The Malaysian Journal of ANALYTICAL SCIENCES ISSN 1394-2506

SYNTHESIS OF RUBBER SEED OIL AND TRIMETHYLOLPROPANE BASED BIOLUBRICANT BASE STOCKS

(Penghasilan Stok Asas Biopelincir Berasaskan Minyak Biji Getah dan Trimetilolpropana)

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Abstract

Esters derived through a chemical combination of vegetable oil with trimethylolpropane (TMP) have the potential for biolubricants usage due to their biodegradable, non toxic and environmentally friendly nature. The synthesis of ester was carried out via esterification of TMP with fatty acid rubber seed oil (FARSO) for 5 hours of reaction at 150 ^{o}C in the present of concentrated sulphuric acid (2% w/w). A Fourier Transform Infrared Spectroscopy (FTIR) and a Gas Chromatography equipped with a Flame Ionization Detector (GC-FID) was used to determine both the presence of the ester carbonyl group (C=O) as well as the ester composition. The results showed that the esterification process has increased the oil flash point (310 ^{o}C), viscosity indices (283) and lower the pour point (-40 ^{o}C). RSOTMP ester produced has shown comparative physicochemical properties that plausible it to be used as good biolubricant base stock oil.

Keywords: ester, biolubricant; fatty acid rubber seed oil; RSOTMP ester

Abstrak

Ester yang diperolehi melalui kombinasi kimia antara minyak tumbuhan dengan trimetilolpropana (TMP) dipercayai mempunyai potensi untuk kegunaan sebagai biopelincir kerana sifatnya yang mudah terbiodegradasikan, tidak toksik dan mesra alam. Sintesis ester telah dijalankan melalui proses pengesteran TMP dengan asid lemak minyak biji getah (FARSO) selama 5 jam pada suhu 150 ^{o}C dengan kehadiran asid sulfurik pekat (2% w/w). Spektroskopi Penyerapan Inframerah (FTIR) dan Kromatografi Gas yang dilengkapi dengan Pengesan Pengionan Api (GC-FID) telah digunakan untuk menentukan kehadiran kumpulan karbonil ester (C=O) dan komposisi ester. Hasil kajian menunjukkan bahawa proses pengesteran telah meningkatkan takat kilat minyak (310 ^{o}C), indeks kelikatan (283) dan takat tuang (-40 ^{o}C). Ester TMPRSO yang dihasilkan menunjukan sifat pelinciran yang baik dan berpotensi untuk digunakan sebagai stok asas dalam penghasilan biopelincir.

Kata kunci: ester; biopelincir; asid lemak minyak biji getah; ester TMPRSO

Introduction

Growing concerns over environmental pollution caused by the use of mineral oil-based lubricants has resulted in lubricant industries expressing interest in environmentally friendly materials that may also be suitable replacements for mineral oil-based lubricants. The nature of vegetable oil that is easily renewable, biodegradable and non toxic makes it the best alternative in replacing mineral oil [1]. It also posses the properties required for lubrication, including excellent lubricity, high flash point and viscosity index, as well as good viscosity [2, 3].

Vegetable oil consists of triacylglycerol molecule which is constructed from three molecules of fatty acid bounded to one molecule of glycerol through ester bonds. However, the existence of β hydrogen on the glycerol backbone in vegetable oil causes few weaknesses which limit its potential use as an industrial lubricant. This includes poor thermal and oxidative stability, [4] easily damaged at high temperature [5] and the fact that it easily undergoes hydrolysis [2]. Chemical modification of vegetable oil, involving the exchanging of glycerol molecule with trimethylolpropane (TMP) forming a typical synthetic ester, has been shown to improve the oil stability [5, 6, 7].

Synthetic esters have been used for many years as base lubricating fluids due to their environmentally friendly nature, despite the high market price of synthetic esters [8]. Synthetic esters are also known for its excellent lubricity such as good thermal and oxidative stability, low volatility, high viscosity index and excellent low temperature fluidity [9].

Typical synthetic esters comprised of vegetable oil with TMP, showed to have good lubrication properties. The esterification of palm kernel oil methyl ester (PKOME) with TMP resulted in a successful conversion of 98 % PKOME to triester (TE) [6]. The esterification between fatty acid *Jatropha curcas* oil with TMP using different catalyst namely nitric acid, perchloric acid, sulphuric acid and *p*-toluenesulfonic acid resulted in TMP ester [4]. The use of perchloric acid produces the highest ester (70 %) with flash point higher than 300 ^{o}C and index viscosity of 150. Esterification of TMP with olive oil, rapeseed oil and lard has shown the resulting TMP ester have good thermal properties [5]. Transesterification of jatropha methyl ester with TMP at 150 ^{o}C using sodium methoxide as the catalyst has improved the oil stability for biolubricant base stock [6]. However the esterification of TMP with rubber seed oil (RSO) has not reported discover.

