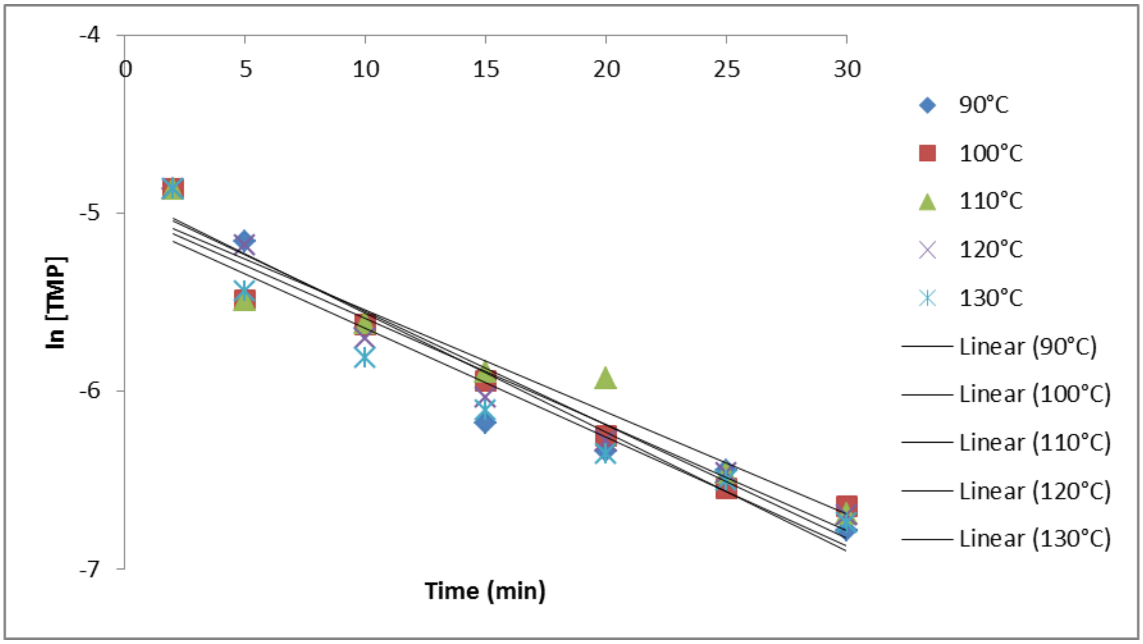


Figure 4.20. First order kinetic model.

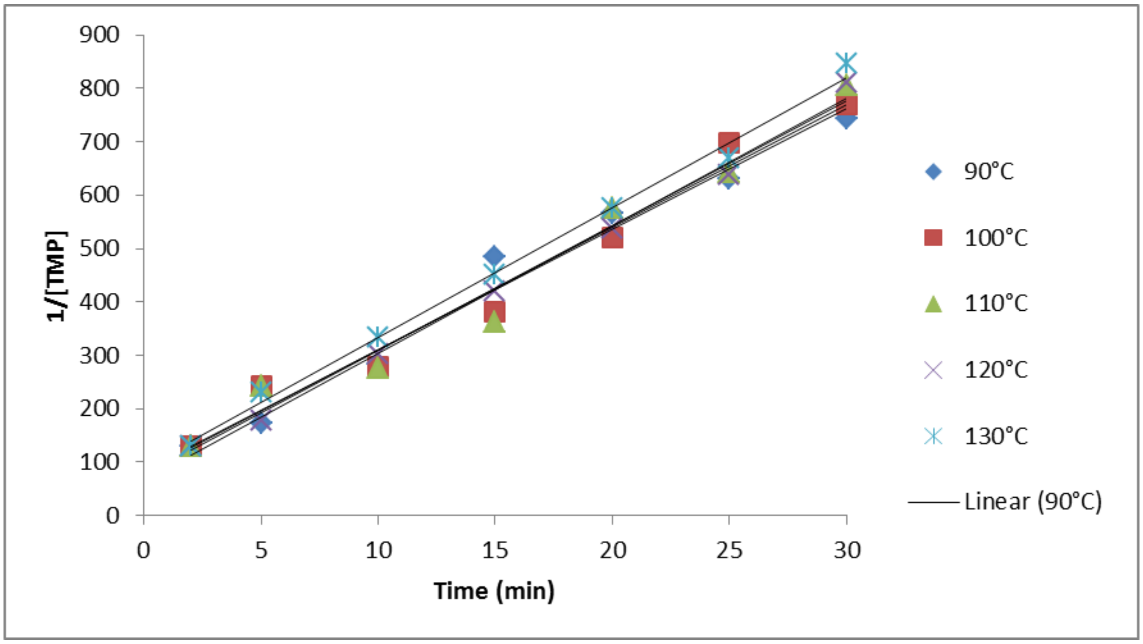


Figure 4.21. Second order kinetic model.

The overall rate constant for both first and second orders were deduced in Figures 4.22 and 4.23.

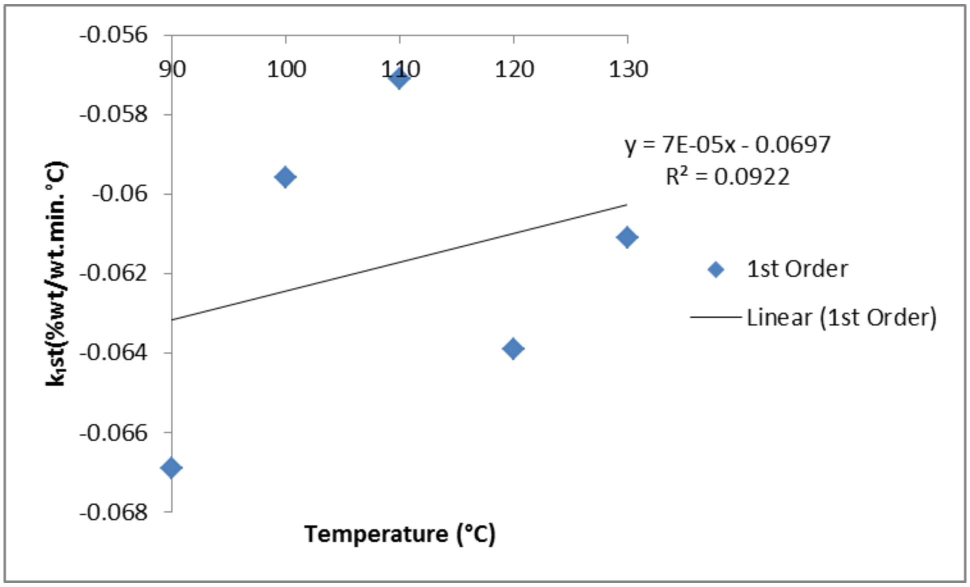


Figure 4.22. Overall First Order.

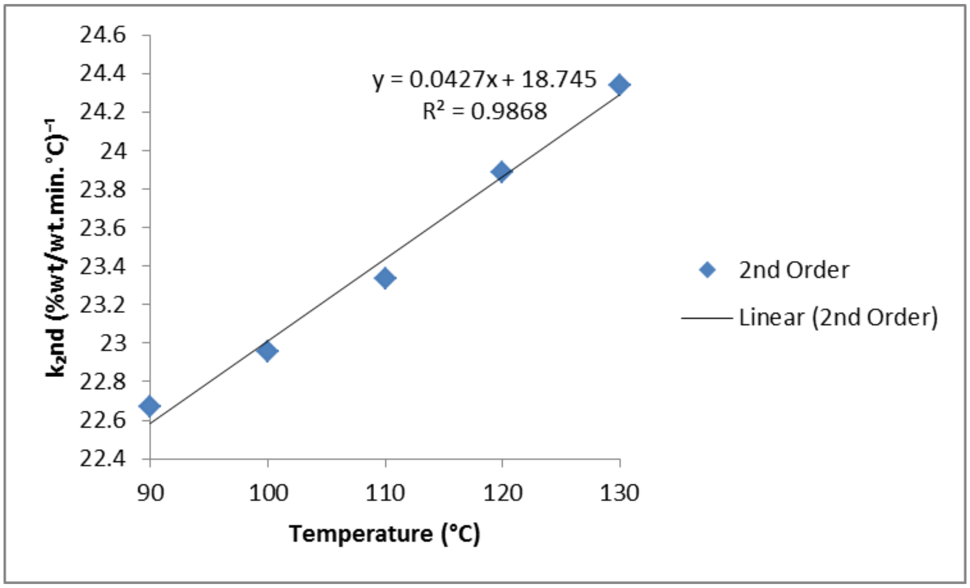


Figure 4.23. Overall Second Order.

Figure 4.23 presents the directly proportional rate of reaction with increased temperature. This also confirms that the reaction followed second order of reaction where R^2 was determined as 0.9868. Table 4.4 represents a comparison between first and second order rates of reaction at various temperatures and Table 4.5 shows a summary of both overall rates of reaction. Based on the overall rate of reaction, the second order rate of reaction was 0.0427 (%wt/wt.min.°C)$^{-1}$.

Table 4.4 Rate constant and regression value at various temperature

Temperature (°C)	**1st Order**	**R^2**	**2nd Order**	**R^2**
90	-0.0669	0.9478	22.671	0.981
100	-0.0596	0.9446	22.956	0.9789
110	-0.0571	0.9314	23.332	0.972
120	-0.0639	0.9577	23.889	0.9953
130	-0.0611	0.9307	24.337	0.9948

Table 4.5 Overall rate of reaction for first and second order of reaction

Rate of reaction	**1st Order**		**2nd Order**	
k_{TMP}	7x10^{-5} %wt/wt.min.°C	0.0922	0.0427 (%wt/wt.min.°C)$^{-1}$	0.9868

In addition, Arrhenius equation was applied to determine the influence of temperature on reaction rate where the rate constant was dependent on activation energy (Thiruvengadaravi *et al.*, 2009). Thus, by plotting the graph of log k against 1/T, the activation energy can be estimated from the graph slope (Resul *et al.*, 2012). The estimated value of activation energy is presented in Figure 4.24 and Table 4.6.

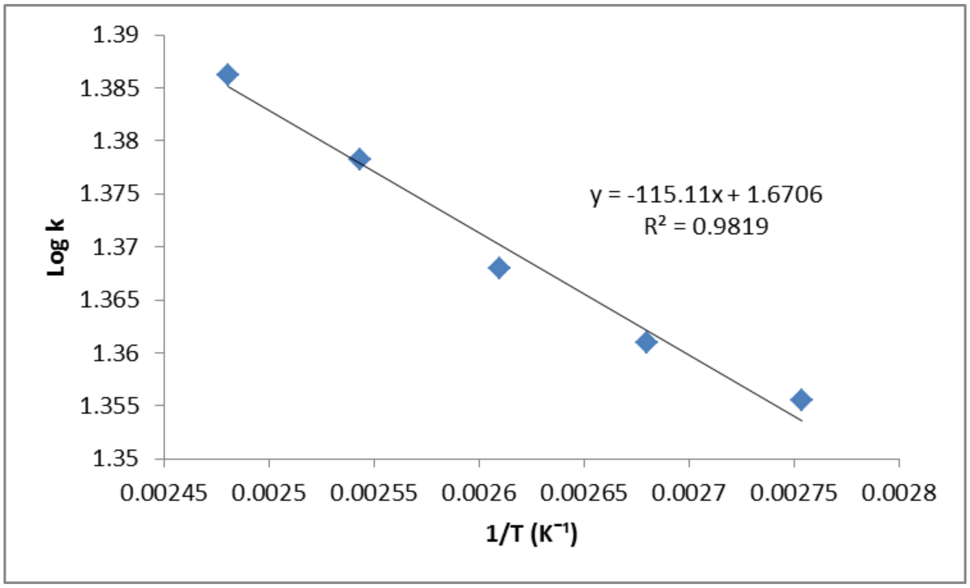


Figure 4.24. Relationship between rate constant and temperature.

Table 4.6: Activation Energy for biolubricant synthesis and comparison

Biolubricant	Activation Energy , Ea (kJol/mol)	R^2
Jatropha (This study)	2.2	0.982
Jatropha (Resul et al , 2011)	3.94	0.887

As a result from this research that applied *Paphia undulata* shell waste as catalyst to produce *Jatropha* biolubricant, the activation energy was found to be much lower (2.2 kJ/mol) in comparison to a previous research that applied sodium methoxide as catalyst (3.94kJ/mol). Theoretically, catalyts accelerate the rate of chemical reactions by stabilizing the transition state of the reaction, hence lowering the activation energy barrier that needs to be overcome for product formation. This shows that this catalyst tends to decrease the activation energy for biolubricant production.

On the other hand, the activation energy for palm oil biolubricant production is much higher than the activation energy obtained for *Jatropha* biolubricant in this research. In this case, the activation energy is lower due to the reaction being less sensitive to temperature (Resul *et al.*, 2012). The temperature reaction of palm oil ranges from 70 to 100 ^{0}C, compared to 90 to 130 ^{0}C in this reaction. Thus, due to low activation energy, the reaction in *Jatropha* biolubricant production followed the optimum condition that was studied before.

4.7 Physico-Chemical Characterization Biolubricant

Biolubricant production must work efficiently with machinery and also be able to work in any climatic condition. Therefore, the viscosity and pour point values are important for indicating the performance of the lubricant. In order to determine viscosity and pour point value, ASTM method was used and the results are presented in Table 4.7.

