CONVERSION OF RUBBER SEED OIL TO BIO-LUBRICANT USING SUPER ACID CATALYST

Dam Thi Thanh Hai[1], Tran Tan Viet[2], Do Chiem Tai[1], Tong Thi Thom[1]
[1]*Petrovietnam University*
[2]*Ho Chi Minh City University of Technology*
Email: haidtt@pvu.edu.vn

Summary

Non-edible vegetable oils can be potential alternatives to mineral oils for lubricant base stocks owing to their inherent properties such as high viscosity, high boiling range and biodegradability. In this research, rubber seed oil fatty acid methyl ester (RSOFAME) polymer was derived by polymerisation reaction from RSOFAME to be used as a bio-lubricant base stock. During the reaction, the super-acid HBF4 was used as a homogeneous catalyst. The reaction efficiency strongly depended on the reaction time (1 - 6 hours), reaction temperature (120 - 220°C) and the mass ratio of oil: catalyst (0 - 6wt%). The resulting products were confirmed by GC-MS, FTIR spectroscopy and also analysed for viscosity. The polymerisation product has a higher viscosity than FAME and RSO (96.98cSt, 5.32cSt and 37.0cSt respectively) but lower iodine value (gI_2/100g) than FAME and RSO (81.2, 132 and 134 respectively). In addition, the properties of the polymerisation product are better than refined mineral oil properties such as high flash point temperature (255°C), and high viscosity index (131.4). The best viscosity value of RSOFAME polymer was 96.98cSt and 12.97cSt at 40°C and 100°C respectively when the conditions of the polymerisation reaction were 200°C, a reaction time of 2 hours, and the oil: catalyst mass ratio of 6wt%.

Key words: *Bio-lubricant, rubber seed oil, polymerisation reaction.*

1. Introduction

The rising demand for mineral-based lubricants continuously adds to the petroleum energy supply tension and their concurrent harmful effects on the environment have led to increasing interests in the development of bio-lubricants from renewable resources.

Plant-based oils are an important part of developing new strategies, policies, and subsidies that aid in reducing the dependence on mineral oil and other non-renewable sources. These oils are promising candidates as base fluid for eco-friendly lubricants and able to replace the mineral-oil-based lubricants because of their unique chemical structures, structurally similar to the long-chained hydrocarbons in mineral oils, and their excellent lubricity, viscosity-temperature characteristics, non-toxicity, renewability and biodegradability. In addition, the development of a lubricant from non-edible vegetable oil feedstock is advantageous as it can overcome the economic, environmental and food versus fuel issues associated with edible vegetable oils [1, 2].

However, these lubricants are limited by low oxidative stability, filter clogging tendency and poor thermal stability. In general, it has been widely understood that the internal 1, 2 disubstituted unconjugated double bonds and the hydrogen atoms on the β-carbon atom of the alcohol fragment in ester molecule lead to poor oxidative and thermal stability [3, 4]. Consequently, vegetable oil has to be chemically modified by transesterification [5] or polymerisation [6] to eliminate vulnerable sites for oxidation and to interrupt the formation of crystals at low temperature. Goodrum and Geller [7] found that castor methyl ester and Lesquerella oil methyl ester also enhanced lubricity to acceptable levels at concentrations below 1%. It is believed that the high concentration of the unique fatty acid methyl ester methyl ricinolate could be responsible for the lubricity enhancing properties of castor oil methyl ester. As a general observation, cationic polymerisation of fatty acids or of fatty acid methyl esters, by using the BF_3 as a catalyst, was described in the literature [8]. The cationic oligomerisation of fatty acids to dimeric and trimeric acids catalysed by acidic clays at higher temperatures (230 - 240°C) is discovered [9].

Cationic polymerisation of natural oils or methyl ester of vegetable oil such as soybean, Jatropha, and palm oil has improved the oil stability for bio-lubricant base stock [10, 11]. However, the cationic polymerisation of rubber seed oil (RSO) has not reported discover. The biggest disadvantage of RSO is very high concentration of free fatty acid (FFA), therefore the oil remains unsuitable for many applications. On the other hand, the presence of high FFA is not a limiting factor in the case of bio-lubricants prepared from fatty acid methyl ester (FAME). Taking this as an advantage, the present study concentrated on the use of unsaturated FAME rich rubber seed oil (82%, unsaturation) for lubricant base stock preparation [12 - 14].