RSO has many potential in industrial applications, but has not been widely used. Such applications include biodiesel [11, 12], surface coating [13, 14], PVC stabilizer [15] and soap [16]. The oil is rich in polyunsaurated fatty acids, comprising up to 79.45 % of its fatty acid composition. The major fatty acid found in RSO is linolenic acid (C18:2), with a total percentage of 37.28 %, followed by oleic acid (22.95 %) and linolenic acid (19.22 %). The total percentage of saturated fatty acid found in RSO is 19.12 % and is comprised of palmitic and stearic acid [17]. In this paper, we reported the esterification of fatty acid RSO (FARSO) with TMP as shown in Figure 1 for biolubricant application. The finding showed that the typical synthetic ester has good physical properties as a biolubricant based stock.

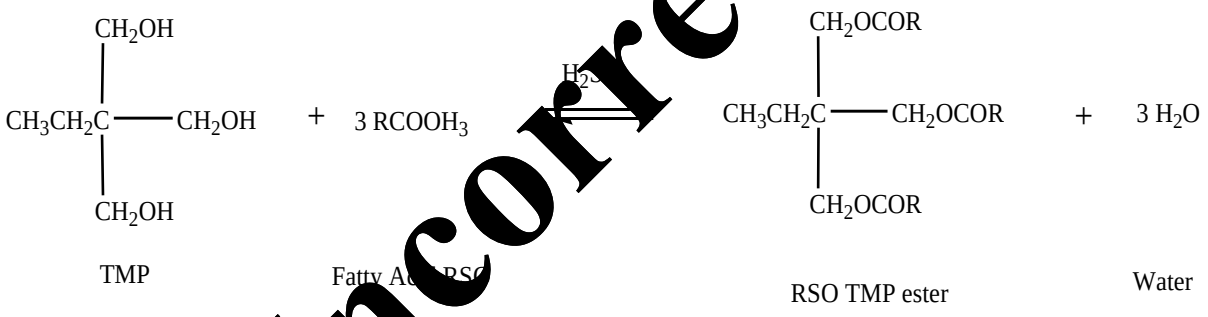

Figure 1. Esterification of fatty acid rubber seed oil (FARSO) with trimethylolpropane (TMP)

Materials and Methods

Raw Materials

Rubber seeds were obtained from a rubber plantation located in Perak, Malaysia. The TMP utilizes for the esterification process was purchased from Fluka. The sulphuric acid, ethyl acetate, hydrochloric acid, *n*-hexane and toluene were purchased from Systerm whereas N,O-Bis(trimethylsilyl)triflouroacetamide (BSTFA) with 1 % trimethylsilyl chloride was purchased from Acros Organic.

Oil Extraction

The collected rubber seeds were dried in an oven for 7 hours sets at 65 ^{o}C. A 500 g of the dried rubber seeds were finely ground and placed in a Soxhlet extraction thimble. The extraction of RSO was performed at 75 ^{o}C for 7 hours period. Hexane was used as an extraction solvent to extract the oil from the rubber seeds and was removed at the end of the process using a rotary evaporator.

Hydrolysis of Rubber Seed Oil (RSO)

The hydrolysis process conducted involves two stages namely saponification and acidification. In the saponification process, 50 g of RSO was mixed with alkaline ethanol and heated in a water bath set at 60 ^{o}C for 2 hours. The mixture then underwent the acidification process in which hydrochloric acid 6 N (HCl 6N) was added to neutralize the alkaline solution. The washing was continued using distilled water and hexane as solvents until the pH was neutral. Solvents were removed at the end using a rotary evaporator and the fatty acid formed was subsequently analysed by FTIR.

Esterification of TMP

The esterification process was conducted by mixing a known quantity of FARSO and TMP at a ratio of 3.9:1 in a 500 mL three neck round bottom flask, equipped with a thermometer and Dean Stark apparatus. Toluene, the azeotropic agent, and 2 % (w/w) sulphuric acid, based on the weight of the fatty acid and acting as a reaction catalyst, were added to the mixture. The reaction was heated for 5 hour at 150 °C with continuous stirring. Mixture was washed thoroughly with alkaline solution and ethyl acetate, followed by distilled water, until pH neutral.