Viscosity is one important charactristic that need to be at high enough to maintain good film between two contacting surface in order to reduce friction that tend to increase heat loss and rapid wear (Salimon et al., 2011). In this reserach, the obtain value of viscosity was fulfills the biolubricant standard (32.29 cst at 40^0C and 5.14 cst at 100^0C). This result slightly higher than biolubricant that using rice bran oil (23.75 cst at 40^0C and 6.06 cst at 100^0C) (Chauhan and Chibber , 2013).

In addition, the high viscosity index is a desirable characteristic in industrial applications due to the ability to resist oxidation and thermal exposure. The ability of biolubricant to adapt with wide range of temperature become critical nowdays. In this research, the results show that the viscosity index (VI) was above the standard limit, which is 81. According to Arbain and Salimon (2010), high viscosity index was obtained due to a higher degree of branching chain in biolubricant base stock. Usually, TMP ester has a higher viscosity due to the three acid group content in its structure.

On the other hand, the pour point for this research was obtained as -5 ^{0}C. Lubricant with lower pour point tends to form macrocristal structure at lower temperature. Thus, improved pour point from transesterification of biolubricant production could be achieved.

Table 4.7

Standard specification of *Jatropha* biolubricant

Properties	**Unit**	**Limit Biolubricant**	**Temperature**	**Result**
Kinemetic Viscosity	c.s.t	>12	40 ^{0}C	32.29
		1.9-6.0	100 ^{0}C	5.14
Viscosity Index		>50		81
Pour Point	°C	-6	10	-5

4.7.1 Biolubricant Analysis

4.7.1.1 FTIR

The results for TMP ester formation for biolubricant using IR analysis are shown in Figure 4.25. According to the IR spectrum of Jatropha biolubricant, C=O ester group formed at wavelength 1741.02 cm^{-1}, while C-O ester group formed at 1242.68 cm^{-1} and 1170.28 cm^{-1}. This result was compared with Salimon and Ishak (2012), in which chemical shift occurred and C=O ester group formed at wavelength 1744.19 cm^{-1} while C-O ester group formed at 1239 and 1164 cm^{-1}. Arbain and Salimon (2010), also showed a shift of wavelength to produce C=O ester at 1743 cm^{-1}. In addition, the alcohol wavelength, -OH (3300-3100cm^{-1}) did not appear in the final result. This shows that all of the OH bonds in TMP fully reacted with JCOME to produce TMP ester.

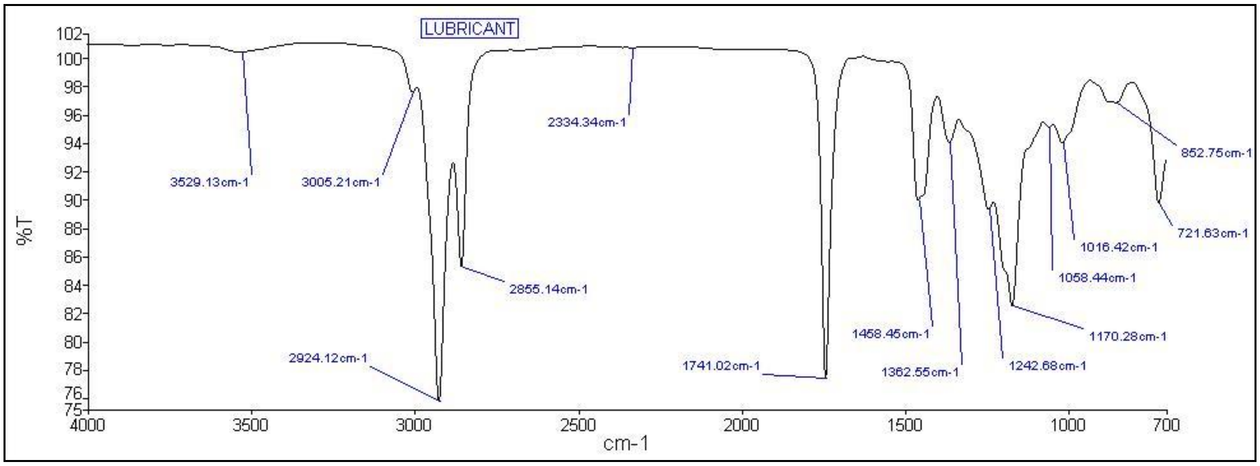


Figure 4.25. IR spectra of TMP ester.

4.7.1.2 Proton and Carbon Nuclear Magnetic Resonance (^{1}H-NMR and ^{13}C-NMR) Spectra

The analysis of ^{1}H-NMR is important to determine the structure of the ester TMP product (Figure 4.26). The signals at 4.03ppm show the existance of methylene proton bound to the –O group of carboxylic acid ester group, -OOR, which is the major methyl ester on this study. Information from the software Chemdraw determined that the value was at 4.00ppm. This result was compared with Arbain and Salimon (2011), where the signals for TMP ester product were at 4.016 ppm.

The ^{13}C-NMR spectrum was also important in proving the existance of TMP ester in the product of the study (Figure 4.27). According to Arbain and Salimon (2011), ester carbonyl group was shown at the range signals of 173-174 ppm in the end-product, while 77.25 ppm refers to the chloroform signals, or CDC13, that was used as solvent in this analysis. The signals at 174 ppm in this study represent ester carbonyl. Meanwhile, the clear signals at 77.34 ppm show the solvent that was used.

From this NMR data analysis, the result of TMP ester formation were shown as expected.

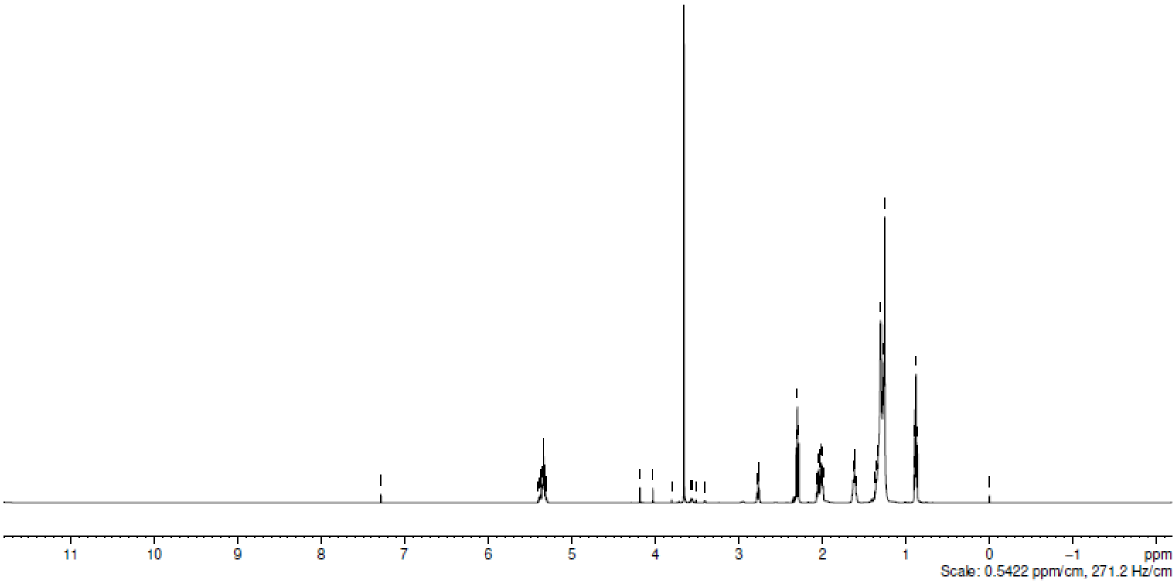


Figure 4.26. ^{1}H-NMR of TMP ester.

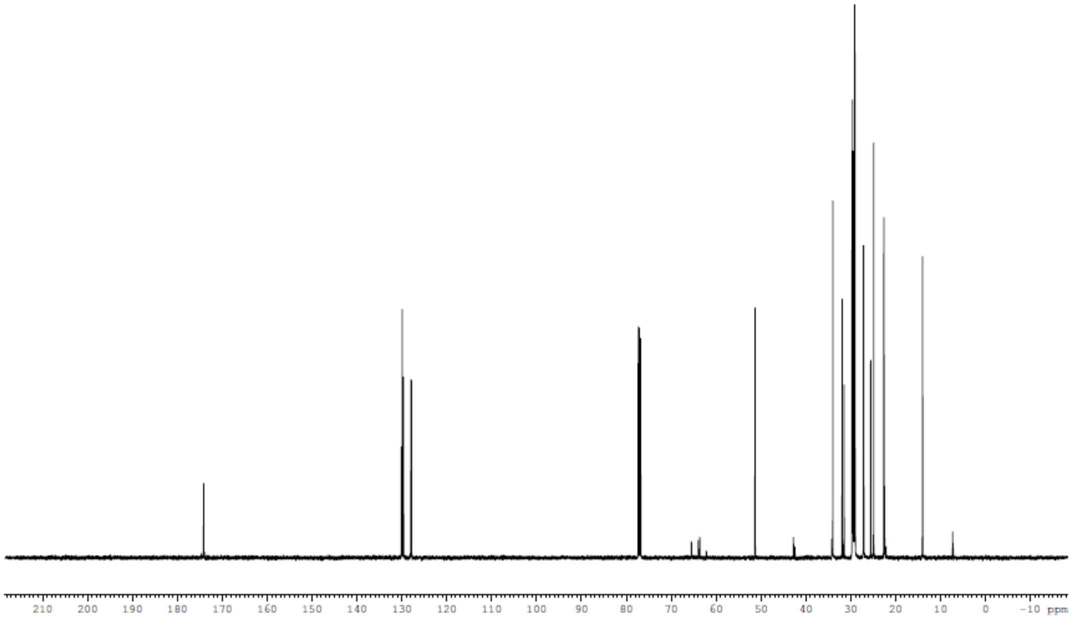


Figure 4.27. ^{13}C-NMR of TMP ester.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Process transesterification of the *Jatropha* biolubricant using *Paphia undulata* shell waste as solid waste catalyst has been successfully achieved. *The Paphia undulata* shell waste as solid catalyst has been successfully characterized and synthesized for biolubricant production. The biolubricant synthesis development from *Jatropha curcas* oil over solid catalyst was achieved using two steps processing.

1) The optimum process conditions were 110 ^{0}C temperature, 3 h reaction time, 4:1 JME: TMP molar ratio and 3% w/w catalyst loading, obtaining the best results of 96.66% TMP conversion and 78.67% TE composition.
2) The catalyst could be reused effectively for up to four production cycles of JCOME transesterification for TE formation.
3) The transesterification reaction of TMP and *Jatropha curcas* oil methyl ester (JCOME) followed second order kinetics with an overall reaction rate constant of 0.0427 $(\%w/w\ min\ °C)^{-1}$ and activation energy of 2.2 kJ/mol.
4) The properties of the resulting *Jatropha* biolubricant (kinematic viscosity, pour point and viscosity index) using *Paphia undulata* shell as solid catalyst fulfills the biolubricant standard which corresponds to better pour point and viscosity.

The utilization of *Paphia undulata* shell waste and renewable feedstock could be an eco-friendly alternative process for biolubricant synthesis.

5.2 RECOMMENDATION

1) The various catalyst can be used for biolubricant from Jatropha curcas oil such as by impregnation with other catalyst.
2) The kinetic model can be developed for biolubricant synthesis such as Hensell wood model and etc.
3) For optimum condition process of biolubricant synthesis can be approving using Response Surface Model Testing.

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APPENDIX A

A.1 Acid Esterification for Reducing Free Fatty Acid Level

i) Percentage of Free fatty acid JCO, FFA (%) = [Titre value × normality of KOH × 56.1] / weight of Jatropha oil

$$= \frac{1.9 \times 0.1 \times 56.1}{0.98}$$

$$= 10.876\ \%$$

ii) Acid value = 2 x % FFA

= 21.752 mg KOH /g

iii) Percentage of free fatty acid in JCO, FFA (%) = [Titre value × normality of KOH × 56.1] / weight of Jatropha oil

$$= \frac{0.1 \times 0.1 \times 56.1}{0.98}$$

$$= 0.57\ \% < 1\%$$

Acid value = 2 X % FFA

= 1.14 mg KOH /g

A.1.1 Catalyst concentration effect on free fatty acid value (FFA)

Catalyst Loading (w/w%)	**FFA%**
0.0%	10.87
0.5%	1.57
1.0%	0.76
1.5%	0.7
2.0%	0.56

A.1.2 Methanol to oil ratio effect on free fatty acid value (FFA)

Methanol to Oil (mol:mol)	**FFA (%)**
3:01	1.3
4:01	0.95
5:01	0.9
6:01	0.63
7:01	0.7

A.1.3 Time of esterification process effect on free fatty acid value (FFA)

Time (Min)	**FFA (%)**		
	E1	**E2**	**E3**
0	10.87	10.775	10.8
10	7.06	7.15	6.91
20	5.5	6	5.01
30	0.89	0.83	0.86
40	0.87	0.8	0.84
50	0.58	0.68	0.63
60	0.57	0.65	0.61

A.2 JCOME Transesterification

A.2.1 Gas Chromatography (GC-MS) Analysis

i) Analysis of Jathropha Crude Oil Methyl Ester (JCOME)

1) Yield Biodiesel, % = $\frac{\text{Weight of Biodiesel}}{\text{Weight of Oil}}$ X 100%

$$= \frac{28\text{ g}}{30\text{ g}} \times 100\ \%$$

$$= 93.33\%$$

A.2.2 Effect of Methanol to oil ratio on JCOME production

Methanol to Oil	Yield (g)			Average	Yield (%)
1:01	23.8	23.7	23.8	23.76	79.2
3:01	25.7	25.6	25.6	25.64	85.45
6:01	27.5	27.4	27.5	27.5	91.67
9:01	27	26.8	26.9	26.95	89.82
12:01	26	26	25.9	25.97	86.57