2. Methods and materials

2.1. Materials

RSO is pressed from the seeds in Binh Phuoc province, Vietnam in December 2014. The oil has a dark yellow colour and no impurities, and is used as a feedstock directly for reaction. Oil samples were analysed to determine the composition of fatty acids by gas chromatography GC-MS analysis and the results were showed on Table 1.

This methanol (grade: chromasolv), tetrafluoroboric acid (HBF_4), acid sulfuric (H_2SO_4) 98% potassium hydroxide powder (ACS reagent, ≥ 85%, pellets) and calcium hydroxide powder (ACS reagent, ≥ 95.0%) were purchased from Sigma-Aldrich and were used directly without further purification.

2.2. Preparation of FAME from RSO

This was due to the fact that RSO oil had a high free fatty acid value; hence, a modified two-step process of Hanny and Shizuko was used to produce FAME from RSO. This method included acid esterification followed by base transesterification [15].

In the first step, RSO was esterified with methanol to lower the fatty acid content catalysed by H_2SO_4. In the second step, the product of the first step was used for the base transesterification. The calculated amount of KOH (catalyst) and methanol was added for each reaction for the temperature and reaction time specified. The residual methanol in the crude FAME was removed by a rotary evaporator and then twice subjected to hot water (80°C) washing to remove residual glycerol and soap. The washed FAME was then dried and purified and FAME was obtained.

2.3. Polymerisation of FAME

The polymerisation was performed under different operating conditions, including various mass percentage value of tetrafluoroboric acid (HBF_4) from 0 to 6%wt, at reaction temperatures from 130°C to 220°C, and five reaction times from 0 to 6 hours.

The synthesis of polymer from FAME was carried out in a three-necked flask. Firstly, FAME was introduced and then the catalyst was loaded with various percentage values. The reaction was conducted under protective atmosphere of nitrogen and using a glass condenser with circulating cooling water, which was connected with the second neck of the flask. The flask was heated by an electric heater with magnetic stirrer. A magnetic stirrer of 2.0cm radius was used to stir the reaction mixture. After the reaction was completed, the mixture was chilled to 60°C and calcium hydroxide powder was added to the mixture to neutralise the catalyst. The mixture was stirred for a period of 20 minutes at 60°C in a heater. Then, the oil was separated by vacuum filtration at 60°C. All experiments were repeated three times, and the value reported in this paper was the average value.

Table 1. *Composition of fatty acids in RSO*

Fatty acid	Formula	Composition (wt. %)
Palmitic acid ($C_{16:0}$)	$C_{16}H_{32}O_2$	10.102
Stearic acid ($C_{18:0}$)	$C_{18}H_{36}O_2$	10.704
Oleic acid ($C_{18:1}$)	$C_{18}H_{34}O_2$	25.605
11-Octadecenoic acid, (Z) ($C_{18:1}$)	$C_{18}H_{34}O_2$	1.436
Linoleic acid ($C_{18:2}$)	$C_{18}H_{32}O_2$	37.054
Linolenic acid ($C_{18:3}$)	$C_{18}H_{30}O_2$	15.099

2.4. GC-MS analysis

Oil samples were analysed to determine the composition of fatty acids by gas chromatography GC-MS analysis with DB-1 column and the FAME produced were analysed on HP-5 column with MSD 5973 equipment (Hewlett Packard) operating in EI mode at 209eV and 1µl of each sample was injected into the column. The carrier gas used was helium at a constant flow rate of 1.4ml/min. The components were identified based on their retention time of peak.

2.5. FT-IR analysis

The identification of functional groups present was carried out through Fourier Transform Infrared Resonance (FT-IR). FT-IR analysis was done by placing the sample on sodium chloride plate (sample holder) to form a thin layer of sample. The second NaCl plate was taken and mounted on the first NaCl plate. The plate was then placed on the sample holder ready for FTIR analysis. The range of wave number used was 4000cm^{-1} to 500cm^{-1}.

2.6. Rheological property

The kinematic viscosity of the RSO-biolubricant was determined according to ASTM D 445 (ASTM Standards, 1995), which is an important characteristic of any lubricating oil, which measures the resistance of a fluid to flow under gravity at a definite temperature.

A Cannon-Fenske Opaque (Reverse-Flow) viscometer with viscometer number Y604 and a size of 150 was selected and used throughout this study. The capability of a lubricant to show good viscosity is determined by its viscosity index. Lubricants with a high viscosity index tend to display less change in viscosity with temperature and this property is desirable for most lubricants. The viscosity index was obtained by referring to ASTM D 2270 after finding the kinematic viscosities at 40°C and 100°C.

