

**LUBRICANT ESTER SYNTHESIS FROM RUBBER
SEEDS WASTE USING COCKLE SHELLS AS
SOLID CATALYST**

NG WEI KEONG

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

**Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG**

JUNE 2013

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ABSTRACT

This paper presents the lubricant ester synthesis from rubber seeds waste using cockle shells as solid catalyst. Rubber seeds were chosen as raw materials in synthesizing lubricant because it is a type non-edible resource and this can avoid the problem of shortcoming on human foods. Rubber seed and cockle shell was abundance in Malaysia and causing waste problem. The kernel of rubber seed was milled into average size of 1mm in diameter. N-hexane is used as solvent in microwave assisted extraction of rubber seed oil. The catalyst that used in this research is cockle shells due to the high content on CaCO_3 which can be converted into CaO. The cockle shells was cleaned and crushed into smaller particles before undergoes calcination process. Then, the activated and inactivated catalysts was analysed using X-ray Fluorescence (XRF), and Fourier transforms infrared (FTIR) spectroscopy analysis. N-hexane was used as solvent in microwave assisted extraction of rubber seed oil. Two steps transesterification process was applied in order to reduce the fatty acid content in the rubber seed oil. The rubber seed oil extracted from rubber seeds underwent two steps esterification process to produce rubber seed methyl ester (RSME). The biolubricant produced through the transesterification process of rubber seed methyl ester (RSME) and trimethylolpropane (TMP) with the presence of CaO catalyst under difference parameter of temperature, reaction time and catalyst loading. Then, the viscosity of biolubricant was analysed using viscometer. The composition of CaO in calcinated cockle shells was 97.06%. Various temperature, reaction time and catalyst loading were applied to seek the optimized result. The results shows RSME has successfully being converted into 37.8% of triester at the temperature of 110°C , 3wt% of CaO catalyst and 3 hours of reaction time. While for viscosity of the lubricant, the kinematics viscosity of lubricant fulfill the ISO VG 46. The viscosity of lubricant was found to be higher than other plant based lubricant such as palm oil.

ABSTRAK

Kertas kerja ini membentangkan kajian sintesis ester pelincir daripada biji getah sisa menggunakan kerang pemangkin pepejal. Biolubricant telah menjadi satu alternatif untuk pelincir berasaskan petrol yang disebabkan oleh isu-isu kelestarian dan alam sekitar. Biji getah dipilih sebagai bahan-bahan mentah dalam menghasilkan pelincir kerana ia adalah sejenis sumber yang tidak boleh dimakan dan ini boleh mengelakkan masalah kekurangan sumber makanan manusia. Biji getah dan kulit kerang adalah banyaknya di Malaysia dan menyebabkan masalah sisa. Isi biji getah kemudiannya dikisar ke dalam saiz purata 1mm diameter. N-hexane digunakan sebagai pelarut dalam ketuhar gelombang mikro membantu pengekstrakan minyak biji getah. Pemangkin yang digunakan dalam kajian ini adalah kerang kerana kandungan yang tinggi pada CaCO_3 yang boleh ditukar menjadi CaO . Kerang yang telah dibersihkan dan dihancurkan menjadi serbuk yang lebih kecil sebelum melalui proses pengkalsinan. Kemudian, pemangkin diaktifkan dan tidak aktif yang diperolehi dianalisis menggunakan sinaran XRF dan Fourier (FTIR) analisis spektroskopi. N-hexane telah digunakan sebagai pelarut dalam ketuhar gelombang mikro membantu pengekstrakan minyak biji getah. Dua proses langkah transesterifikasi telah digunakan untuk mengurangkan kandungan asid lemak dalam minyak biji getah. Minyak biji getah diekstrak daripada biji getah adalah melalui proses dua langkah pengesteran untuk menghasilkan benih getah metil ester (RSME). Biolubricant yang telah dihasilkan melalui proses transesterifikasi getah benih metil ester (RSME) dan trimethylolpropane (TMP) dengan kehadiran pemangkin CaO bawah parameter perbezaan suhu, masa tindak balas dan pemangkin muatan. Akhirnya kelikatan biolubricant dihasilkan dianalisis menggunakan meter kelikatan. Komposisi CaO dalam cengkerang kerang calcinated didapati 97.06%. Suhu pelbagai, masa tindak balas dan pemangkin muatan telah digunakan untuk mendapatkan tindak balas optimum. Keputusan menunjukkan RSME telah berjaya ditukarkan kepada 37.8% daripada triester pada suhu $110\text{ }^\circ\text{C}$, dengan menggunakan 3wt% daripada CaO pemangkin pada 3 jam masa tindak balas. Manakala bagi kelikatan minyak pelincir, kelikatan kinematik dan kelikatan pelincir didapati memenuhi standard ISO VG 46. Kelikatan minyak pelincir telah didapati lebih tinggi daripada loji berasaskan lain pelincir seperti minyak sawit dan cursas jatropha. Keputusan ini menunjukkan pelincir RSO mempunyai potensi untuk menggantikan loji berasaskan lain pelincir. Penambahan bahan tambahan telah dicadangkan untuk meningkatkan kelikatan dan kualiti pelincir dihasilkan.

