Journal of Science and Technology

Optimization Process for Esterification of Rubber Seed Oil (RSO) with Trimethylolpropane (TMP)

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Abstract

Trimethylolpropane (TMP) ester has the potential to serve as a basic material in the biolubricant production due to its biodegradability, environmental friendly and good thermal properties. Thus, an investigation on the optimization of esterification of TMP with rubber seed oil (RSO) fatty acid was carried out with sulphuric acid acting as the catalyst. In seeking optimised reaction, various temperature levels, durations and catalyst concentrations were applied. The results show that RSO has successfully being converted to TMP ester with 78% of TE at the temperature of 150^{o}C using 2% (w/w) of sulphuric acid at 5 hours reaction time. Purification of TMP ester resulted in percentage yield of 66.8% of TMP ester with a mixture of DE and TE at 0.9% and 99.1%, respectively. TMP ester was analysed using high temperature gas chromatography (GC-FID) to determine the percentage composition of ester formed and fourier transform infrared spectroscopy (FTIR) to confirm the structure.

Keywords: esterification; rubber seed oil; trimethylolpropane; biolubricant

1. INTRODUCTION

The awareness of environmental pollution caused by mineral oil has led the lubricant industries to produce environmental friendly products by replacing mineral oil with biodegradable materials. In the U.S, 60% of lubricant oil used is lost to the environment which in turn leads to air pollution [1]. Only 25% of biodegradable properties are found in mineral oil-based lubricant [2]. Besides environmental pollution, the extensive usage of mineral oil has caused depletion in its quantity and requires millions of years to replenish. Vegetable oil is found to be the best alternative in replacing mineral oil. This is due to its non toxic, biodegradable and renewable properties [3]. It also has the properties required as lubricant such as high index viscosity, low volatility and good lubricity [4]. However, several disadvantages that cause its instability and easily damaged nature have limit its application in the lubricant industries. This includes hydrolytic instability, poor low temperature properties, poor thermal and oxidative properties [5]. Nonetheless, this problem can be solved through combining the oil with additives or through chemical modification such as esterification, epoxidation and hydrogenation [1]. Vegetable oil consists of triacylglycerol which is made up of three fatty acid molecules bounded to a glycerol molecule. The instability of vegetable oil is caused by the presence of β-hydrogen of the hydroxyl group in the glycerol which makes it unstable at high temperature, thus damaging the oil and cause precipitation [6,7]. However, the glycerol can be replaced with polyol which does not contain β-hydrogen through the esterification process. Previous study reported on the esterification of palm oil methyl ester (POME) and palm kernel oil (PKO) with TMP has successfully converted 98% of POME and PKO to TE [8,9]. Another study use TMP and neopentylglycol (NPG) as polyol; and samples are comprised of olive oil, rapeseed oil and lard [6]. The finding shows that the TMP esters and NPG esters have good high thermal properties.

In this study, rubber seed oil is use in producing TMP ester which can be use as base stock in lubricant production. Rubber seed oil is a semi-drying [10] rich in unsaturated fatty acid (oleic, lenoleic and lenolenic) which make up 79.45 ± 0.31% of its total fatty acid composition in the oil [11]. Presently, many studies on RSO shown that it has many potential for industrial application such as biodiesel [12,13], surface coating [10,14] and soap [15]. The objective of this study is to optimize the esterification of fatty acid (FA) RSO with TMP to achieve the maximum production of TE. Through this process, TMP ester which is formed can be used as a basic material in the lubricant production. The esterification of rubber seed oil fatty acid with TMP is shown in Figure 1.

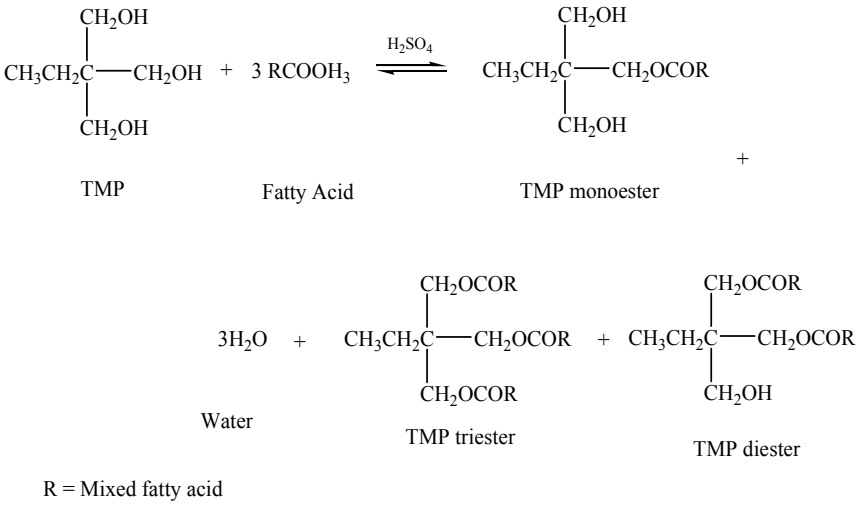

Figure 1: Esterification of FA with TMP

2. MATERIALS AND METHOD

2.1 Materials

Rubber seed used in this study was obtained from a rubber plantation in Kampung Sungai Mati, Perak and extracted using the Soxhlet extraction method. The trimethylolpropane (TMP) was purchased from Fluka; N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% trimethylsilyl chloride was purchased from Acros Organic. Meanwhile, the Sulphuric acid, sodium chloride, sodium hydrogen bicarbonate, ethyl acetate, hydrochloric acid, *n*-hexane and toluene were purchased from Systerm.