2.7. Physical characterisation

Standard ASTM (American Society for Testing and Materials) methods were followed to study the physical and chemical properties which included the iodine value, acid value, water content, and density. All the analysis was carried out in triplicate and an average was taken.

3. Results and discussion

The present study explored the potential of the unsaturated non-edible RSO for the development of a biodegradable lubricant base stock. Table 2 shows the results of the physicochemical characterisation of RSO compared with FAME from RSO. The colour of rubber seed oil was light brown after clarification and it remained liquid at room temperature. The density of RSO and FAME was found to be 0.915g/cm^3 and 0.886g/cm^3 respectively which implies that both oils are less dense than water and that there is no heavy element present in the oil. The physicochemical characters seem to be similar to that of common vegetable oils and hence validate the claim that RSO can be exploited as a base stock for developing an environment friendly lubricant. Iodine number gives an idea about the degree of unsaturation of the oil and its oxidation stability. The iodine value of 134gI$_2$/100g indicates that RSO is a semi drying oil. The acid value of RSO is 42.7, extremely higher than that of FAME, which indicates high levels of free fatty acids which might be a limiting factor in its use as a biolubricant directly. It is true that RSO has higher free fatty acids compared with some other vegetable oils. But there are several approaches which can be adopted to deacidify RSO such as chemical re-esterification, physical refining or conventional alkali de-acidification [2]. In this research, transesterification by two steps method reduced acid value from 42.7 (RSO) to 0.4 (FAME).

Table 2. Physicochemical characterisation of RSO and FAME

Oil type	RSO	FAME
Colour	Light brown	Light yellow
Density (g/cm^3)	0.915	0.886
Acid value (mg KOH/g)	42.7	0.4
Iodine value (gI$_2$/100g)	134	132
Water content mass %	0.223	0.01
Viscosity at 40°C (cSt)	37	5.32

The characteristic formation of the oil strongly depends on fatty acid composition. According to the GC-MS result, RSO consists of five types major fatty acids and the percentage composition of them was in the following order: linoleic acid, oleic acid, linolenic acid, stearic acid, palmitic acid (37.054%, 25.605%, 15.099%, 10.704% and 10.102% respectively). Similar trends were observed by M.Mahbub et al. when conducting quantitative analysis of RSO. The high percentage of unsaturated fatty acid in RSO (more than 80%) provides compelling evidence of the liquid form of oil at room temperature.

3.1. Effect of temperature on the synthesis of biolubricant

Temperature is the major focus of parameter in this present study because it strongly affects the rate of reaction. Polymerisation is a temperature dependent reaction, where higher temperatures enable more energy delivery to overcome the minimum activation energy required in the reaction in order to result in more successful particle collisions. Thus, the product yield can be improved. The effect of temperature on the conversion of FAME to biolubricant was carried out in the batch reactor via polymerisation of FAME with tetrafluoroboric acid as the catalyst. The reaction temperatures investigated were ranging from 130°C to 220°C. Some literatures and published research work of optimum parameters for palm based biolubricant production have also been referred prior to carry out this study [11]. Therefore, in this temperature study, the molar ratio, the amount of catalyst used as well as the oscillation settings remain constant throughout the experiments. The effect of temperature on viscosity of the reaction during cationic polymerisation of FAME is presented in Figure 1. According to Ionescu et al., the increase of viscosity is a direct measure of the efficiency of the polymerisation process and the linoleic acid polymerises more rapidly to high molecular weight polymers. As can be seen, the viscosity of the reaction product was almost increased 2 times when the reaction temperature changed from 130°C to 200°C, which is consistent with the results obtained in previous studies. In addition, the conjugated double bonds in hydrocarbon chain are significantly reactive in cationic polymerisation reaction condition with superacids [16]. As expected, the reaction product has higher viscosity than FAME as a result of cationic polymerisation involving double bonds which are consumed during the reaction. The reaction temperature is higher than 200°C, resulting in solid polymers, therefore, the liquid product is less in amount and less in viscosity values.

3.2. Effect of reaction time on the synthesis of biolubricant

Beside the temperature, the reaction time plays an important role in cationic polymerisation reaction on the conversion efficiency in biolubricant production with superacid catalyst. The increase of viscosity during the cationic polymerisation of FAME is small in the first 1 - 2 hours of reaction but very strong after 3 - 6 hours. Figure 2 shows the viscosity increase during the polymerisation of FAME with tetrafluoroboric acid (3% mass), at 200°C. The increase of viscosity proved the increase of high molecular weight species with time.