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LIST OF ABBREVIATIONS

<i>RSO</i>	Rubber seed oil
<i>TMP</i>	Trimethylolpropane
<i>ME</i>	Methyl ester
<i>DE</i>	<i>Di-ester</i>
<i>TE</i>	Tri-ester
<i>CaO</i>	Calcium oxide
<i>CH₃OH</i>	Methanol
<i>CaCO₃</i>	Calcium carbonate
<i>CO₂</i>	Carbon dioxide
<i>XRF</i>	X-ray fluorescence
<i>FTIR</i>	Fourier transform infrared
<i>GC-MS</i>	Gas Chromatography Mass Spectrometry

1 INTRODUCTION

1.1 *Motivation and statement of problem*

Lubricants are oils that used in the machinery to reduce friction and the total application of lubricant in the world used is about 37 million tons per year. The most commonly lubricant that consumed in the market is automotive lubricants followed by hydraulic fluids. Nowadays, the lubricants are formulated of 70-90% base oils combined with functional additives in order to change their natural properties in term of cold stability, oxidation stability, hydrolytic stability, viscosity and viscosity index to suit their specific application respectively (Akerman et al., 2011).

Due to the rapid economic growth, demands on lubricant are growing and caught the public's attention on the limitation of the fossil fuel and environment degradability (Arumugam & Sriram, 2012).The widely use of petroleum based oil have caused depletion in quantity and it takes million year to restore back (Salimon et al., 2011).In the last decades, the use of mineral based oil had led to a serious pollution soil and water source problems. For example, 1 liter of mineral oil leaked will contaminates 1 million liter of clean water sources. There are only 10-50% used lubricants oil are recycled on the industries. While for the remaining of millions tons of lubricants are dumped to the environment through leakages and careless disposal method. Most of them are mineral based oil and they are non-biodegradable (Silva, n.d). Thus there is a need in finding lubricants that are environmentally friendly and without leaving aside its basic properties compared to petroleum based lubricant.

The issue on developing alternative bio-lubricant has been raised over the years. Biolubricant was gaining interest to choose as an alternative because it is non-toxic, biodegradable, produced from renewable resources, good lubricity, low volatility, and high viscosity as compared to mineral based lubricant. However, the disadvantages on biolubricant are they easy to oxidize, low thermal stability and poor flow properties at low temperature as compared to mineral based lubricant. The stability of the bio based lubricant can be improved through the process of transesterification, epoxidation and selective hydrogenation (Madankar et al., 2012).

Production of biofuel and biolubricant from edible food crops such as corns, and soya will cause a shortcoming of food material for human (Arbain & Salimon, 2010). In 2012, the total rubber plantation in Malaysia is 1041540 hectares and they produce (Malaysian Rubber Board, 2012). A total range of 800-1200 of rubber seeds per hectare per year will be produce in a rubber plantation and they will be treated as waste (Eka et al., 2010). These figures indicate the vast availability of rubber seed product in a year and also the amount of rubber seed treated as waste. A total of 40-50% of pale yellow oil can be extracted from the rubber seed kernels (Ramadas et al., 2005). This made rubber seed oil an alternative for the main supply in the vegetable oil (Aigbodion & Pillai, 2000).