A.2.3 Effect of catalyst loading on JCOME production

Catalyst Loading (%)	Yield (g)			Average	Yield (%)
1	14.9	14.9	14.8	14.85	49.5
2	19.7	19.6	19.8	19.72	65.73
3	20.9	20.9	20.9	20.9	69.67
4	27.5	27.4	27.5	27.5	91.67
5	27	27	27	27.0	90

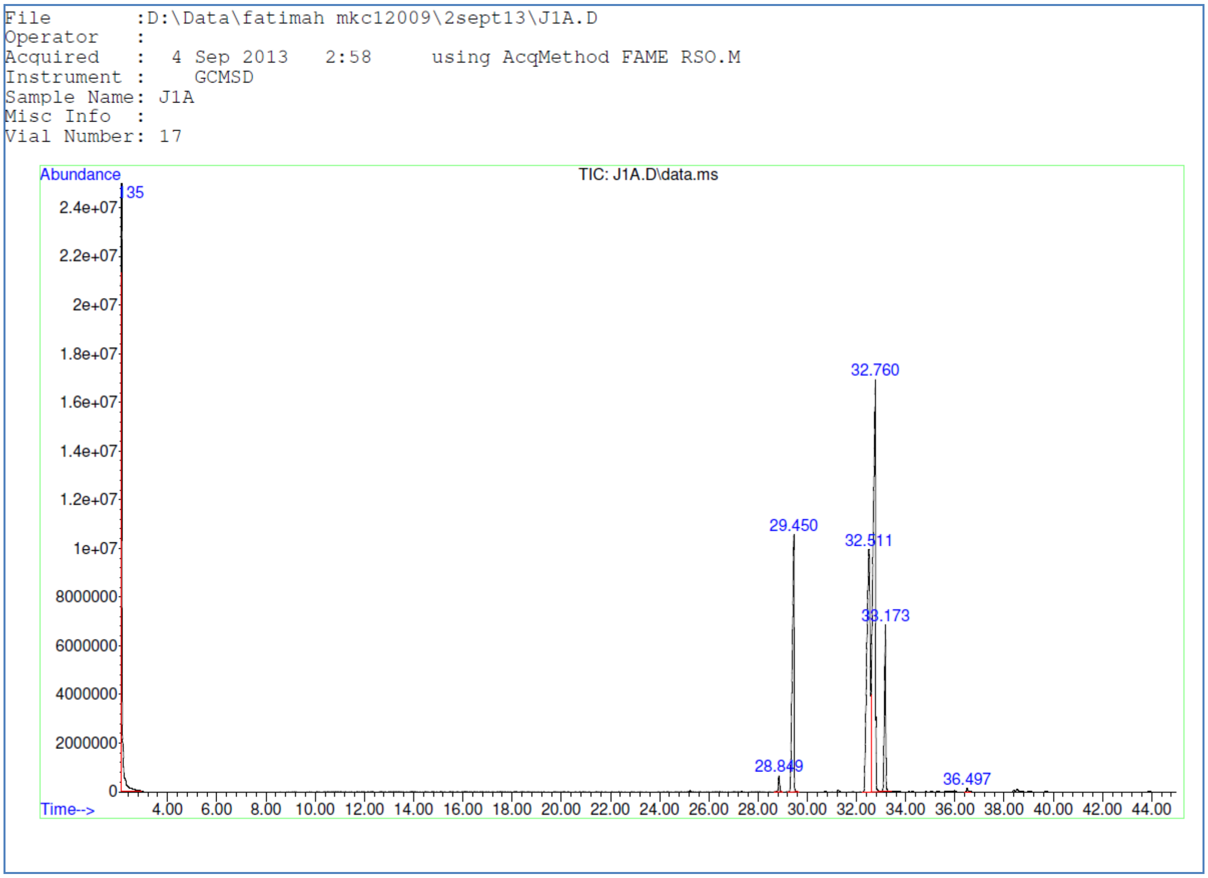
A.2.4 Effect of time on JCOME production

Reaction Time (Hour)	Yield (g)			Average	Yield (%)
1	23.8	23.7	23.8	23.80	79.36
2	26.4	26.4	26.5	26.44	88.13
3	27.8	27.8	27.8	27.80	92.67
4	27.3	27.4	27.4	27.33	91.10
5	27	26.6	26.6	26.74	89.14

A.2.5 Effect of temperature on JCOME production

Temperature (°C)	Yield (g)			Average	Yield (%)
45	21.3	21.4	21.4	21.34	71.13
50	24.0	24.0	24.0	24.0	80
55	24.5	24.4	25.5	25.47	84.9
60	28.0	28.0	28.0	28.0	93.33
65	26.4	26.5	26.5	26.46	88.2

A.3 GC-MS for JCOME



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Operator    :
Acquired    :  4 Sep 2013   2:58     using AcqMethod FAME RSO.M
Instrument :    GCMSD
Sample Name: J1A
Misc Info   :
Vial Number: 17
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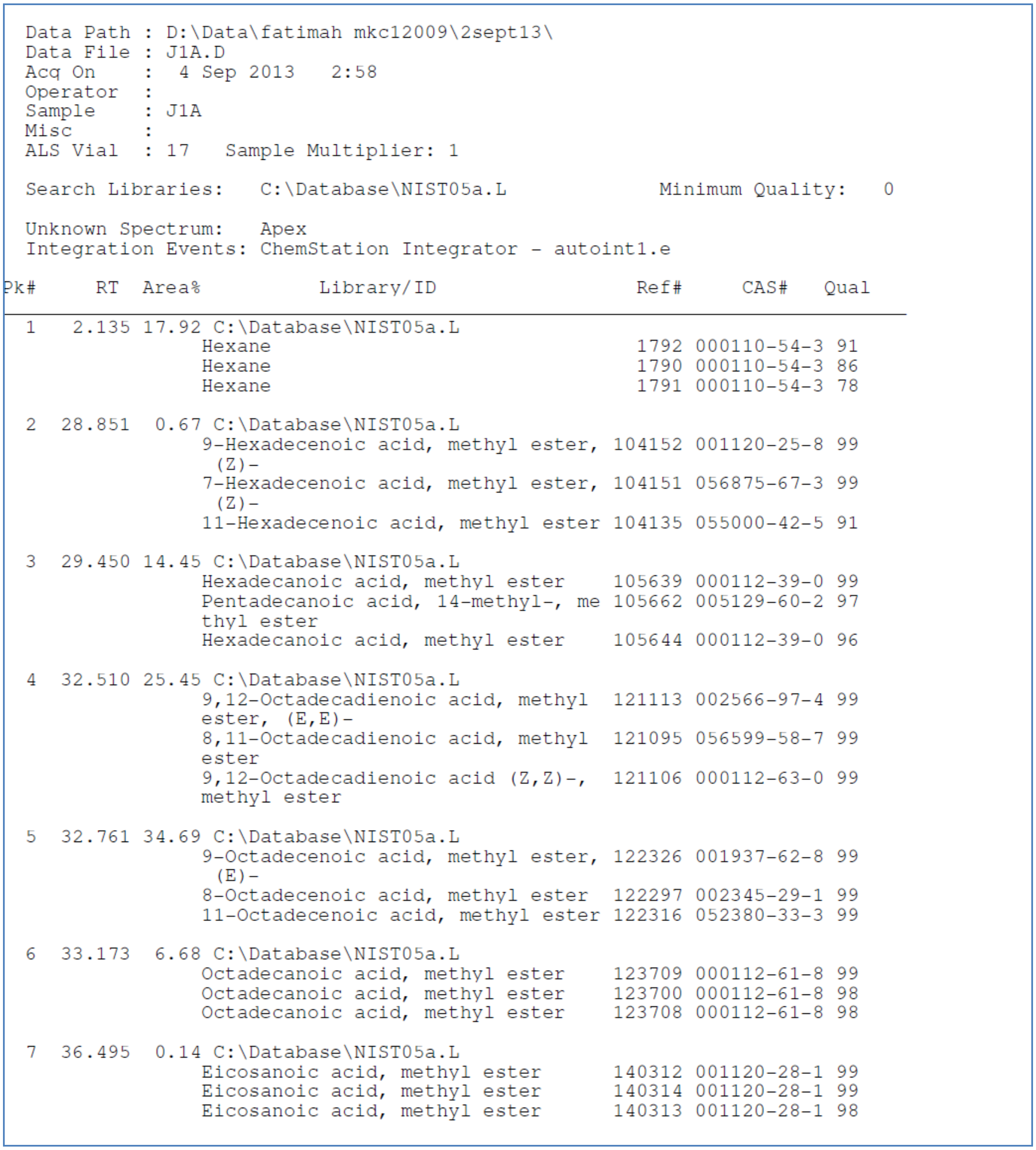

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 Data File : J1A.D
 Acq On    :  4 Sep 2013   2:58
 Operator  :
 Sample    : J1A
 Misc      :
 ALS Vial  : 17   Sample Multiplier: 1

 Search Libraries:   C:\Database\NIST05a.L            Minimum Quality:   0

 Unknown Spectrum:   Apex
 Integration Events: ChemStation Integrator - autoint1.e

Pk#     RT  Area%          Library/ID                 Ref#     CAS#   Qual
______________________________________________________________________________
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               Hexane                                 1792 000110-54-3 91
               Hexane                                 1790 000110-54-3 86
               Hexane                                 1791 000110-54-3 78

 2  28.851  0.67 C:\Database\NIST05a.L
               9-Hexadecenoic acid, methyl ester,  104152 001120-25-8 99
                (Z)-
               7-Hexadecenoic acid, methyl ester,  104151 056875-67-3 99
                (Z)-
               11-Hexadecenoic acid, methyl ester 104135 055000-42-5 91

 3  29.450 14.45 C:\Database\NIST05a.L
               Hexadecanoic acid, methyl ester    105639 000112-39-0 99
               Pentadecanoic acid, 14-methyl-, me 105662 005129-60-2 97
               thyl ester
               Hexadecanoic acid, methyl ester    105644 000112-39-0 96

 4  32.510 25.45 C:\Database\NIST05a.L
               9,12-Octadecadienoic acid, methyl  121113 002566-97-4 99
               ester, (E,E)-
               8,11-Octadecadienoic acid, methyl  121095 056599-58-7 99
               ester
               9,12-Octadecadienoic acid (Z,Z)-,  121106 000112-63-0 99
               methyl ester

 5  32.761 34.69 C:\Database\NIST05a.L
               9-Octadecenoic acid, methyl ester, 122326 001937-62-8 99
                (E)-
               8-Octadecenoic acid, methyl ester  122297 002345-29-1 99
               11-Octadecenoic acid, methyl ester 122316 052380-33-3 99

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               Octadecanoic acid, methyl ester    123709 000112-61-8 99
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               Octadecanoic acid, methyl ester    123708 000112-61-8 98