GC-FID Analysis

To determine the percentage composition, the end product was analysed using a gas chromatograph equipped with a flame ionization detector (GC-FID). Sample was prepared by heating a small portion of the sample mixed with ethyl acetate (GC grade) and BSTFA in a 60 °C water bath for 30 minutes. The analysis was performed by using the DB-5HT (30 m x 0.25 mm x 0.10 μm), the injector and detector were set at 380 and 400 °C, respectively. The initial oven temperature was set at 100 °C with 1 minute of initial holding time. Ramping rate was increased for 5 °C/min until it reached 380 °C; and held for 25 minutes.

FTIR Analysis

Identification of functional groups present was determined through Fourier Transform Infrared Resonance (FTIR). FTIR analysis was done by placing the sample on sodium chloride (NaCl) plate (sample holder) forming thin layer of sampel. Second NaCl plate was taken and mounted on the first NaCl plate. Plate was then placed on the sample holder ready for FTIR analysis. The range of wave number used was 4000 cm^{-1} to 700 cm^{-1}.

Physical Characterization

The characterization tests, including flash point (ASTM D92), pour point (ASTM D97), viscosity (ASTM D445) and oxidative stability [20] test were performed on the formed RSOTMP ester.

Results and Discussion

Rubber Seed Oil (RSO)

Rubber seed oil (RSO) is known as non edible vegetable oil. The oil at present has not been used for any major application [12]. The extraction of rubber seed oil shows the seeds contained 48.4% of oil. This value was comparable with other RSO such as 40% by Jumat and Bashar (2009) and 40 – 50% by Ramadhas et al. (2005) [12, 17]. Different in oil content indicates RSO and its fatty acid obtained from the rubber seeds vary depends on the countries and area. Table 1 shows the properties comparison of RSO from different area in Malaysia and from other countries.

Fatty acid composition plays an important role in characteristic formation of the oil. RSO consist from five types of fatty acids. The major fatty acid was linoleic acid with the percentage composition of 40.5 % followed by linolenic acid (13.5 %), oleic acid (28.9 %), stearic acid (9.0 %) and palmitic (7.9 %). This was compareable with Nigeria RSO [18] where 2.2 % of meristic acid was detected in the oil. The high percentage of unsaturated fatty acid in RSO makes up to a total of 82.9 % of its fatty acid composition. This explains the liquid form of the oil at room temperature.

Table 1. Physicochemical properties of Rubber Seed Oil (RSO)

Analysis	**MRSO**	**MRSO [17]**	**IRSO [12]**	**NRSO [18]**
Source of rubber seeds	Malaysia (Perak)	Malaysia (Selangor)	India	Nigeria
Oil content, %	48.4	40	40 – 50	NA
Fatty acid composition, %				
i. Myristic acid	-	-	-	2.2
ii. Palmitic acid	7.9	8.6	10.2	7.6
iii. Stearic acid	9.0	10.6	8.7	10.7
iv. Oleic acid	28.9	22.3	24.6	20.0
v. Linoleic acid	40.5	37.3	39.6	36.0
vi. Linolenic acid	13.5	19.2	[illegible]8	23.5
Iodine value, mgI_2/g	124.2	135.8	[illegible]	155.6
Acid value, mgKOH/g	6.35	15.0	[illegible]4	23.00
Free fatty acid (as oleic), %	3.19	7.6	[illegible]	11.29

NA – not available

RSOTMP ester

The esterification between FARSO and TMP at high temperature with sulphuric acid as the catalyst has successfully formed ester TMP based on rubber seed oil (RSOTMP ester). The presence of catalyst encourages the protonation of carbonyl oxygen of fatty acid [19] as shown in Figure 2. Increase in electrophilicity of the carbon atom led to alcohol (TMP) nucleophilic attack forming a tetrahedral intermediate. Proton migration of the intermediate eventually forms an ester. Formation of water as by-product throughout the process was removed through Dean Stark apparatus to avoid from reverse hydrolysis causing the breakdown of triester (TE) to diester (DE) and monoester (ME).