Among of the alkaline catalysts, calcium oxide is one of the best alternative catalysts as it has a lower solubility, higher alkalinity, cheaper and is easier to handle as compare with potassium hydroxide. Its catalytic activity can be improved by applying calcination at 973K in order to remove the impurities such as surface carbonate and the hydroxyl groups (Kawashima et al., 2008). Cockle is a cheap protein source which is utilized as local dishes. During Ninth Malaysia Plan, 13000 metric tons of cockles are expected to be produced in Malaysia. In 2007, there are total of 1055 farmers focus in growing cockles which involving 6000 hectare of cultivation area. These statistic not only show the huge availability of cockles but also the amounts of waste shells produced. These shells will be dumped and caused unpleasant smells which disturb the environment (Mohamed et al., 2012). Cockle shell is discarded abundantly in Malaysia from the seafood industry. In this study, cockle shell will be utilized as solid catalyst in the production of biolubricant because it contains calcium carbonate which can be converted into calcium oxide during calcination. This research is to synthesis the lubricant from rubber seed oil using calcium oxide from cockle shell as catalyst. The characteristic of the solid catalyst will be studied and the optimum amount of catalyst required for production of bio-lubricant from rubber seed.

1.2 Objectives

The following is the objective of this research:

- To characterize activated catalyst from cockle shell for lubricant synthesis based on parameter.

1.3 Scope of this research

In order to achieve the objective of the study, there are some scopes have to be done as follows:

- i) Characterize and activation of the catalyst performance from cockle shell for lubricant ester synthesis.
- ii) Synthesizing of lubricant from extracted rubber seed oil based on process parameter.
- iii) Analysing of lubricant synthesized using Gas Chromatography Mass Spectrometry
- iv) Analysing viscosity of synthesized lubricant.

2 LITERATURE REVIEW

2.1 *Biolubricant*

Bio-lubricant is a renewable resource which is produce from animal fats or vegetable oils (Salimon et al., 2011). Bio-lubricant is a biodegradable product and is proven can be decomposed within one year. Vegetable oil consists of triglycerides which are made up of three fatty acid molecules bounded to a glycerol molecule. For a good biolubricant, the basic properties that it must achieve are high viscosity, low pour point, low corrosion, high biodegradability, and low oxidative stability.

Below shows the explanation on parameter of lubricant properties:

- a. Viscosity: It is one of the main parameter of biolubricant. It relates to the film formation which protects the surfaces of machinery parts by reducing friction between them. Fluid velocity is the resistance to the flow, which also means the required energy to happen sliding between its molecules. The minimum requirement of biolubricant in market is range from 8 to 15cSt at 100⁰C.

- b. Viscosity Index: It is an arbitrary number used to distingue the range of kinetic viscosity of oil with the temperature. A high viscosity means when the temperature of product is increase, a low viscosity is decrease. Oils with value of viscosity index higher than 130 will have wider application. Viscosity index is measured through ASTM D2270 calculation method.

- c. Pour point: It is behavior of fluid flow at low temperature. The lowest temperature at which the movement of lubricant can observe is named as pour point. The lower the pour point of the lubricant, better quality of the lubricant will be obtained. Lubricants which have lower value of -36⁰C pour point having wider market.

- d. Corrosion: Lubricant must not be corrosive. The maximum value that lubricants have is 1B on the test of ASTM D130, which is observation of corrosion in a copper place for 3 hours and immersed in lubricant after taken out from the oven at 150⁰C.

e. Biodegradability: Vegetable and synthetic ester in market are usually biodegradable. This means that they are not permanent and will undergo physical and chemical changes as the time going when exposed to the environment. To measure the lubricants degradability, the tests of CEC L-33-T-82 and modified STURM can be used. On the CEC test, the lubricant which presents a reading higher than 67% only can considered as biodegradable.

f. Oxidative stability: Most of the vegetable oil are unsaturated and tends to be less stable on oxidation compared to mineral based oil. Mineral based oil required low amounts of antioxidants which are about 0.1-0.2% in their formulation. On the other hand, vegetable oil requires larger amounts of antioxidant which is about 1-5% to prevent the process of oxidative degradation. Rotary Pressure Vessel (RPVOT – ASTM D2272) can be applied to measure the oxidative stability of lubricant. The requirement of a good lubricant must show the oxidation time more than 180 minutes from the test (Silva, 2011).

2.2 Vegetable oil

Vegetable oil can be classified as edible and non-edible. Examples of edible oil are soya beans; canola and sunflower oil can be used for human consumptions. On the other hand, examples of non-edible oil are waste cooking oil and *Jatropha curcas*. This both type of vegetable oils are suitable for both production of biofuel and also biolubricant. In the past, there is people use vegetable oil to produce the lubricant.