 7  36.495  0.14 C:\Database\NIST05a.L
               Eicosanoic acid, methyl ester      140312 001120-28-1 99
               Eicosanoic acid, methyl ester      140314 001120-28-1 99
               Eicosanoic acid, methyl ester      140313 001120-28-1 98
```

APPENDIX B

Synthesis of biolubricant from JCOME

B.1 Final Product

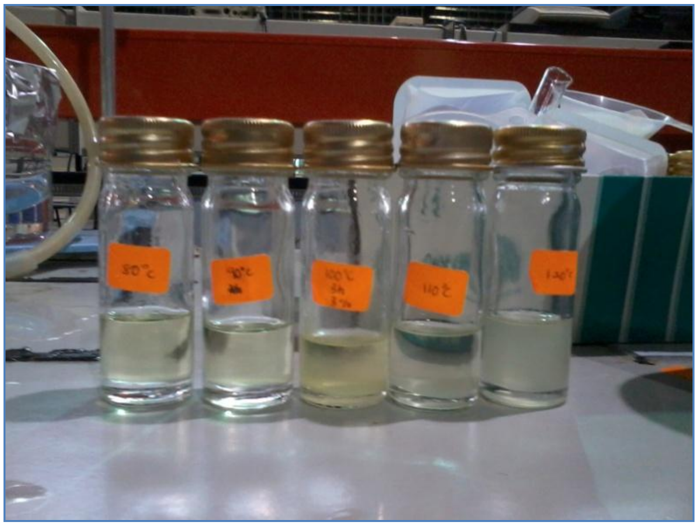


Figure B.1. Final product of Biolubricant

B.2 Standard Curve

B.2.1 Calibration curve for TMP Conversion

TMP: 9.942

Concentration (g/L)	**Peak Area (p.A*s)**
0	0
10	28.34
20	46
30	63.98
40	80.9
50	94.25

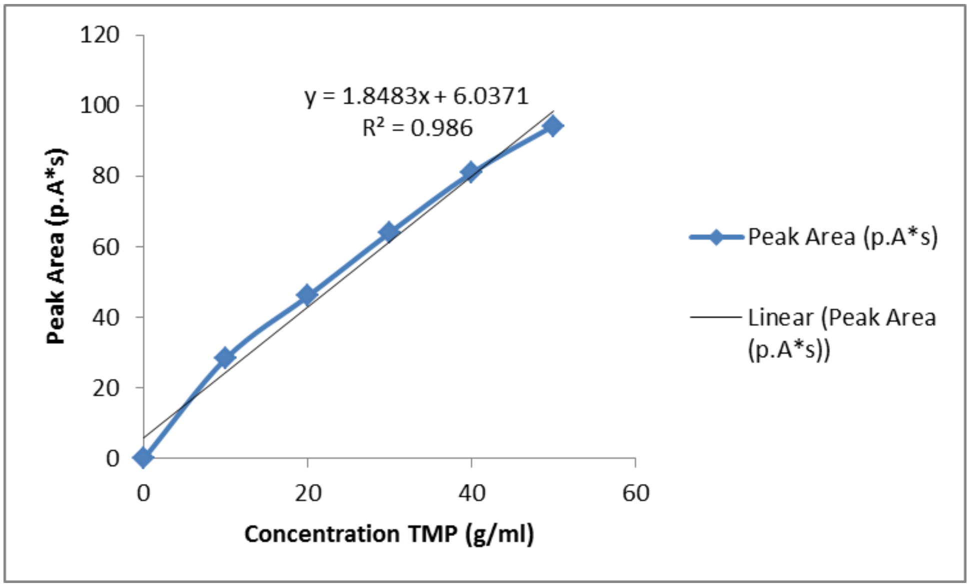


Figure B.3. Calibration curve for TMP

B.2.2 The calibration curve for partial glyceride as GC-FID standard

Monolinoleate : 26.219

Concentration (w/w%)	**Peak Area (p.A*s)**
0	0
0.004	138.049
0.008	277.198
0.012	377.874
0.016	503.908
0.021	645.442

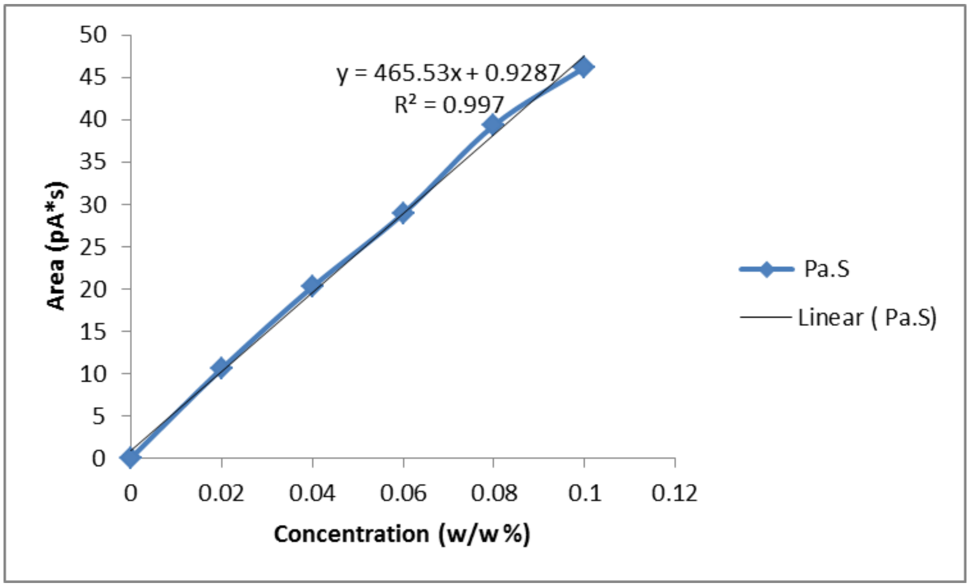


Figure B.4. Monolinoleate standard curve

Dilinoleate: 31.800

Concentration (w/w%)	**Peak Area (p.A*s)**
0	0
0.002	392.399
0.004	735.922
0.006	1137.037
0.008	1429.511
0.01	1777.363

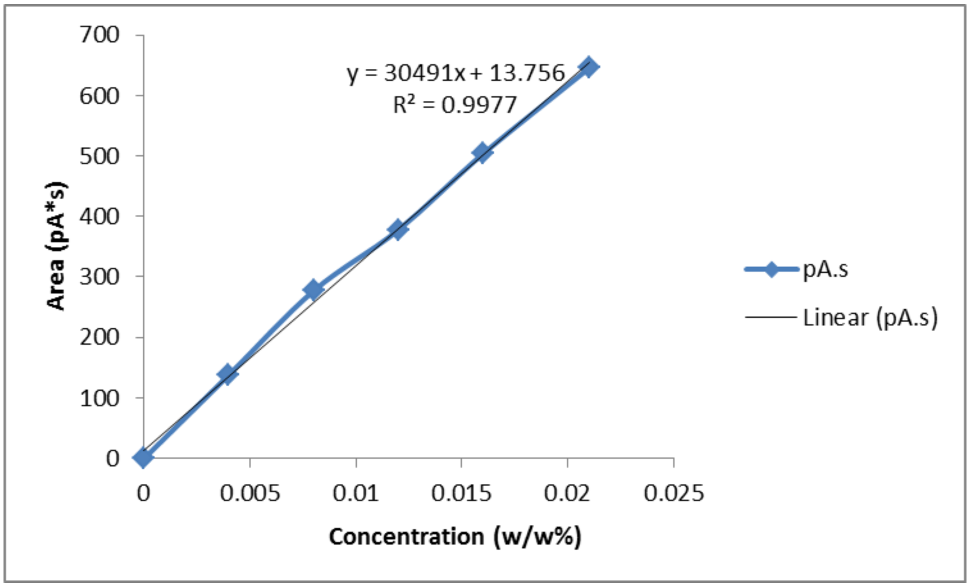


Figure B.5. Dilenoleate standard curve

Trilinoleate: 44.797

Concentration (w/w%)	**Peak Area (p.A*s)**
0	0
0.002	392.399
0.004	735.922
0.006	1137.037
0.008	1429.511
0.01	1777.363

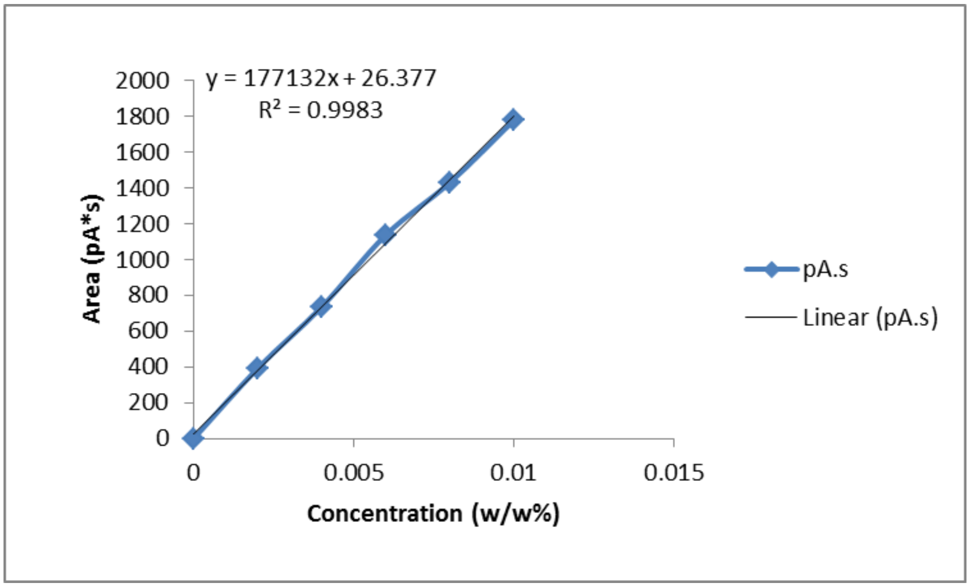


Figure B.6. Trilenoleate standard curve

Monopalimitate: 23.485

Concentration (w/w)	Peak Area (p.A*s)
0	0
0.001	21.437
0.002	57.098
0.003	85.231
0.004	118.772
0.005	143.503

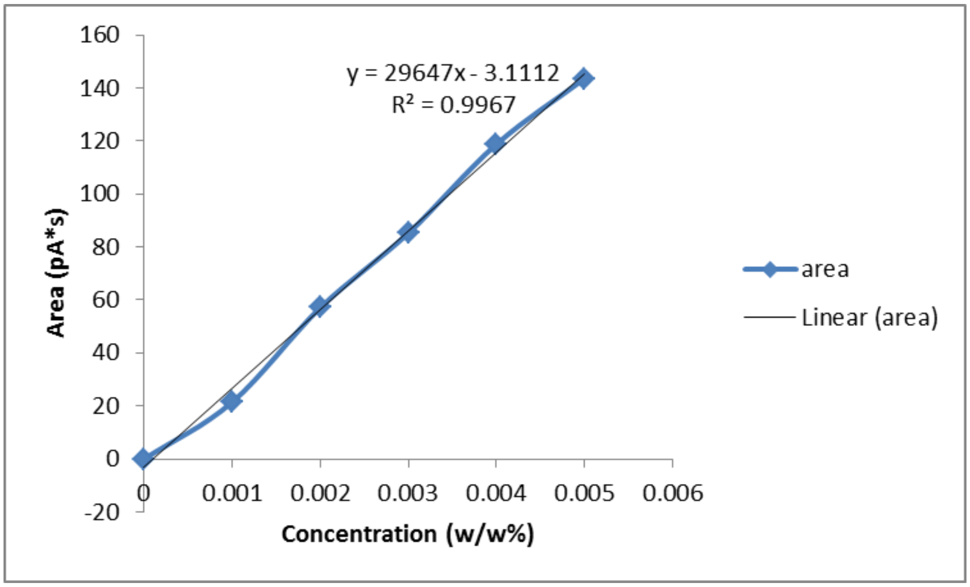


Figure B.7. Monopalmitate standard curve

Dipalmitate: 29.605

Concentration (w/w)	Peak Area (p.A*s)
0	0
0.001	4.748
0.002	10.1433
0.003	15.569
0.004	20.149
0.005	25.409

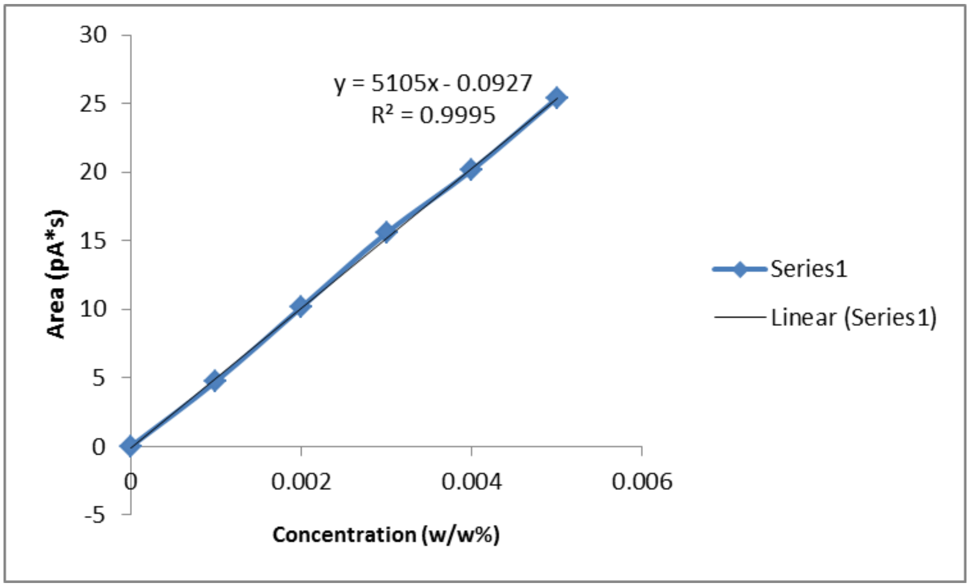


Figure B.8. Dipalmitate standard curve

Tripalmitate: 43.33

Concentration (w/w)	Peak Area (p.A*s)
0	0
0.0005	29.209
0.001	44.529
0.002	86.242
0.003	126.1
0.004	158.699

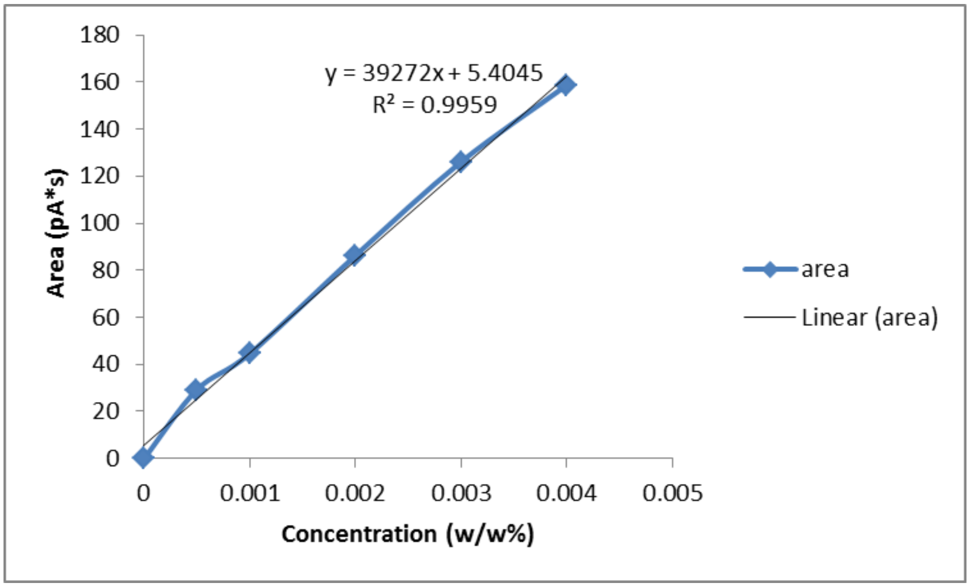


Figure B.9. Tripalmitate standard curve

Monooleate: 24.4

Concentration (w/w%)	Peak Area (p.A*s)
0	0
0.001	127.793
0.002	224.5419
0.003	345.985
0.004	431.46
0.005	536.3143

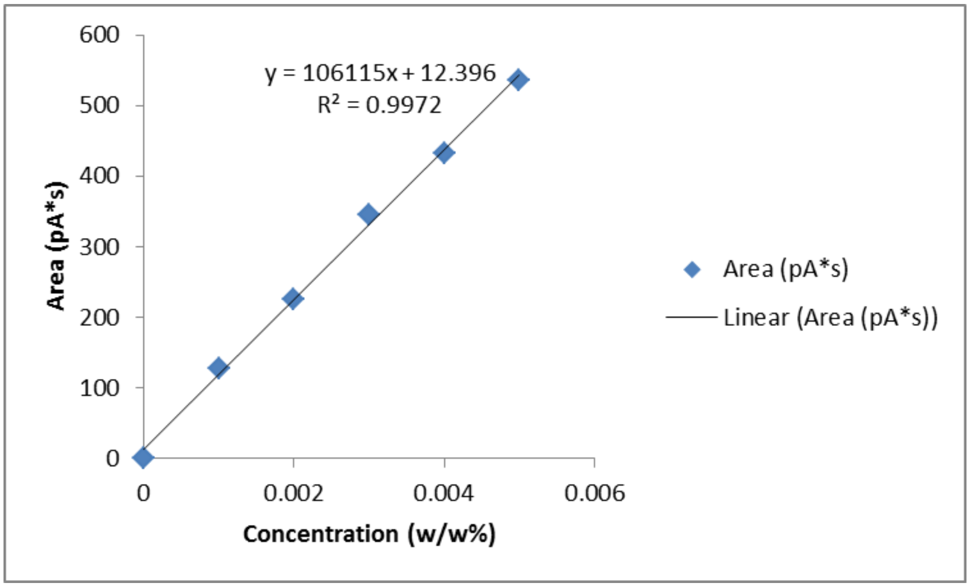


Figure B.10. Monooleate standard curve

Dioleate: 31.559

Concentration (w/w%)	**Peak Area (p.A*s)**
0	0
0.001	1529.928
0.002	2600
0.003	4271
0.004	5525.08
0.005	6865.589

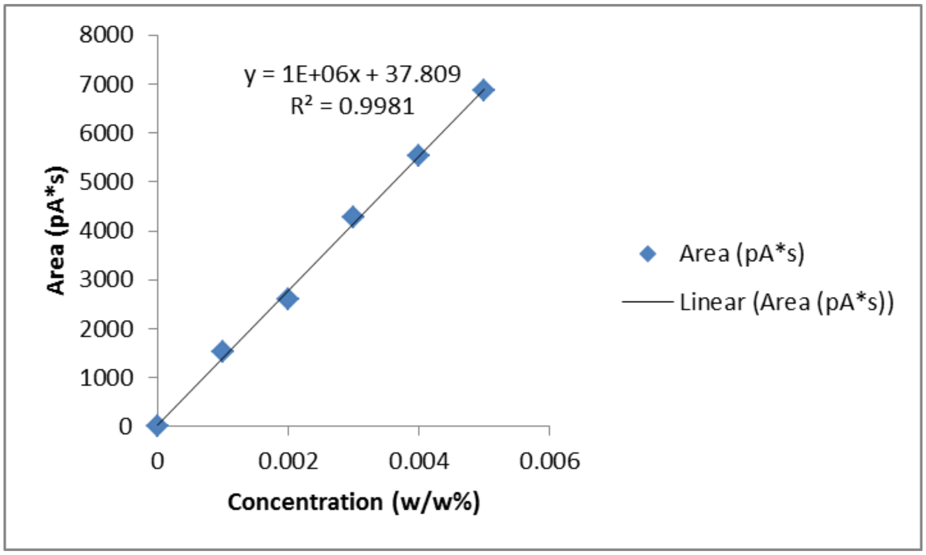


Figure B.11. Dioleate standard curve

Trioleate: 44.65

Concentration (w/w%)	**Peak Area (p.A*s)**
0	0
0.0005	119.064
0.001	220.2031
0.002	429.28
0.003	616.81
0.004	810.89

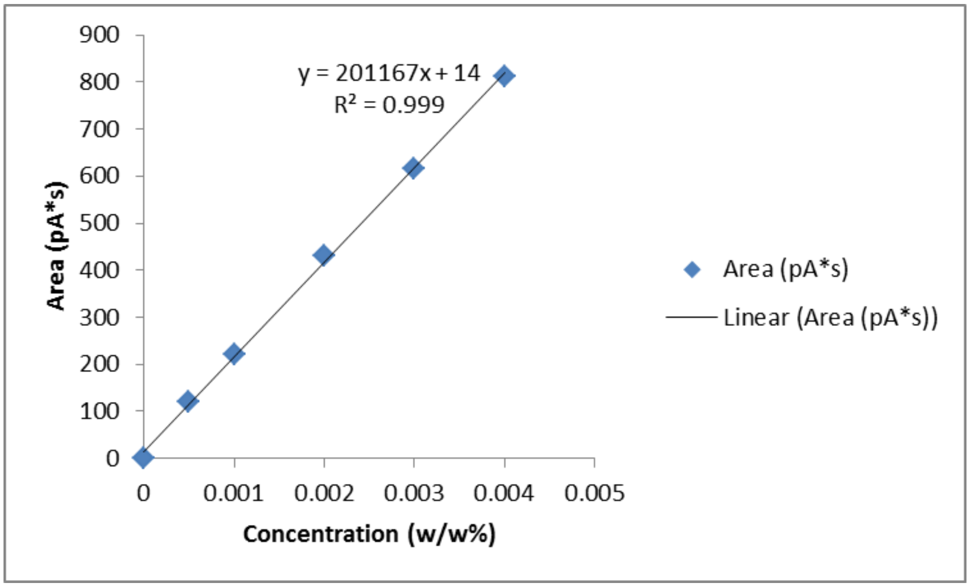


Figure B.12. Trioleate standard curve

B.3 TMP Standard Curve for Kinetic Study

Concentration TMP (wt/ wt%)	**Peak Area (p.A*s)**
0	0
0.02	4738.618
0.04	8055.784
0.06	12143.8
0.08	17214.4
0.1	19834.1

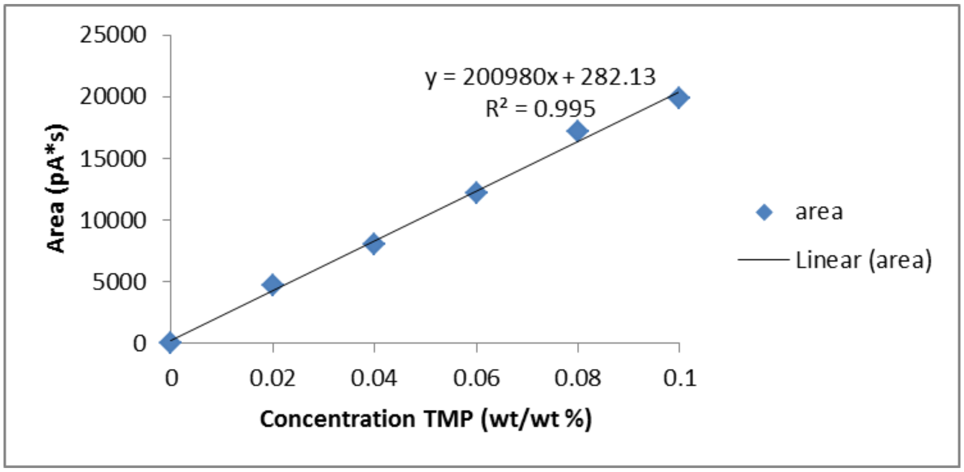


Figure B.13. TMP standard curve for kinetic

B.4 GC-FID Result for *Jatropha* Biolubricant

B.4.1 Effect of JCOME to TMP molar ratio

Concentration	**Replication**	**Monopalmitate**		**Monolinoleate**		**Monooleate**	
		Area (pA*s)	**Concentration (w/w %)**	**Area (pA*s)**	**Concentration (w/w %)**	**Area (pA*s)**	**Concentration (w/w %)**
1:3 mol/mol	1	55.834	0.00199	0.000	0.00000	316.702	0.00287
	2	55.346	0.00197	0.000	0.00000	326.988	0.00296
	3	54.981	0.00196	0.000	0.00000	327.269	0.00297
	Average		0.00197		0.00000		0.00293
	Total (w/w%)	0.00492					
1:4 mol/mol	1	22.158	0.00085	0.000	0.000	264.569	0.00238
	2	22.209	0.00085	0.000	0.000	264.543	0.00238
	3	22.418	0.00086	0.000	0.000	264.920	0.00238
	Average		0.00086		0.000		0.00238
	Total (w/w%)	0.00323					
1:5 mol/mol	1	12.564	0.00053	0.000	0.000	420.314	0.00384
	2	12.612	0.00053	0.000	0.000	420.184	0.00384
	3	12.981	0.00054	0.000	0.000	420.612	0.00385

	Average		0.00053		0.000		0.00384
	Total (w/w%)	0.00438					
1:6 mol/mol	1	0.000	0.00010	0.000	0.000	660.887	0.00611
	2	0.000	0.00010	0.000	0.000	660.349	0.00611
	3	0.000	0.00010	0.000	0.000	660.385	0.00611
	Average		0.00010		0.000		0.00611
	Total (w/w%)	0.00621					
1:7 mol/mol	1	26.614	0.00100	0.000	0.000	194.612	0.00172
	2	16.823	0.00067	0.000	0.000	194.312	0.00171
	3	26.612	0.00100	0.000	0.000	194.765	0.00172
	Average		0.00089		0.000		0.00172
	Total (w/w%)	0.00261					

Concentration	**Replication**	**Dipalmitate**		**Dilinoliate**		**Dioleate**	
		Area (pA*s)	**Concentration (w/w %)**	**Area (pA*s)**	**Concentration (w/w %)**	**Area (pA*s)**	**Concentration (w/w %)**
1:3 mol/mol	1	26.532	0.00522	0	0.000	2255.928	0.00215
	2	26.512	0.00521	0	0.000	2256.934	0.00216
	3	29.555	0.00581	0	0.000	2254.920	0.00215
	Average		0.00541		0.000		0.00215
	Total (w/w%)	0.00756					
1:4 mol/mol	1	299.269	0.05864	0.000	0.000	1995.64500	0.00189
	2	299.452	0.05868	0.000	0.000	1995.41000	0.00189
	3	294.896	0.05778	0.000	0.000	1995.93400	0.00189
	Average		0.05837		0.000		0.00189
	Total (w/w%)	0.05981					
1:5 mol/mol	1	419.341	0.08216	0.000	0.000	1134.614	0.00103
	2	418.945	0.08208	0.000	0.000	1134.610	0.00103
	3	419.124	0.08212	0.000	0.000	1134.590	0.00103
	Average		0.08212		0.000		0.00103

	Total (w/w%)	0.08270					
1:6 mol/mol	1	249.192	0.04883	0.000	0.000	188.734	0.00009
	2	249.249	0.04884	0.000	0.000	188.004	0.00009
	3	249.395	0.04887	0.000	0.000	188.612	0.00009
	Average		0.04885		0.000		0.00009
	Total (w/w%)	0.04848					
1:7 mol/mol	1	329.457	0.06455	0.000	0.000	184.630	0.00008
	2	349.423	0.06847	0.000	0.000	184.634	0.00008
	3	349.412	0.06846	0.000	0.000	184.794	0.00008
	Average		0.06716		0.000		0.00008
	Total (w/w%)	0.06679					