3.3. Effect of the percentage of catalyst on the synthesis of biolubricant

A tetraflouroboric acid (HBF_4) which is the most common superacid was used in the present study because HBF_4 is one of the cheapest superacids available commercially. It is known from the literature that superacids in pure form or as a solution in organic nonprotic solvents are catalytically active for oil polymerisation because water in solution destroys the carbocations, which is important species of cationic polymerisation. In addition, the polymerisation reaction of fatty acid derivatives with only one internal double bond does not occur even though superacid has been used.

Figure 3 shows the effect of tetrafluoroboric acid concentration on viscosity after 3 hours of reaction. In this figure, the viscosity of biolubricant product of reaction with 0% mass of catalyst is small (8cSt compared with 5.32cSt of reactant), which implies that thermal polymerisation occurs in this case but the reaction rate is too slow.

When the percentage of catalyst increases from 0 to 6wt%, the viscosity of product increases rapidly. However, the concentration of superacid was more than 6wt%, the rate of reaction was very difficult to control and generated solid polymerisation product.

Figure 4 illustrates the decrease of iodine value, which is a direct measure of the double bond content, with time, during the cationic polymerisation of FAME. In addition, iodine number gives an idea about the degree of unsaturation of the oil and its oxidation stability. The iodine value was reduced from 134 (RSO) to 81.2 (polymerisation product), which implied that a huge number of double bone content in RSO was reacted under superacid condition.

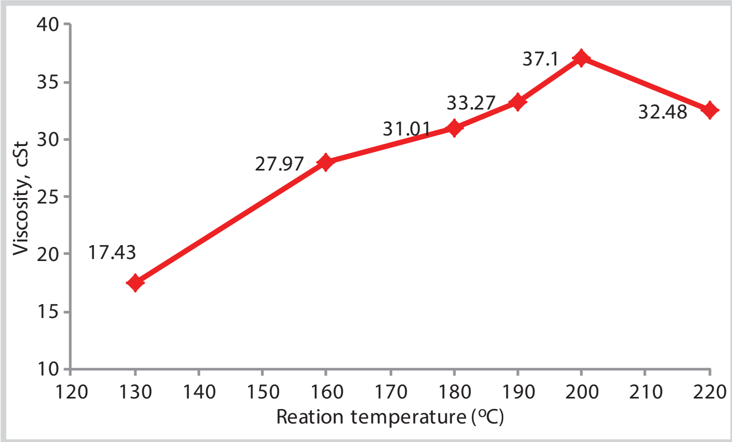

Figure 1. *Effect of reaction temperature on the product's viscosity (reaction time: 3 hours, 3% mass of catalyst)*

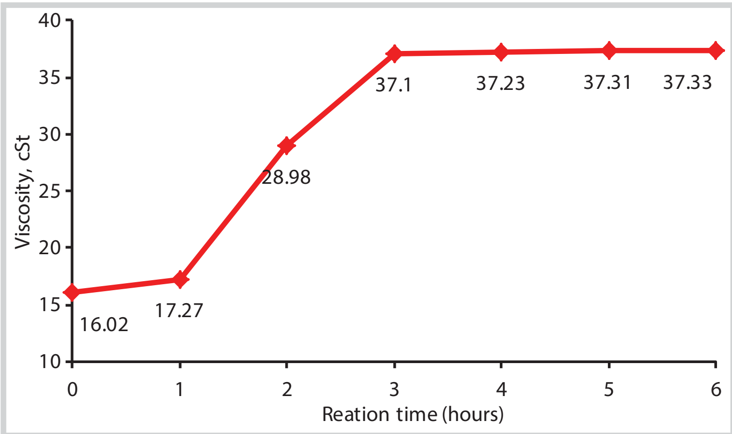

Figure 2. *Effect of reaction time on the product's viscosity (reaction temperature: 200°C, 3% mass of catalyst)*