The main constituents of vegetable oils are triglycerides. Triglyceride is an ester where glycerol is combined with three molecules of fatty acids. The glycerol contains three hydroxyl groups while each of the fatty acid has a carboxyl group. The composition and distribution of fatty acid is the key on determining the chemical and physical properties of vegetable oil rather than glycerol structure in the triglycerides. Most of the triglycerides of vegetable oil consist of fatty acid that has 14-15 carbons with different saturation level. The long fatty acid chains combined with polar carbonyl groups in triglycerides structure make it provide excellent lubrication. The interaction of triglycerides with metallic surfaces is stronger than hydrocarbon and this make it more effective in reducing friction and wear on the metal surfaces (Nie, 2012).

Although vegetable oil has advantages in providing excellent lubrication, there are some drawbacks; poor low temperature performance and poor oxidative stability. The presence of β -hydrogen of hydroxyl group in the glycerol which makes vegetable oil becomes unstable at high temperatures and this will damage the quality of oil and cause precipitation. However, by using the esterification process, the glycerol can be replaced with polyol such as TMP which does not contain β -hydrogen using the esterification process (Silva, 2011).

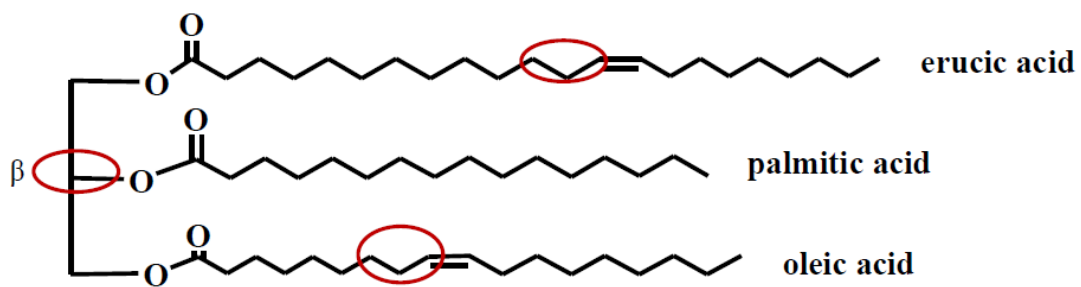


Figure 2- 1: Chemical structure of a triglyceride molecule and its oxidation susceptible sites (Nie, 2012).

Vegetable oil can be easily oxidized when they are heated or exposed to the air. The oxidative stability affected by the number of polyunsaturated fatty acid. The relationship between number of polyunsaturated fatty acid and oxidative stability is inversely proportional. Although increasing the number of polyunsaturated fatty acid will decreases the oxidative stability, but it increases the low temperature performance. As show as below figure, the β -hydrogen is easy to undergo elimination process and this will cause degradation of the particular vegetable oil (Nie, 2012).

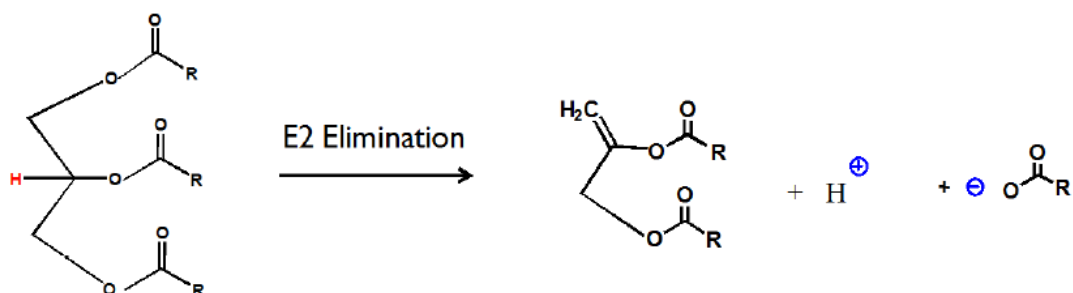


Figure 2- 2: Branched polyols with neopentyl structure (Nie, 2012).

Below table show the fatty acid composition in different type of vegetable oils.

Table 2- 1: Fatty acid composition in different types of vegetable oils (Ramadhas et al., 2005).