Concentration	Replication	Tripalmitate		Trilinoleate		Trioleate	
		Area (pA*s)	Concentration (w/w %)	Area (pA*s)	Concentration (w/w %)	Area (pA*s)	Concentration (w/w %)
1:3 mol/mol	1	487.443	0.01227	0.00000	0.00000	0.00000	0.00000
	2	486.941	0.01226	0.00000	0.00000	0.00000	0.00000
	3	400.194	0.01005	0.00000	0.00000	0.00000	0.00000
	Average		0.01153		0.00000		0.00000
	Total (w/w%)	0.01153					
1:4 mol/mol	1	3442.802	0.08753	402.682	0.00212	7845.448	0.03893
	2	3442.467	0.08752	402.722	0.00212	7845.576	0.03893
	3	3442.512	0.08752	402.691	0.00212	7845.321	0.03893
	Average		0.08752		0.00212		0.03893
	Total (w/w%)	0.12858					
1:5 mol/mol	1	3317.130	0.08433	226.732	0.00113	6823.133	0.03385
	2	3317.213	0.08433	226.425	0.00113	6823.985	0.03385
	3	3317.413	0.08434	227.423	0.00114	6823.532	0.03385
	Average		0.08433		0.00113		0.03385
	Total (w/w%)	0.11931					
1:6 mol/mol	1	1277.046	0.03238	374.327	0.00196	6652.913	0.03300

	2	1277.631	0.03240	374.637	0.00197	6652.413	0.03300
	3	1277.412	0.03239	374.952	0.00197	6652.783	0.03300
	Average		0.03239		0.00197		0.03300
	Total (w/w%)	0.06736					
1:7 mol/mol	1	1597.346	0.04054	373.642	0.00196	6612.120	0.03280
	2	1798.546	0.04566	373.894	0.00196	6612.943	0.03280
	3	1698.312	0.04311	373.987	0.00196	6412.893	0.03181
	Average		0.04310		0.00196		0.03247
	Total (w/w%)	0.07753					

TMP to Oil Molar ratio (mol/mol)	**TMP $_p$ (g/ml)**	**Conversion (%)**
3:1	2.22	83.18
4:1	0.67	94.92
5:1	1.87	85.83
6:1	2.02	84.66
7:1	2.09	84.17

TMP to Oil Molar ratio (mol/mol)	**Percent Composition (wt/wt%)**			**Conversion (%)**
	ME	**DE**	**TE**	
3:1	20.48	31.48	48.04	83.18
4:1	1.701	30.64	67.659	94.92
5:1	2.121	40.07	57.808	85.83
6:1	5.09	39.724	55.186	84.66
7:1	1.78	45.453	52.767	84.17

B.4.2 Effect of Catalyst Loading

Catalyst	**Replication**	**Monopalmitate**		**Monolinoleate**		**Monooleate**	
		Area (pA*s)	**Concentration (w/w %)**	**Area (pA*s)**	**Concentration (w/w %)**	**Area (pA*s)**	**Concentration (w/w %)**
0%	1	0.000	0.000	0.000	0.000	0.000	0.000
	2	0.000	0.000	0.000	0.000	0.000	0.000
	3	0.000	0.000	0.000	0.000	0.000	0.000
	Average		0.000		0.000		0.000
	Total (w/w%)	0.000					
1%	1	101.078	0.00351	5.52	0.00986	586.933	0.00541
	2	100.185	0.00348	5.491	0.00980	586.41	0.00541
	3	100.01	0.00348	5.521	0.00986	586.899	0.00541
	Average		0.00349		0.00984		0.00541
	Total (w/w%)	0.01875					

2%	1	22.078	0.00085	9.000	0.01734	26.933	0.00014
	2	22.185	0.00085	7.311	0.01371	26.410	0.00013
	3	22.010	0.00085	6.501	0.01197	22.899	0.00010
	Average		0.00085		0.01434		0.00012
	Total (w/w%)	0.01531					
3%	1	5.907	0.00030	3.839	0.00625	19.305	0.00007
	2	5.900	0.00030	1.930	0.00215	19.301	0.00007
	3	5.985	0.00031	1.935	0.00216	19.300	0.00007
	Average		0.00031		0.00352		0.00007
	Total (w/w%)	0.00389					
4%	1	7.535	0.00036	3.430	0.00537	10.291	-0.00002
	2	7.534	0.00036	3.431	0.00538	10.295	-0.00002
	3	7.538	0.00036	3.410	0.00533	10.290	-0.00002

	Average		0.00036		0.00536		-0.00002
	Total (w/w%)	0.00570					

Catalyst	**Replication**	**Dipalmitate**		**Dilinoliate**		**Dioleate**	
		Area (pA*s)	**Concentration (w/w %)**	**Area (pA*s)**	**Concentration (w/w %)**	**Area (pA*s)**	**Concentration (w/w %)**
0%	1	0.000	0.000	0	0.000	24.627	0.000
	2	0.000	0.000	0	0.000	24.617	0.000
	3	0.000	0.000	0	0.000	24.625	0.000
	Average		0.000		0.000		0.000
	Total (w/w%)	0.000					
1%	1	469.852	0.09206	0.000	0.000	1024.204	0.00092
	2	469.75	0.09204	0.000	0.000	1024.2	0.00092
	3	669.554	0.13117	0.000	0.000	1024.206	0.00092
	Average		0.10509		0.000		0.00092
	Total (w/w%)	0.10556					
2%	1	466.852	0.09147	0.000	0.000	924.204	0.00082
	2	567.850	0.11125	0.000	0.000	924.200	0.00082
	3	267.654	0.05245	0.000	0.000	921.206	0.00082
	Average		0.08506		0.000		0.00082
	Total (w/w%)	0.08543					

3%	1	380.096	0.07447	851.206	0.027	903.711	0.00080
	2	380.090	0.07447	860.209	0.028	903.715	0.00080
	3	380.000	0.07445	860.200	0.028	903.691	0.00080
	Average		0.07447		0.028		0.00080
	Total (w/w%)	0.10293					
4%	1	208.061	0.04077	194.520	0.00593	976.952	0.00088
	2	209.060	0.04097	194.730	0.00594	976.950	0.00088
	3	209.059	0.04097	194.725	0.00594	976.958	0.00088
	Average		0.04090		0.00593		0.00088
	Total (w/w%)	0.04771					

Tripalmitate		Trilinoleate		Trioleate	
Area (pA*s)	**Concentration (w/w %)**	**Area (pA*s)**	**Concentration (w/w %)**	**Area (pA*s)**	**Concentration (w/w %)**
0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000
	0.000		0.000		0.000
0.000					
6382.422	0.16238	0.000	0.000	0.000	0.000
6382.512	0.16238	0.000	0.000	0.000	0.000
3499.453	0.08897	0.000	0.000	0.000	0.000
	0.13791		0.000		0.000
0.13769					
7122.422	0.18122	0.000	0.000	0.000	0.000
7132.512	0.18148	0.000	0.000	0.000	0.000
7142.453	0.18173	0.000	0.000	0.000	0.000
	0.18148		0.000		0.000
0.18126					
6636.015	0.16884	4454.404	0.02500	8994.074	0.04464
6736.818	0.17140	4454.410	0.02500	8994.067	0.04464
6736.871	0.17141	4444.400	0.02494	8994.079	0.04464
	0.17055		0.02498		0.04464

0.24017					
4709.490	0.11978	0.000	0.000	4480.910	0.02220
4709.495	0.11978	0.000	0.000	4480.919	0.02221
1966.489	0.04994	0.000	0.000	4490.909	0.02225
	0.09650		0.000		0.02222
0.11857					

Catalyst w/w%	**TMP_p (g/ml)**	**Conversion (%)**
0	8.82	33.18
1	1.99	84.92
2	1.87	85.83
3	0.44	96.66
4	1.43	89.17

Catalyst (w/w %)	Composition (%)			Conversion (%)
	ME	DE	TE	
0	0.30	0	0	33.18
1	7.157	40.29	52.553	84.92
2	5.43	30.293	64.277	85.83
3	1.123	29.663	69.214	90.66
4	3.315	27.738	68.947	89.17

B.4.3 Effect of Time

Time	Replication	Monopalmitate		Monolinoleate		Monooleate	
		Area (pA*s)	Concentration (w/w %)	Area (pA*s)	Concentration (w/w %)	Area (pA*s)	Concentration (w/w %)