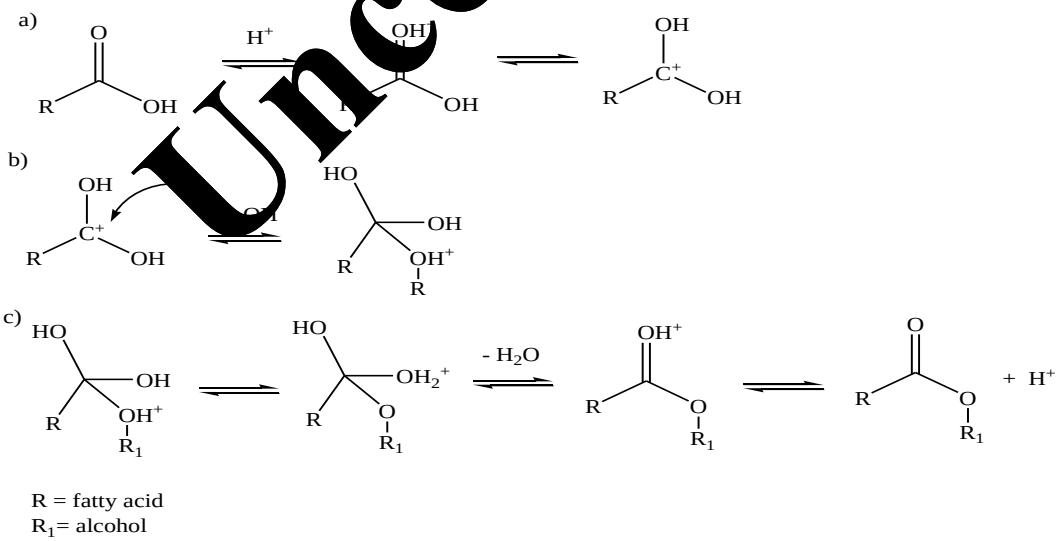

Figure 2. Reaction mechanism for esterification: a) protonation of the carbonyl by acid catalyst; b) nucleophilic attack of alcohol forming tetrahedaral intermediate; c) proton migration of tetrahedral intermediate forming an ester.

The formation of ester was confirmed by the presence of ester groups following FTIR analysis as shown in Figure 3. The IR spectrum of RSOTMP ester shows the emergence of C=O ester peak at a wavenumber 1744 cm^{-1}. This was different from the IR spectrum of the FARSO, whereby the stretching of C=O group of the fatty acid appeared at a wavenumber of 1713 cm^{-1} [21]. The stretching of the C-O ester group exists at wavenumbers of 1239 cm^{-1} and 1164 cm^{-1} in the RSOTMP ester spectrum. The C-O of the fatty acids appears at the wavenumbers of 1285 cm^{-1} and 1247 cm^{-1}. The change in wavenumber indicates that the fatty acid been has reacted with TMP forming RSOTMP ester. In addition, changes in the –OH peak occurred for both spectra in which the peak (3400-2400 cm^{-1}) is no longer visible in the spectrum of RSOTMP ester [21].