Property	Rubber seed oil	Sunflower oil	Rapeseed oil	Cotton seed oil
Fatty acid composition (%)				
(i) Palmitic acid, C _{16:0}	10.2	6.8	3.49	11.67
(ii) Stearic acid, C _{18:0}	8.7	3.26	0.85	0.89
(iii) Oleic acid, C _{18:1}	24.6	16.93	64.4	13.27
(iv) Linoleic acid, C _{18:2}	39.6	73.73	22.3	57.51
(v) Linoleic acid, C _{18:3}	16.3	0	8.23	0
Specific gravity	0.91	0.918	0.914	0.912
Viscosity (mm ² /s) at 40 ⁰ C	66.2	58	39.5	50
Flash point (⁰ C)	198	220	280	210
Calorific value (MJ/kg)	37.5	39.5	37.6	39.6
Acid value	34	0.15	1.14	0.11

2.3 Esterification process of methyl ester synthesis

The transesterification of triglycerides with methanol in the presence of catalyst produce fatty acid methyl ester. The general equation of esterification between triglyceride with methanol is described as equation below:

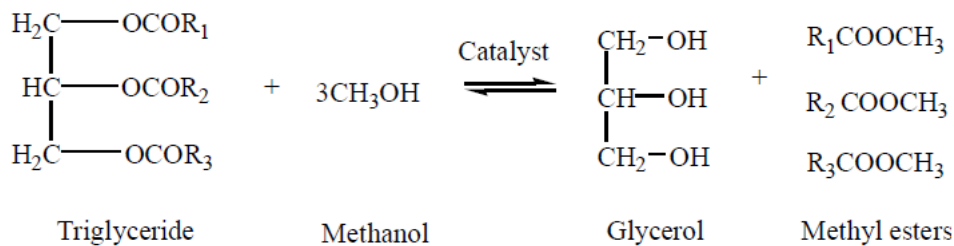


Figure 2- 3: General equation of esterification process (Nie, 2012).

From above stoichiometry reaction equation, it shows that three moles of methanol/1 mole of triglyceride to produce methyl esters. Transesterification of triglyceride is a step by step and reversible process where monoglyceride and diglyceride are produced as intermediates.

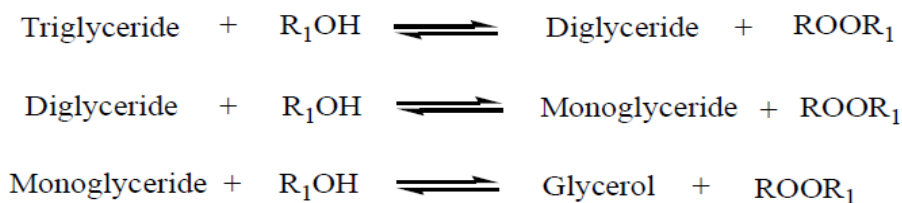


Figure 2- 4: Overall reaction equation of transesterification process (Nie, 2012).

Rubber seed oil has a high content in free fatty acids and this has caused the use of alkaline catalyst such as potassium hydroxide and sodium hydroxide is not suggestible (Ramadas et al., 2005) when the acid value is more than 4.0 because of formation major product of soap will cause to the loss and increased the difficulty in separation between biodiesel and glycerol (Sharma et al., 2008). The yield of esterification process will be reduced when the content of free fatty acid in the oil is higher. Thus, two step transesterification method is use to reduce the acid value in the vegetable oil (Ramadas et al., 2005). Acidic catalyst is not effective as compared alkaline catalyst because it needed longer reaction time, higher operating temperature and has weaker catalytic

activities (Yang et al., 2011). In order to solve the problem on saponification, two steps process is suggested namely acid esterification and alkaline esterification.

- a) Acid esterification: The first step using methanol and hydrochloric acid to reduce the free fatty acid value of crude rubber seed oil to about 2%.
- b) Alkaline esterification: After removing excess methanol from first step, it is transesterification to mono-esters of fatty acids, using alkaline catalyst (Ramadas et al., 2005).