1h	1	1709.220	0.05776	0.000	0.0000	8884.540	0.08361
	2	1660.221	0.05610	0.000	0.0000	8884.550	0.08361
	3	1659.21	0.05607	0.000	0.0000	8884.650	0.08361
	Average		0.05664		0.0000		0.08361
	Total (w/w%)	0.14025					
2h	1	505.969	0.01717	100.686	0.21429	306.607	0.00277
	2	505.970	0.01717	100.780	0.21449	306.610	0.00277

	3	505.660	0.01716	113.690	0.24222	306.600	0.00277
	Average		0.01717		0.22367		0.00277
	Total (w/w%)	0.24361					
3h	1	197.474	0.00677	0.000	0.000	33.177	0.000
	2	196.417	0.00673	0.000	0.000	33.167	0.000
	3	188.469	0.00646	0.000	0.000	33.187	0.000
	Average		0.00665		0.000		0.000
	Total (w/w%)	0.00685					
4h	1	74.732	0.00263	0.000	0.0000	0.000	0.000
	2	80.730	0.00283	0.000	0.0000	0.000	0.000
	3	80.750	0.00283	0.000	0.0000	0.000	0.000
	Average		0.00276		0.0000		0.000
	Total (w/w%)	0.00264					
5h	1	88.787	0.00310	0.000	0.000	1580.695	0.01478
	2	88.780	0.00310	0.000	0.000	1590.690	0.01487
	3	88.790	0.00310	0.000	0.000	1564.700	0.01463
	Average		0.00310		0.000		0.01476
	Total (w/w%)	0.01786					

Time	**Replication**	**Dipalmitate**		**Dilinoliate**		**Dioleate**	
		Area (pA*s)	**Concentration (w/w %)**	**Area (pA*s)**	**Concentration (w/w %)**	**Area (pA*s)**	**Concentration (w/w %)**
1h	1	614.521	0.12039	884.337	0.02855	3148.934	0.00305
	2	135.520	0.02656	884.338	0.02855	3148.950	0.00305
	3	132.529	0.02598	884.340	0.02855	3148.930	0.00305
	Average		0.05765		0.02855		0.00305
	Total (w/w%)	0.08925					
2h	1	216.893	0.04250	59.253	0.00149	679.461	0.00058
	2	225.890	0.04427	59.250	0.00149	679.462	0.00058
	3	255.895	0.05014	59.257	0.00149	679.460	0.00058
	Average		0.04564		0.00149		0.00058
	Total (w/w%)	0.04771					
3h	1	156.682	0.03071	0.000	0.000	462.435	0.00036
	2	150.280	0.02946	0.000	0.000	462.456	0.00036
	3	170.281	0.03337	0.000	0.000	462.451	0.00036
	Average		0.03118		0.000		0.00036
	Total (w/w%)	0.03109					

4h	1	88.813	0.01742	0.000	0.000	0.000	0.000
	2	87.910	0.01724	0.000	0.000	0.000	0.000
	3	86.915	0.01704	0.000	0.000	0.000	0.000
	Average		0.01723		0.000		0.000
	Total (w/w%)	0.01668					
5h	1	470.763	0.09223	225.711	0.00695	9320.000	0.00922
	2	470.345	0.09215	225.772	0.00695	9320.010	0.00922
	3	670.000	0.13126	225.770	0.00695	9320.014	0.00922
	Average		0.10522		0.00695		0.00922
	Total (w/w%)	0.12139					

Time	**Replication**	**Tripalmitate**		**Trilinoleate**		**Trioleate**	
		Area (pA*s)	**Concentration (w/w %)**	**Area (pA*s)**	**Concentration (w/w %)**	**Area (pA*s)**	**Concentration (w/w %)**
1h	1	5389.880	0.13711	694.176	0.00377	9384.769	0.04658
	2	5389.881	0.13711	694.172	0.00377	9384.770	0.04658
	3	6387.890	0.16252	694.179	0.00377	9384.765	0.04658
	Average		0.14558		0.00377		0.04658
	Total (w/w%)	0.19593					

2h	1	19231.413	0.48956	16700.000	0.09413	29691.924	0.14753
	2	19229.410	0.48951	16706.900	0.09417	29690.925	0.14752
	3	18225.415	0.46394	16705.000	0.09416	29690.920	0.14752
	Average		0.48100		0.09415		0.14753
	Total (w/w%)	0.72268					
3h	1	2980.604	0.07576	1974.784	0.01100	2497.424	0.01235
	2	2980.600	0.07576	1974.780	0.01100	2497.425	0.01235
	3	2974.699	0.07561	1974.785	0.01100	2497.420	0.01235
	Average		0.07571		0.01100		0.01235
	Total (w/w%)	0.09905					
4h	1	811.698	0.02053	33.248	0.00004	4049.970	0.02006
	2	813.700	0.02058	33.254	0.00004	4049.978	0.02006
	3	815.690	0.02063	33.250	0.00004	4049.941	0.02006
	Average		0.02058		0.00004		0.02006
	Total (w/w%)	0.04068					
5h	1	8407.570	0.21395	0.000	0.000	9956.625	0.04942

	2	8614.571	0.21922	0.000	0.000	9956.630	0.04942
	3	8614.575	0.21922	0.000	0.000	9956.645	0.04942
	Average		0.21746		0.000		0.04942
	Total (w/w%)	0.26674					

Time (h)	**TMP$_p$ (g/ml)**	**TMP Conversion (%)**
1	2.21	83.26
2	0.52	96
3	0.44	96.66
4	0.82	93.79
5	0.5	96.2

Time (h)	**Composition (%)**			**Conversion (%)**
	ME	**DE**	**TE**	
1	33	21	46.1	83.26
2	24	4.7	71.2	90
3	5	22.7	72.3	95.6
4	4.4	27.8	67.8	93.99
5	4.4	29.9	65.7	93.82

B.4.4 Effect of Temperature

Temperature	**Replication**	**Monopalmitate**		**Monolinoleate**		**Monooleate**	
		Area (pA*s)	**Concentration (w/w %)**	**Area (pA*s)**	**Concentration (w/w %)**	**Area (pA*s)**	**Concentration (w/w %)**
90°C	1	1355.479	0.04583	0.000	0.00000	225.003	0.00200
	2	1355.480	0.04583	0.000	0.00000	225.006	0.00200
	3	1363.465	0.04609	0.000	0.00000	225.001	0.00200
	Average		0.04592		0.00000		0.00200
	Total (w/w%)	0.04792					
100°C	1	69.609	0.00245	0.000	0.000	66.889	0.00051
	2	69.610	0.00245	0.000	0.000	67.890	0.00052
	3	69.608	0.00245	0.000	0.000	68.891	0.00053
	Average		0.00245		0.000		0.00052
	Total (w/w%)	0.00298					
110°C	1	43.917	0.00159	9.929	0.01933	187.660	0.00165
	2	43.910	0.00159	9.930	0.01934	187.650	0.00165
	3	44.915	0.00162	9.926	0.01933	187.665	0.00165
	Average		0.00160		0.01933		0.00165
	Total	0.02258					

	(w/w%)						
120°C	1	160.178	0.00551	29.419	0.06120	144.212	0.00124
	2	160.200	0.00551	29.417	0.06120	144.173	0.00124
	3	160.180	0.00551	29.413	0.06119	144.214	0.00124
	Average		0.00551		0.06119		0.00124
	Total (w/w%)	0.06794					
130°C	1	429.839	0.01460	73.144	0.15513	954.600	0.00888
	2	429.840	0.01460	73.431	0.15574	954.670	0.00888
	3	428.850	0.01457	73.351	0.15557	954.600	0.00888
	Average		0.01459		0.15548		0.00888
	Total (w/w%)	0.17895					

Temperature	**Replication**	**Dipalmitate**		**Dilinoliate**		**Dioleate**	
		Area (pA*s)	**Concentration (w/w %)**	**Area (pA*s)**	**Concentration (w/w %)**	**Area (pA*s)**	**Concentration (w/w %)**
90°C	1	241.061	0.04724	0	0.000	668.195	0.00057
	2	245.150	0.04804	0	0.000	567.190	0.00047
	3	245.065	0.04802	0	0.000	667.198	0.00057
	Average		0.04777		0.000		0.00053
	Total (w/w%)	0.04785					