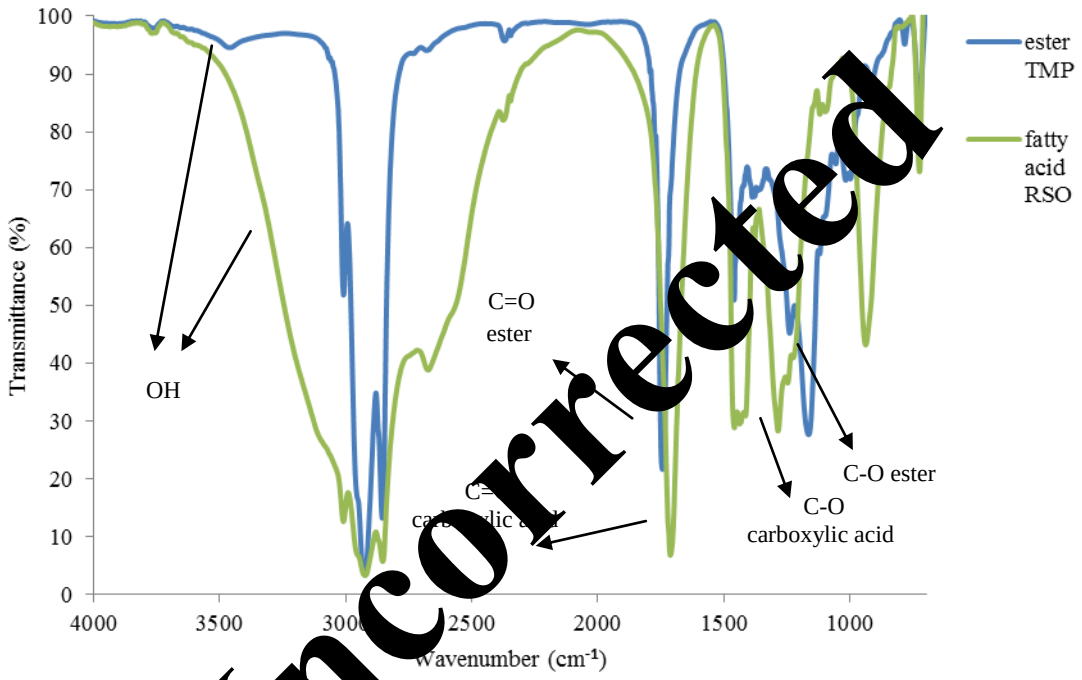

Figure 3. FTIR spectra comparison between fatty acid RSO and RSOTMP ester

The GC-FID chromatogram of RSOTMP ester is shown in Figure 4. The ester consist mixture of TE, DE, unreacted fatty acid and no presence of ME. Table 2 shows the percentage composition of each component. The major component of RSOTMP ester was 79.6% of TE followed by 18.9% of unreacted fatty acid and 1.49% of DE. The peaks in the GC chromatogram refer to the number of carbons from the alkyl group attached to the TMP. Ester of the same carbon number appears as one peak in the chromatogram [22]. Based on Figure 4, TE 54 is a triester which is made up of three fatty acids with the same carbon number, such as C18:0, C18:1, C18:2 or C18:3. TE 48 is also a triester which consists of three C16:0 (palmitic acid) that have a carbon number of 16, bringing the total to 48.

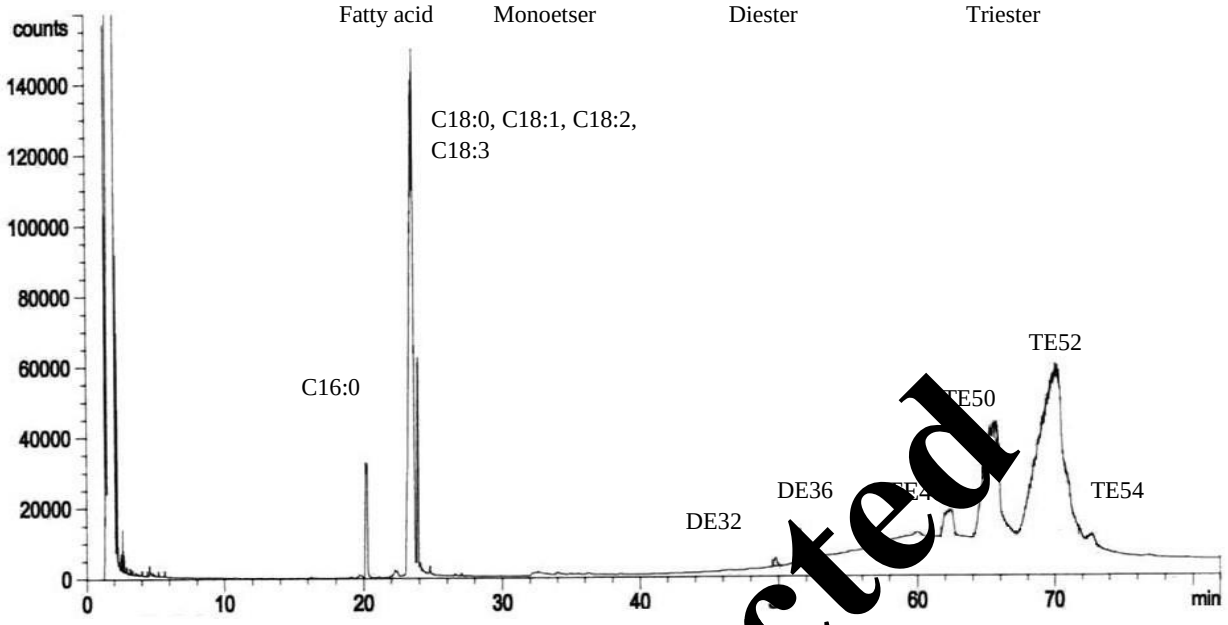

Figure 4. GC-FID chromatogram of RSOTMP ester

Table 2. The composition of RSOTMP ester

Product	Identified	Composition (%)
Unreacted fatty acid	C16:0, C18:0, C18:1, C18:2, C18:3	18.9
Monoester	-	-
Diester	DE32, DE36	1.49
Triester	TE48, TE50, TE52, TE54	79.6

Since the lubricating properties depends on the ester structure [7], the RSOTMP ester was purified by removing any excess fatty acid or monoester as it can affect the lubrication properties. Excess fatty acids were removed from the ester by using methanol extraction.