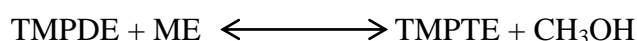
Adding excess amount of methanol can help in shifting the equilibrium to the right and this favor the production of methyl ester. The final products will be separated into two phases when the transesterification process is completed. Fatty acid methyl ester and methanol are low density product while glycerol is higher density polar liquid. The difference in density makes glycerol can be separated out by using separating funnel. Excess methanol can be recycled back and separated out from the solution through the distillation process (Nie, 2012). On the other hand, there is another research from Margaretha et al. (2011), shows that over excessive amount of methanol added will affect the production of methyl ester to be affected. When the methanol to palm oil ratio is increase from 5:1 to 7:1, the amount of methyl ester produced from triglycerides increase. However, continuous increase of methanol / oil ratio decreased the amount of methyl ester produced. The production of methyl ester and glycerol become faster when there is excessive amount of methanol. With the sufficient amount of glycerol produced, it will react with the catalytically active sites of CaO and formed calcium glyceroxide. The calcium glyceroxide produced tends to be less reactive than CaO for the transesterification process. Thus, less methyl ester produce due to consumption of catalyst.

Previous study using *Jatropha* seeds as raw materials showed that the ester produced must be washed and purified before synthesizing the biolubricant. The two step transesterification is a must because the process used to produce biolubricant needed methyl ester and not fatty acids (Resul et al., 2012).

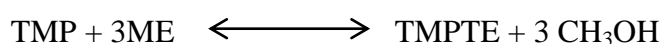
Previous study also shows that the performance of alkaline catalyst will be affected if there is presence of water in vegetable oil during the process of transesterification. The moisture in raw material will causes the triglycerides undergoes hydrolysis. Consequently, the reaction between the fatty acids and alkaline cations will cause the soap formation and consume and reduce the base catalyst efficiency. As a result, in order to get a good conversion of vegetable oil using alkaline catalyst, the water content of raw material must be less than 0.06wt. % (Yang et al., 2011).

2.4 *Transesterification process with TMP for lubricant synthesis*

From previous study, 98% of palm oil methyl ester and palm kernel oil was successfully converted to triesters through the esterification process using trimethylolpropane. Another finding was varying the samples to olive oil, rapeseed oil and lard and at the same time using trimethylolpropane (TMP) as polyol (Salimon, 2012). TMP was chosen as reactant in previous study because it is cheaper. Besides that, it also reacts at lower temperature comparing other polyol such as neopentylglycol and pentaerythritol. The weakness of vegetable oil such as low thermal stability can be solved through transesterification process (Resul, 2012). Transesterification of vegetable oil to biolubricant using polyol will minimize the limitation of biolubricant properties by elimination of hydrogen atom from beta-carbon of vegetable oil structure. The synthesis of biolubricant through transesterification process with presence of catalyst involves 3 phases. Trimethylolpropane monoester (TMPME) was converted into trimethylolpropane diester (TMPDE) as intermediate product and finally becomes trimethylolpropane trimer (TMPTE). The reaction is shown as below when 3 mol of methyl ester (ME) react with 1 mol of trimethylolpropane to become TMPTE (Nie, 2012).



Overall reaction:



2.5 Rubber seed

The rubber seed from the rubber tree (*Hevea brasiliensis*) will be used as raw material for synthesis of bio-lubricant in this research. The Hevea tree produces latex (Oladoja, 2007). The dry kernels of the rubber seeds have been found to be rich in non-edible oil varies from 35 to 45%. According to Ramadhas et al. (2012), the fatty acid composition of rubber seed oil are 18.9% of saturated acid , 80.5% of unsaturated acid and 0.6% others. Rubber seed oil is commercially extracted from the rubber seed for various purposes such as production of bio-diesel, bio-lubricant, and alkyd resin that can used in paints as well as coatings.

In this research, rubber seed oil-based biolubricant and the synthetic lubricant (SAE 20W 40) will be compared on the properties of viscosity index, flash point and pour point. Below table shows comparison properties of rapeseed oil based bio-lubricant and standard mineral based lubricant from previous study.

Table 2- 2: Properties of Synthetic and Rape seed Oil-Based Biolubricant (Arumugam & Sriram, 2012).