100°C	1	64.889	0.01273	0.000	0.000	0.000	0.000
	2	62.890	0.01234	0.000	0.000	0.000	0.000
	3	61.891	0.01214	0.000	0.000	0.000	0.000
	Average		0.01240		0.000		0.000
	Total (w/w%)	0.01185					
110°C	1	116.625	0.02286	63.206	0.00162	503.711	0.00040
	2	115.930	0.02273	63.210	0.00162	503.710	0.00040
	3	115.620	0.02267	63.202	0.00162	503.712	0.00040
	Average		0.02275		0.00162		0.00040
	Total (w/w%)	0.02478					
120°C	1	246.743	0.04835	193.402	0.00589	698.008	0.00060

	2	247.150	0.04843	193.400	0.00589	698.010	0.00060
	3	247.145	0.04843	193.110	0.00588	698.003	0.00060
	Average		0.04840		0.00589		0.00060
	Total (w/w%)	0.05489					
130°C	1	514.514	0.10080	100.000	0.00283	1656.177	0.00155
	2	512.920	0.10049	104.000	0.00296	1656.180	0.00155
	3	512.915	0.10049	103.000	0.00293	1656.175	0.00155
	Average		0.10060		0.00291		0.00155
	Total (w/w%)	0.10506					

Temperature	Replication	Tripalmitate		Trilinoleate		Trioleate	
		Area (pA*s)	**Concentration (w/w %)**	**Area (pA*s)**	**Concentration (w/w %)**	**Area (pA*s)**	**Concentration (w/w %)**
90°C	1	1497.440	0.03799	0.000	0.000	95.259	0.00040
	2	1497.439	0.03799	0.000	0.000	95.250	0.00040
	3	1496.043	0.03796	0.000	0.000	94.230	0.00040
	Average		0.03798		0.000		0.00040
	Total (w/w%)	0.03823					
100°C	1	1526.490	0.03873	0.000	0.000	1023.389	0.00502
	2	1516.495	0.03848	0.000	0.000	1023.390	0.00502
	3	1603.480	0.04069	0.000	0.000	1023.395	0.00502
	Average		0.03930		0.000		0.00502
	Total (w/w%)	0.04417					
110°C	1	6334.030	0.16115	384.404	0.00202	2312.000	0.01142
	2	6334.030	0.16115	384.410	0.00202	2312.000	0.01142
	3	6341.031	0.16133	384.407	0.00202	2312.000	0.01142
	Average		0.16121		0.00202		0.01142
	Total (w/w%)	0.17465					

120°C	1	1067.846	0.0271	128.374	0.00058	928.654	0.00455
	2	1067.850	0.0271	128.380	0.00058	928.670	0.00455
	3	1066.890	0.0270	128.350	0.00058	928.650	0.00455
	Average		0.0270		0.00058		0.00455
	Total (w/w%)	0.03217					
130°C	1	829.205	0.02098	211.685	0.00105	1013.140	0.00497
	2	829.210	0.02098	211.630	0.00105	1013.150	0.00497
	3	829.207	0.02098	211.650	0.00105	1013.130	0.00497
	Average		0.02098		0.00105		0.00497
	Total (w/w%)	0.02699					

Temperature (°C)	TMP $_P$ (g/mL)	Conversion (%)
90	2.69	79.62
100	1.35	89.77
110	0.44	96.66
120	2.82	78.64
130	3.85	70.83

Temperature (°C)	Composition (%)			Conversion (%)
	ME	DE	TE	
90	35.761	35.709	28.529	79.62
100	5.051	20.084	74.861	89.77
110	10.171	11.162	78.671	96.66
120	43.832	35.413	20.755	78.64
130	57.540	33.782	8.679	70.83

B.4.5 Reuseability

	ME	**DE**	**TE**
R1	5.175	16.573	78.252
R2	5.810	34.100	60.090
R3	2.881	38.575	58.543
R4	24.674	34.800	40.526

B.4.6 Kinetics

TE composition at different Temperature

Time (min)	**Temperature**				
	90 °C	**100 °C**	**110 °C**	**120 °C**	**130 °C**
0	0	0	0	0	0
5	2.413	3.415	5.345	1.564	1.23
10	10.014	10.014	25.345	12.356	2.345
20	15.16	20.45	40.456	13.456	3.879
30	17.083	62.989	70.456	14.029	4.567
60	18.793	63.671	72.669	14.148	4.71
90	19.828	63.872	74.456	14.534	4.985
120	20.433	68.551	75.453	15.956	5.751
150	27.371	70.567	76.564	16.124	6.534
180	28.529	74.861	78.67	20.752	8.679

90 °C

Time	p.A*	[TMP]	lnx	1/x
2	1836.185	0.008	-4.862	129.326
5	1437.363	0.006	-5.159	173.974
10	991.1383	0.004	-5.647	283.466
15	697.7874	0.002	-6.181	483.523
20	637.8593	0.002	-6.337	564.980
25	600.472	0.002	-6.448	631.334
30	509.7062	0.001	-6.783	883.133

100 °C

Time	p.A*	[TMP]	lnx	1/x
2	1836.185	0.008	-4.862	129.326
5	1112.41	0.004	-5.489	242.063
10	1003.768	0.004	-5.629	278.505
15	807.954	0.003	-5.946	382.219
20	668.126	0.002	-6.255	520.679
25	569.848	0.001	-6.549	698.531
30	543.384	0.001	-6.645	769.290

110°C

Time	p.A*	[TMP]	lnx	1/x
2	1836.185	0.008	-4.862	129.326
5	1108.61	0.004	-5.494	243.176
10	1012.486	0.004	-5.617	275.181
15	837.386	0.003	-5.892	361.959
20	817.531	0.003	-5.928	375.382
25	595.423	0.002	-6.464	641.508
30	531.789	0.001	-6.691	805.018

120°C

Time	p.A*	[TMP]	lnx	1/x
2	1836.185	0.008	-4.862	129.326
5	1407.381	0.006	-5.185	178.609
10	949.3476	0.003	-5.708	301.221
15	761.278	0.002	-6.039	419.453
20	656.891	0.002	-6.285	536.288
25	596.982	0.002	-6.459	638.332
30	530.322	0.001	-6.697	809.776

130°C

Time	p.A*	[TMP]	lnx	1/x
2	1836.185	0.008	-4.862	129.327
5	1156.408	0.004	-5.438	229.884
10	883.33	0.003	-5.812	334.304
15	727.613	0.002	-6.112	451.161
20	631.942	0.002	-6.354	574.554
25	582.905	0.001	-6.505	668.229
30	519.891	0.001	-6.740	845.338

1st order

Time	90°C	100°C	110°C	120°C	130°C
2	-4.862	-4.862	-4.862	-4.862	-4.862
5	-5.159	-5.489	-5.494	-5.185	-5.438
10	-5.647	-5.629	-5.617	-5.708	-5.812
15	-6.181	-5.946	-5.892	-6.039	-6.112
20	-6.337	-6.255	-5.928	-6.285	-6.354
25	-6.448	-6.549	-6.464	-6.459	-6.505
30	-6.783	-6.645	-6.691	-6.697	-6.74

2nd order

Time	90°C	100°C	110°C	120°C	130°C
2	129.326	129.326	129.326	129.326	129.327
5	173.974	242.063	243.176	178.609	229.884
10	283.466	278.505	275.181	301.221	334.304
15	483.523	382.219	361.959	419.453	451.161
20	564.98	520.679	575.382	536.288	574.554
25	631.334	698.531	641.508	638.332	668.229
30	743.133	769.29	805.018	809.776	845.338

Overall

Temperature (°C)	1ST ORDER	R^2	2ND ORDER	R^2
90	-0.0669	0.9478	22.671	0.981
100	-0.0596	0.9446	22.956	0.9789
110	-0.0571	0.9314	23.332	0.972
120	-0.0639	0.9577	23.889	0.9953
130	-0.0611	0.9307	24.337	0.9948

Rate of Reaction	Overall 1st order		Overall 2nd Order	
	(%wt/wt min °C)	R^2	(%wt/wt min °C)	R^2
k_{TMP}	7E-05	0.0922	0.0427	0.9868

Activation Energy, Ea

$$\frac{-Ea}{RT} = \text{Slope of graph log k versus 1/T}$$

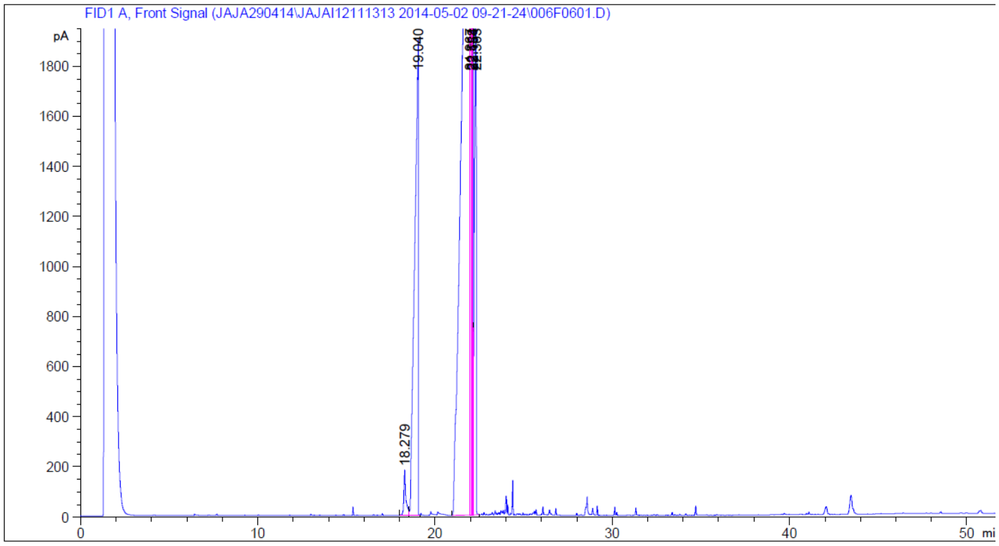
$$\frac{-Ea}{(2.303)(8.314)} = -115.11$$

-Ea = 2204.03 J/mol = 2.2 kJ/mol

Jatropha methyl ester