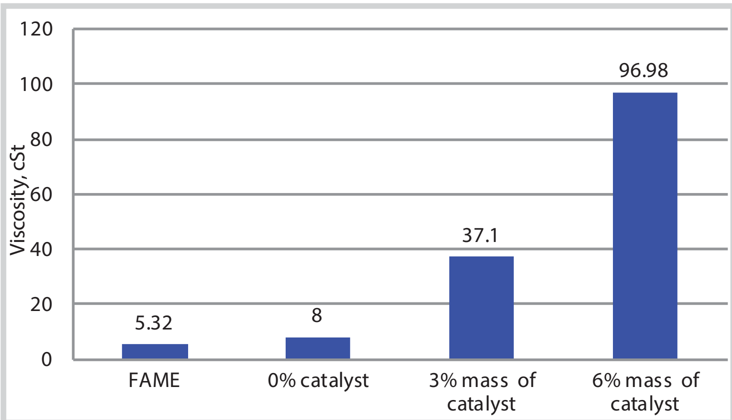

Figure 3. *Effect of percentage of catalyst on the product's viscosity (reaction temperature: 200°C, reaction time: 3 hours)*

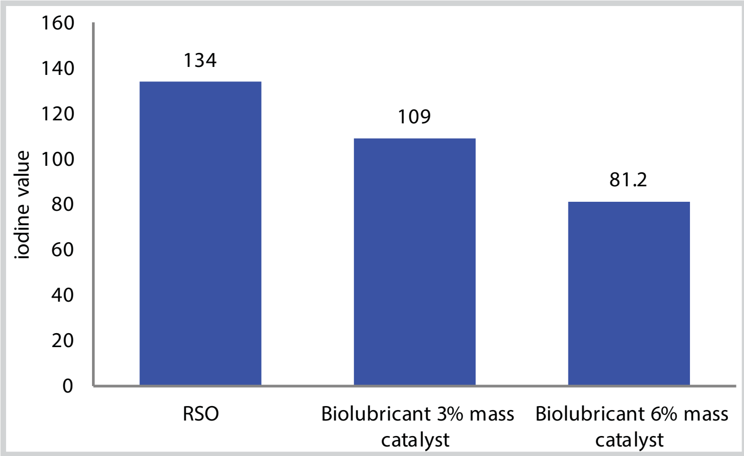

Figure 4. *Iodine value of RSO and various biolubricant products*

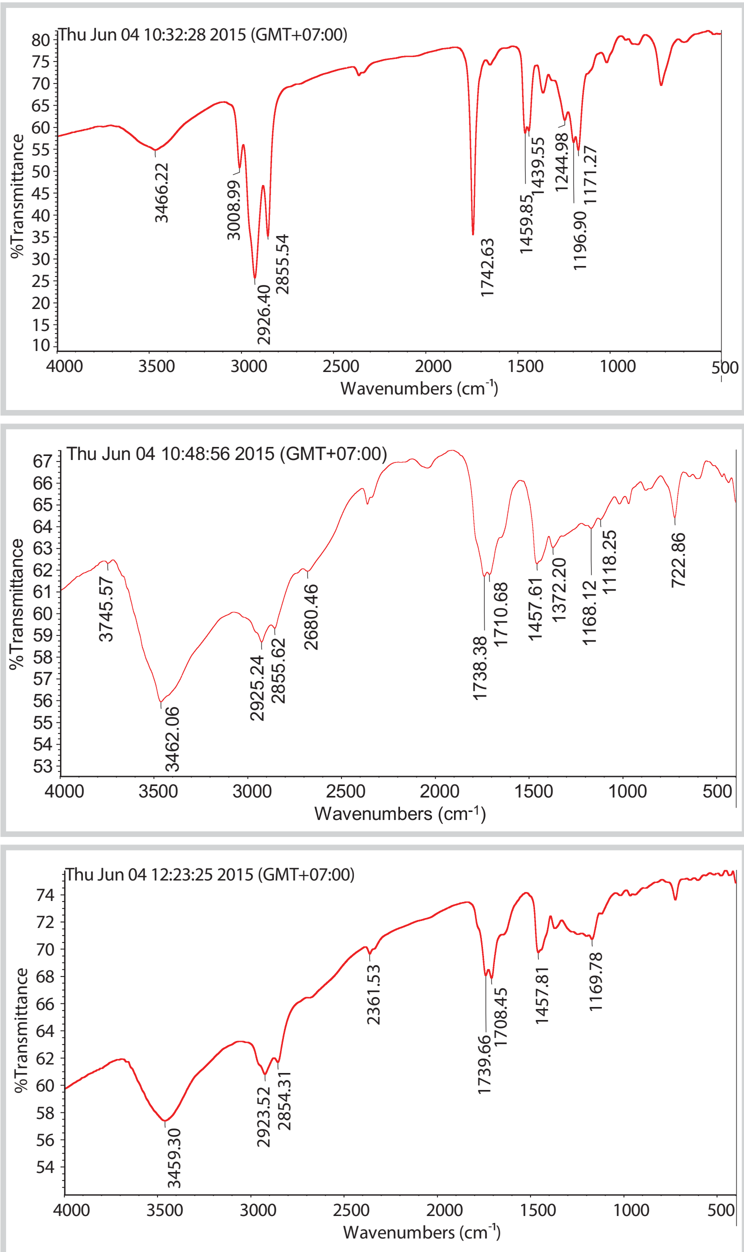

Figure 5. *FT-IR spectra of initial RSO, FAME and polymerised FAME*

Moreover, the formation of polymer was confirmed by the disappearance of C=C groups following FTIR analysis.

Figures 5 shows the FT-IR spectra of initial RSO, FAME and polymerised FAME after 6 hours of reaction, respectively. The spectrum from the FTIR analysis displays several absorption peaks of C-C=C symmetric stretch double bonds at 1675 - 1600cm^{-1}, of various C-H from CH_2 groups, CH groups and CH_3 groups (2925cm^{-1}, 2854cm^{-1}, 1163 - 1463cm^{-1}). Functional groups representing C = O (1737, 1738cm^{-1}) and the C-O bands of esters (1117 - 1118cm^{-1}) are clearly visible in the spectra.

The important peaks observed in the FTIR spectrum of polymerised FAME is the absorption characteristic of "cis" double bonds at 790cm^{-1}. On the other hand, the FTIR spectra of FAME, the absorption bands from the "cis" double bonds were lower intensity. This result suggests that the rearrangement of some initial "trans" double bonds of FAME to "cis" double bonds occurs under the polymerisation reaction conditions.

The polymerisation of FAME with superacid has increased the oil stability. Table 3 shows the lubricant characterisation of the polymerisation product in comparison with FAME. Based on this table, the flash point of polymerisation product is high at 255°C compared to the flash point of FAME which was at 140°C.

The polymerisation of FAME with superacid has increased the oil stability. Table 3 shows the lubricant characterisation of the polymerisation product in comparison with FAME. Based on this table, the flash point of polymerisation product is high at 255°C compared to the flash point of FAME or normal lubricating oil which is at 140°C and 210°C, respectively. The high value of flash point and the less amount of double bond content in the polymerisation product suggest that the oil thermal stability has been increased.