Properties	SAE 20W 40	Rape Seed Oil-Based Bio- Lubricant
Ash content (%) (ASTM D874)	0.45	0.027
Kinematic viscosity @ 100 ⁰ C (cSt) (ASTM D5800)	15.2	11.8
Viscosity index (ASTM D2270)	133	131
Noack volatility (% wt) (ASTM D5800)	6.5	0.18
Flash point (⁰ C) (ASTM D92)	250	188
Pour point (⁰ C) (ASTM D97)	-21	6
Copper strip corrosion test (ASTM D130)	Slight tarnish	Nil
Four ball wear scar diameter (mm) (ASTM D4172)	0.68	0.55

2.6 Extraction method

In past study, there are many type of method of oil extraction from seeds such as mechanical pressing (Morshed et al., 2011), soxhlet extractor (Ikwuagu et al., 1999), and microwave assisted extraction (Boldor et al., 2010).

The method we use in in this research is microwave assisted extraction because rapidity of extraction is higher, lower energy consumption, and reduced formation of byproduct and lower solvent needed in this extraction process. Furthermore, the major reason on using microwave assisted extraction is because reaction can be performed faster, safer and efficiently (Boldor et al., 2010).

2.7 Catalyst

Generally, there are three types of catalyst that usually used by industry for production of biodiesel. They are homogeneous catalyst, heterogeneous catalyst, and enzymes type catalyst. Examples of homogeneous catalyst are sodium hydroxide, potassium hydroxide and sulphuric acid. On the other hand, examples of heterogeneous catalyst are cation-exchange resin and hydrotalcites. Moreover, examples for enzymes catalyst are *Chromobacterium viscosum*, *Candida rugosa* and *Porcine pancreas*. Homogeneous catalyst was used to be the most common type catalyst use for production of biodiesel. However, the usage of this catalyst is beginning to decrease due to its weakness. The weakness of homogeneous catalyst is it cannot be recovered and reused after the production. Besides that, it also produced toxic wastewater. The use enzyme type catalyst is not preferable because it is more expensive compared to homogeneous catalyst. Homogeneous acid catalysts have drawbacks on using higher molar ratio of methanol/oil and the reaction required longer time to accomplish (Margaretha et al., 2011). The advantages of using heterogeneous based catalyst are it can be recycle back to reuse, non-corrosive, and improve product yield and purity. Besides that, it also show better tolerance to water and free fatty acid in feed stream, having a simpler purification process and easy to separated out from the product (Gimbun et al., 2013).

Cockle is also known as *anadara granosa*. It is a type of bivalve shellfish that grows well in muddy coastal area. The composition of CaCO_3 in seashells is 95-99% and this enable the can be applied into many purpose.

The applications of sea shells are very wide and they are used in many countries for different purpose as shown in table below.

Table 2- 3: Application of difference types of shells (Mohamed et al., 2012).

Type of Seashell	Country	Application
Oysters	Japan	Cement clinkers
	Korea	Fertilizers, water eutrophication
Scallops	UK	Construction road forestry\
	Peru	Obtain lime as the input for other industrial sector
Mussels	Spain	Animal feed additives, liming agent, constituent
	US	Fertilizers
	Holland	Salt conditioner, liming agent, mussel tiles

Currently in Malaysia, cockle shell is found to be a potential biomass resource for bone repair material. Equation below shows the decomposition of CaCO_3 .



CaCO_3 converted into CaO through the process of calcination. In industry, CaO is usually used in water and sewage treatment, glass production, construction material and more. There are 3 factors which can affect the kinetic of calcination such as concentration of CO_2 , size of particles and impurities in the catalyst. The process of calcination is favors at high temperature because it is an endothermic reaction and it needs to process in low pressure in order to drive the equilibrium reaction forward (Mohamed et al., 2012).

Previous study from Margaretha et al. (2012) show that by increasing the amount of the calcium oxide produced from Pomacea sp. shell, the total yield of production of biodiesel will be increased. In the process of transesterification, the CaO basic sites transform the methanol into a more reactive nucleophile molecule. These molecules are then attack the carbonyl carbon structure of glyceride molecules more effectively. As a nutshell, when the amount of CaO catalyst is increased, the number of basic sites is also increased and this increased the production of biodiesel (Margaretha et al., 2012).

3 MATERIALS AND METHODS

3.1 *Materials*

Rubber seed is obtained from a rubber plantation which is situated in Malacca. Cockles shell is collected from a seafood restaurant in Tanjung Lumpur, Kuantan. Analytical grade chemicals will be purchased from various sources namely, Taat Bestari, Sigma-Aldrich, Permula Chemicals, Chemart Asia and others depending on the availability and price quotation.