```
Data File C:\CHEM32\1\DATA\JAJA290414\JAJAI12111313 2014-05-02 09-21-24\006F0601.D
Sample Name: JME

    =====================================================================
    Acq. Operator   : JAJA                          Seq. Line :    6
    Acq. Instrument : Instrument 1                   Location : Vial 6
    Injection Date  : 5/2/2014 2:47:10 PM                 Inj :    1
                                                   Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\DATA\JAJA290414\JAJAI12111313 2014-05-02 09-21-24\JAJA.M
    Last changed    : 4/29/2014 11:56:01 AM by JAJA
    Analysis Method : C:\CHEM32\1\METHODS\SHUTDOWN.M
    Last changed    : 5/5/2014 1:53:08 PM by JAJA
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



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

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

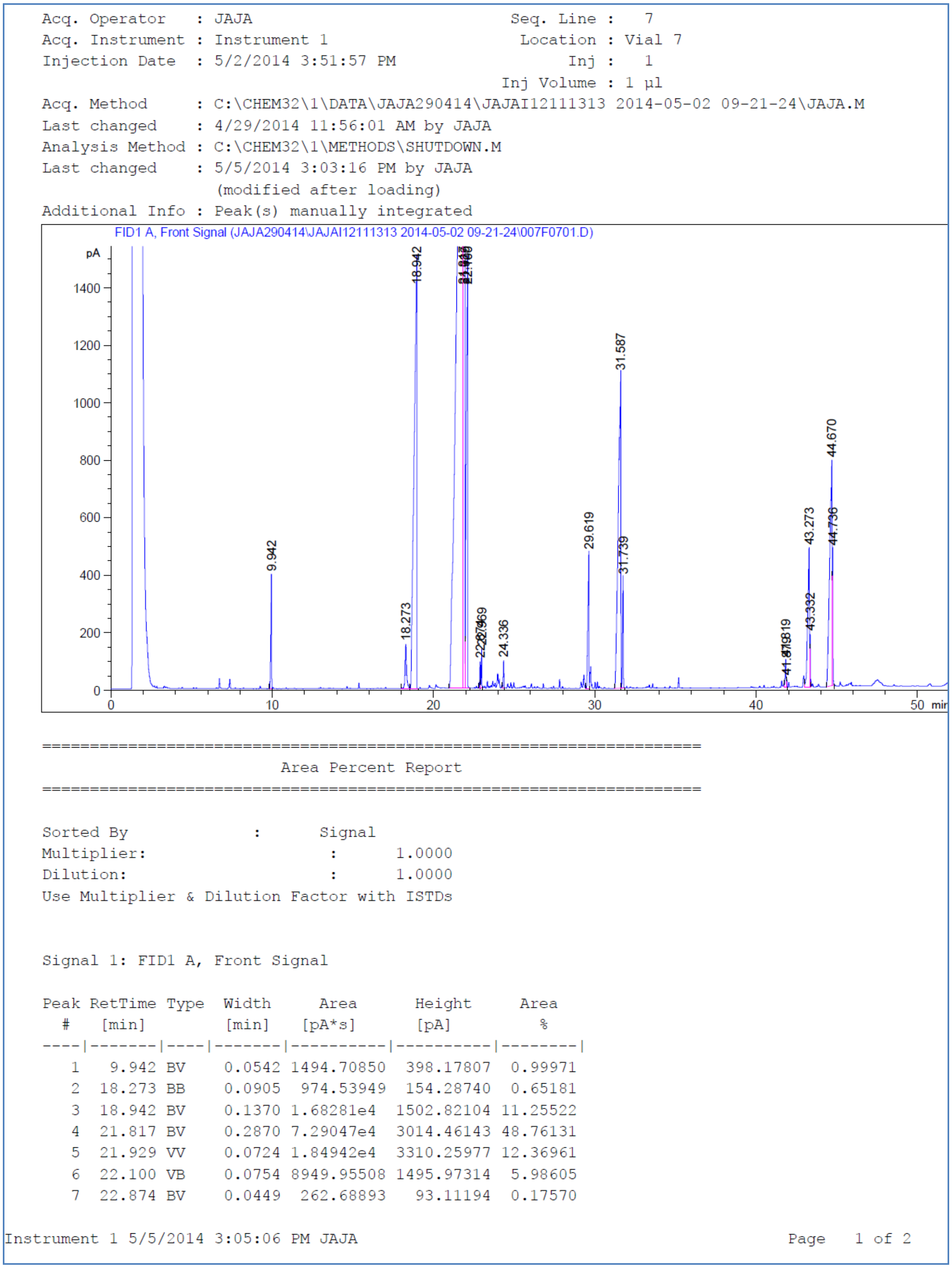

    Signal 1: FID1 A, Front Signal

    Peak RetTime Type  Width      Area      Height     Area
      #   [min]        [min]    [pA*s]      [pA]        %
    ----|-------|----|-------|----------|----------|--------|
       1  18.279 BV     0.1110 1482.66113  183.58101  0.79192
       2  19.040 VV     0.1737 2.68691e4  1892.23682 14.35138
       3  21.967 BV     0.3148 9.98546e4  3758.19702 53.33453
       4  22.044 VV     0.0660 2.11548e4  4084.84155 11.29925
       5  22.109 VV     0.0425 1.26858e4  4010.47559  6.77576
       6  22.154 VV     0.0385 1.16067e4  4218.00000  6.19936
       7  22.303 VB     0.0820 1.35696e4  2116.04175  7.24780

  ----|-------|----|-------|----------|----------|--------|
  Totals :                  1.87223e5  2.02634e4

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

Trimethylolpropane Ester



```
Acq. Operator   : JAJA                              Seq. Line :    7
Acq. Instrument : Instrument 1                       Location : Vial 7
Injection Date  : 5/2/2014 3:51:57 PM                     Inj :    1
                                                   Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\DATA\JAJA290414\JAJAI12111313 2014-05-02 09-21-24\JAJA.M
Last changed    : 4/29/2014 11:56:01 AM by JAJA
Analysis Method : C:\CHEM32\1\METHODS\SHUTDOWN.M
Last changed    : 5/5/2014 3:03:16 PM by JAJA
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

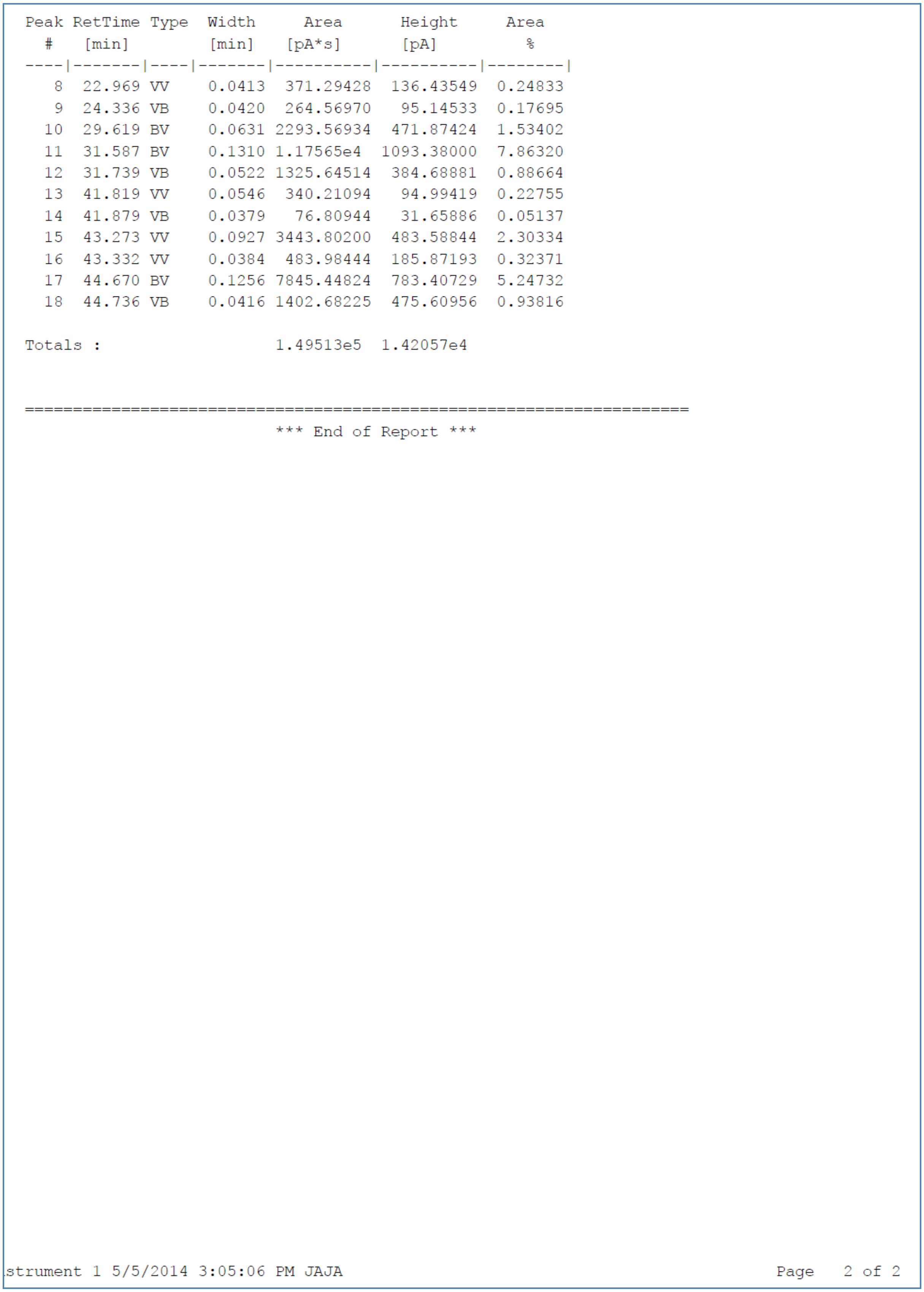
```
=====================================================================
                         Area Percent Report
=====================================================================

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


Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]         %
----|-------|----|-------|----------|----------|--------|
   1   9.942 BV    0.0542 1494.70850  398.17807  0.99971
   2  18.273 BB    0.0905  974.53949  154.28740  0.65181
   3  18.942 BV    0.1370 1.68281e4  1502.82104 11.25522
   4  21.817 BV    0.2870 7.29047e4  3014.46143 48.76131
   5  21.929 VV    0.0724 1.84942e4  3310.25977 12.36961
   6  22.100 VB    0.0754 8949.95508 1495.97314  5.98605
   7  22.874 BV    0.0449  262.68893   93.11194  0.17570

Instrument 1 5/5/2014 3:05:06 PM JAJA                                   Page    1 of 2
```



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   8  22.969 VV    0.0413  371.29428  136.43549  0.24833
   9  24.336 VB    0.0420  264.56970   95.14533  0.17695
  10  29.619 BV    0.0631 2293.56934  471.87424  1.53402
  11  31.587 BV    0.1310 1.17565e4  1093.38000  7.86320
  12  31.739 VB    0.0522 1325.64514  384.68881  0.88664
  13  41.819 VV    0.0546  340.21094   94.99419  0.22755
  14  41.879 VB    0.0379   76.80944   31.65886  0.05137
  15  43.273 VV    0.0927 3443.80200  483.58844  2.30334
  16  43.332 VV    0.0384  483.98444  185.87193  0.32371
  17  44.670 BV    0.1256 7845.44824  783.40729  5.24732
  18  44.736 VB    0.0416 1402.68225  475.60956  0.93816

Totals :                  1.49513e5  1.42057e4



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

```
strument 1 5/5/2014 3:05:06 PM JAJA                                              Page    2 of 2
```

APPENDIX C

LIST OF PUBLICATION

A) Journal

1) Nurdin, S., Sukri, H.A.M., Yunus, R.M., Gimbun, J., Abbakar, M.S.A, Shah, L.A., Ghazali, N.S., Misebah, F.A. and Harun, S.F. (2013). Kinetics and adsorption equilibrium of cadmium, silver and copper onto rubber seeds shell waste. *Journal of Engineering and Applied Sciences.* (In the publication process)(ISI/Scopus Format)

2) Nurdin,S., Misebah, F.A., Yunus, R.M., Mahmud, M.S., and Sulaiman, A.Z. (2014) Conversion of Jatropha curcas Oil to Ester Biolubricant Using Solid Catalyst Derived from Saltwater Clam Shell Waste (SCSW). *World Academy of Science, Engineering and Technology International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering, 8* (9), 939-945. (ISI Journal).

3) Nurdin, S., Misebah, F.A., Haron, S.F., Ghazali, N.S., Yunus, R.M., and Gimbun, J. (2014). Activated Paphia undulate Shells Waste (APSW): A Cost-Effective Catalyst for Biodiesel Synthesis from Rubber and Jatropha curcas Seeds Oil (RSOME & JSOME). *International Journal of Chemical Engineering and Applications, 5*(6), 483-488. (Indexed / Peer reviewed journal).

4) Nurdin, S., Misebah, F.A., Haron, S.F., and Yunus, R.M. (2014). Transesterification Kinetics of *Jatropha* Methyl Ester and Trimethylolpropane for Biolubricant Synthesis Using *Paphia undulata* Shell Waste.*Advances in Environmental Biology*, 9(1), 35-43. (ISI / Scorpus journal)

5) Nurdin, S., Z. Jema'at, Zakaria, N.F., Haron, S.F., Ghazali, N.S., and Misebah, F.A. (2014). Mixture of S.Rebaudiana Leaves And Stems Waste For Steviosides

Synthesis Using Ethanol-Water Solvents. *Journal of Engineering and Technology,* 5(2), 51-62. (Indexed / Scorpus journal).

B) Patent

Nurdin, S., Yunus, R.M., Gimbun, J., Sulaiman, S.Z., Sukri, H.A.M., Shah, L.A. and Misebah, F.A. (2013). Rubber Seeds Shell Adsorbent. P.I.2013004511.

C) Presented Papers at Conferences / Symposiums / Seminars

Authors: S. Nurdin, H.A.M sukri, R.M Yunus, J.Gimbun, M.S Abbakar, L.A.Shah, N.S. Ghazali, F.A. Misebah, S.F Harun
Title of Paper : Kinetics and adsorption equilibrium of Cadmium, silver and copper onto rubber seeds shell waste.
Name and Country of Conference: ICCEIB2013 Kuantan, Pahang (National)

Authors: Fatimah A. Misebah, Said Nurdin, Rosli M.Yunus, Mohd S. Mahmud, Ahmad Z. Sulaiman, Syafiqah A.Khairuddin
Title of Paper: Conversion of *Jatropha curcas* Oil to Biolubricant Using Solid Catalyst Derived from Saltwater Clam Shell Waste (SCSW)
Name and Country of Conference: CITREX 2014, Kuantan, Pahang

Author: Nurdin,S., Misebah, F.A., Haron, S.F., & Yunus, R.M.
Tittle of Paper: Transesterification Kinetics of *Jatropha* Methyl Ester and Trimethylolpropane for Biolubricant Synthesis Using *Paphia undulata* Shell Waste.
Name and Country of Conference: ICGT 2015, Kota Kinabalu, Sabah

D) Awards

1) IID 2014: GOLD MEDAL
2) CITREX 2014: SILVER MEDAL