Lubricant Characterization

The esterification of FARSO with TMP has increased the oil stability. Table 3 shows the lubricant characterization of the RSOTMP ester in comparison with RSO and other synthetic ester. Based on Table 3, the flash point of RSOTMP ester is high at 310 ^{o}C compared to the flash point of RSO which was at 281 ^{o}C. This indicates the esterification with TMP has increase the oil thermal stability due to the absence of β hydrogen in the ester structure. In comparison with other synthetic ester, the obtained flash point was similar to TMP ester of PKOME (310 ^{o}C) but slightly higher than TMP ester of POME (304 ^{o}C) [6]. Typical lubricating oil has flash point around 210 ^{o}C [23]. The high flash point indicates RSOTMP ester has high potential for biolubricant production.

Table 3. The physicochemical properties of RSO, RSOTMP ester and other synthetic ester

Synthetic ester based on natural fats	Flash point, ^{o}C	Pour point, ^{o}C	Oxidative stability, ^{o}C	Viscosity at 40 ^{o}C	Viscosity at 100 ^{o}C	Viscosity index
RSO	281	-36	137	31.5	49	271
RSOTMP ester	310	-40	144	8.6	13.3	283
Palm kernel oil methyl ester (PKOME) + TMP [6]	310	2	NA	39.7	7.7	167
Palm oil methyl ester (POME) + TMP [6]	304	-1	NA	49.7	9.8	187
Olive oil + TMP [5]	NA	-13	NA	36	8.3	218.3
Rapeseed oil + TMP [5]	NA	-15.5	NA	35.3	7.9	209.2

NA – not available

The pour point of the RSOTMP ester is -40 ^{o}C. The obtained pour point was lower than RSO which was -36 ^{o}C. The slight branching structure of RSOTMP ester due to the presence of ethyl group (CH_2CH_2) in the TMP structure has improved the pour point lowering it to -40 ^{o}C. Presence of branch structure can lower the pour point by reducing the crystallization process [24]. This value was comparable with other synthetic ester such as TMP ester of PKOME, POME [6], rapeseed oil and olive oil [5] each recorded a pour point of 2 ^{o}C, -1 ^{o}C, -13 ^{o}C and -15.5 ^{o}C respectively. Esterification with TMP has produced RSOTMP ester with higher oxidative stability than RSO. The esterification has managed to replace glycerol containing β hydrogen, an active site for oxidation, with TMP increasing the oxidative to 144 ^{o}C.

RSOTMP ester has a higher viscosity than RSO. The viscosity of RSOTMP ester at 40 ^{o}C and 100 ^{o}C was 49 cSt and 13.3 cSt. Increase in viscosity was caused by the slight branching and mass increases in the ester structure. From the viscosity reading on both temperatures, the viscosity index was determined. Most refine mineral oil and synthetic oil in the market has the viscosity index around 100 and 150 [23]. The results showed that both RSO and RSOTMP ester have high viscosity index of more than 100. However, RSOTMP ester has a slightly higher viscosity index than RSO. The value of 28 for viscosity index of RSOTMP ester was the highest in comparison with other synthetic ester (PKOME, POME, rapeseed oil and olive oil). High viscosity index indicates little changes in oil viscosity with temperature [5, 23]. This performs better protective layer or film surrounding the metal surfaces.

Conclusion

The esterification of fatty acid RSO with TMP produces a typical synthetic ester with a slight close to the triacylglycerol of RSO. The absence of β hydrogen in the synthetic ester structure has increase the oil stability. Good physicochemical properties of RSOTMP ester such as viscosity index, high flash point and low pour point made RSOTMP ester of a suitable synthetic ester to be utilised as biolubricant base stock. An excellent lubricity and environmentally nature of the synthetic ester derived from natural oils and fats and TMP made them an appropriate biolubricant base stock for replacing mineral oil based lubricant.

Acknowledgement

The authors would like to thanks to the School of Chemical Science and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia of the financial support of this research.

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