3.2 *Overall Methodology Flowchart*

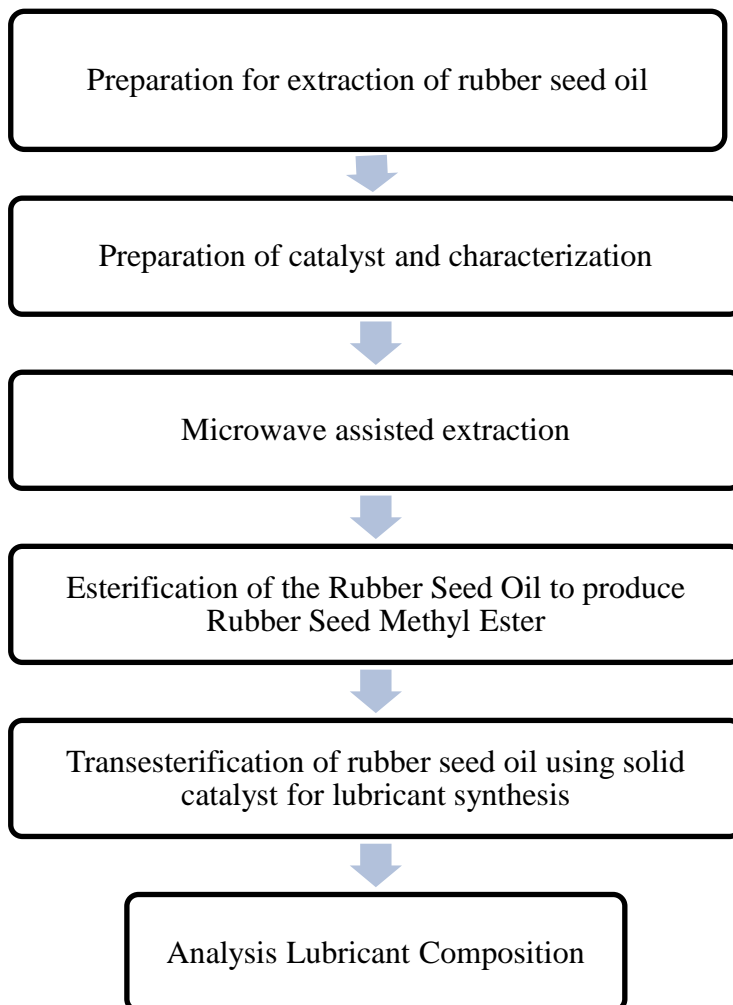


Figure 3- 1: Overall Methodology Flowchart

3.3 Experiment Procedures

3.3.1 Preparation for extraction of rubber seed oil

The rubber seed obtained was cleaned and dried in an oven at 100⁰C for 4 hours. The shell was removed manually from the kernel. Then, rubber seed is milled to average size diameter of 1mm.

3.2.2 Preparation of catalyst and characterization

The cockle shell was cleaned up using tap water and dried overnight. It was crushed and calcinated in furnace (Carbolite, CWF1215) at 900⁰C for 2 hours (Margaretha et al., 2012). The raw material and solid catalyst will be characterized using X-ray fluorescence (XRF) spectrometry and Fourier transform infrared (FTIR) spectroscopy analysis.

3.2.3 Microwave assisted extraction

Milled rubber seed and n-hexane in 1:3 weight ratio were put into a extraction flask for 30 minutes at 60 °C with the power of 200W using the microwave. The mixture of hexane and extracted rubber seed oil is then separated using a rotary evaporator.

3.2.4 Esterification of the rubber seed oil to produce rubber seed methyl ester

Rubber seed oil needs to undergo two step esterification processes with methanol to reduce free fatty acids content and produce ethyl ester and glycerol.

3.2.4.1 Acid esterification

100ml of rubber seed oil was put in a three necked bottom flask and equipped with reflux condenser. Amount of methanol used to rubber seed oil ratio (wt/wt) is 6:1. A total of 3% of hydrochloric acid was added into the mixture. The mixture was heated to 60⁰C for 30 minutes in continuous stirring condition. On completion of this reaction, the mixture was poured into separating funnel to separate the excess methanol. Top layer which was excess methanol, hydrochloric acid and impurities moves to the top surface which is removed, while the lower layer was separated for alkaline esterification.