In addition, the lubricant characterisation of polymerisation product was compared with the properties of FAME and RSO. As shown in Tables 2 and 3, the value of viscosity followed the order polymerisation product > RSO > FAME at 40°C (96.98cSt, 37cSt and 5.32cSt respectively). The

Table 3. *Lubricant characterisation of the polymerisation product and FAME*

Oil type	FAME	Polymerisation product
Density (g/cm^3)	0.886	0.929
Viscosity at 40°C (cSt)	5.32	96.98
Viscosity at 100°C (cSt)	0.03	12.97
Flash point, °C	140	255
Iodine value ($gI_2/100g$)	132	81.2
Viscosity index	-	131.4

evidence points to the possibility that in many cases, increase in viscosity can contribute to certain types of the slight branching and mass increases in the ester structure.

Based on the viscosity at 40°C and 100°C, the viscosity index of polymerisation product was determined and compared with the viscosity index of refined mineral oil and synthetic oil in the market. Generally, their viscosity index is around 100 and 150 and the result implied that the polymerisation product has high viscosity index. High viscosity index indicates little changes in oil viscosity with temperature therefore it forms better protective layer or film surrounding the metal surfaces [2].

4. Conclusion

By chemically modifying plant oil through polymerisation reaction of FAME of RSO with super acid HBF_4 catalyst, the characteristics of products such as viscosity, flash point, and oil thermal stability can be improved. The effect of temperature reaction, reaction time, the percentage of superacid catalyst on the synthesis of biolubricant was studied and the best reaction conditions were 200°C, reaction time 2 hours, and oil: catalyst mass ratio of 6wt%. Our results provide compelling evidence that the oil stability has increased and reduced the amount of double bond content in the synthetic ester structure by the polymerisation of FAME. The polymerisation synthetic ester with high lubricant characteristics such as viscosity, viscosity index, and flash point allowed it to be utilised as biolubricant base stock.

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