2.2 Hydrolysis of Rubber Seed Oil (RSO)

Hydrolysis involves the use of alkaline ethanol to separate FA from glycerol backbone. The process was conducted in accordance to PORIM Test Method (1995) [16] by mixing 50g of RSO with alkaline ethanol. This mixture was then heated in a water bath setup at 60^{o}C for 2 hours. The reaction mixture was washed with 150 mL of 6N HCl, 200 mL of distilled water and 100 mL of *n*-hexane. The washing process was then continued with 100 mL of hexane followed by 50 mL of distilled water until the pH became neutral. Solvent was removed by using the rotary evaporator and the FA formed was subsequently analysed by Gas Chromatografi (GC).

2.3 Esterification of trimethylolpropane (TMP)

The esterification process began by adding the FA RSO with TMP at a ratio of 3.9:1 in a 250 mL three necks round bottom flask equipped with a thermometer and Dean Stark. 2% (w/w) of sulphuric acid based on the weight of FA was then added as the reaction catalyst and 80 mL of toluene as the azeotopic agent. The optimization process was conducted for 8 hours at various temperature levels ($110^{o}C$–$160^{o}C$). The process was then repeated for different reactions at various durations (hours). The sulphuric acid concentration used ranged from 1% (w/w) to 5% (w/w). The ester produced was then washed thoroughly with sodium bicarbonate, sodium chloride and ethyl acetate followed by distilled water until neutral. The end product of each condition was analysed through the Gas Chromatografi – Flame Ionization Detector (GC-FID) to calculate the ester percentage.

2.4 TMP Ester Analysis

The percentage composition of the resulting esters was determined by using GC equipped with flame ionization detector (FID). Sample was prepared by heating a small portion of the sample mixed with ethyl acetate (GC grade) and BSTFA in a $60^{o}C$ water bath for 40 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 $380^{o}C$ and $400^{o}C$, respectively. The initial oven temperature was set at $100^{o}C$ with 1 minute of initial holding time. Ramping rate was increased for $5^{o}C$/min until it reached $380^{o}C$; and held for 25 minutes. The structure of optimized TMP ester was confirmed using FTIR.

3. RESULTS AND DISCUSSION

RSO is golden yellow and is known as non-edible oil. Hydrolysis process conducted in this study has successfully separated 90 – 97 % of the fatty acids from the glycerol backbone. The gas chromatography (GC) analysis on hydrolysed RSO shows high percentages of unsaturated and saturated fatty acid with a total of 82.9% and 16.9%, respectively. The types of fatty acid and its composition in RSO are shown in Table 1.

Table 1: Percentage composition of fatty acid in RSO

Fatty acid	Percentage composition (%)
Saturated fatty acid:	
Palmitic acid (C16:0)	7.9
Stearic acid (C18:0)	9.0
Total	16.9
Unsaturated fatty acid	
Oleic acid (C18:1)	28.9
Lenoleic acid (C18:2)	40.5
Lenolenic acid (C18:3)	13.5
Total	82.9

3.1 The Effect of Temperature

The results show that the reaction temperature influences the formation of ME, DE and TE. The formation of TE increases with the increase of reaction temperature but drops slightly at 160^{o}C (Figure 2). FA content in the reaction mixture also decreases during the reaction as it being transformed into ME, DE and TE. High temperature can cause the vaporization of FA from the reaction mixture and thus, encouraging forward reaction to form TE [9]. Vaporised FA however, has the potential to re-condense into reaction mixture and produce a reversible reaction [8]. The aim of the study is to focus on TE production as it has good high temperature properties compared to ME and DE [17]. The production of TE is high at 150^{o}C with few DE (1.32%) and ME (0.25%) formation in the final product. Although ME formation records the lowest (0.70%) at 110^{o}C, and DE (1.02%) at 140^{o}C, both temperatures however record lower TE compare with when it was at 150^{o}C. Low temperature results in reversible reaction as toluene fails to carry water out from the reaction mixture through Dean-Stark, turning TE back to DE and ME.

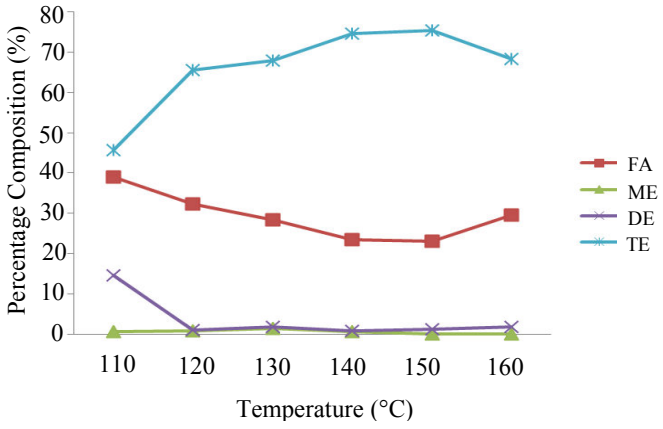

Figure 2: Effect of temperature on esterification at 8 hoursof reaction using 2% (w/w) of sulphuric acid

3.2 Effect of Time

The effect of time on esterification reaction is shown in Figure 3. As reaction time increases from 2 to 11 hours, the percentage composition of ME in the final product becomes lesser and approaches zero. This shows improvement as ME has low temperature stability which can easily damage the oil. In order to produce bio-lubricant with good lubrication properties, high composition of TE is required because it can give high viscosity and thermal properties [17] [6]. The lowest DE production is at 2 hours of reaction where the percentage composition is at 0.95%. However, the formation of TE is only at 71.40% which is considered low compared with the 5 hours of reaction which records 79.6% of TE formation. Based on Figure 3, it shows that 5 hours of reaction has the highest TE (79.60%) followed by 8 hours (75.25%), 2 hours (71.40%) and 11 hours (63.71%). Longer reaction duration causes the percentage composition of TE to reduce as it composes and hydrolyses to ME and DE.

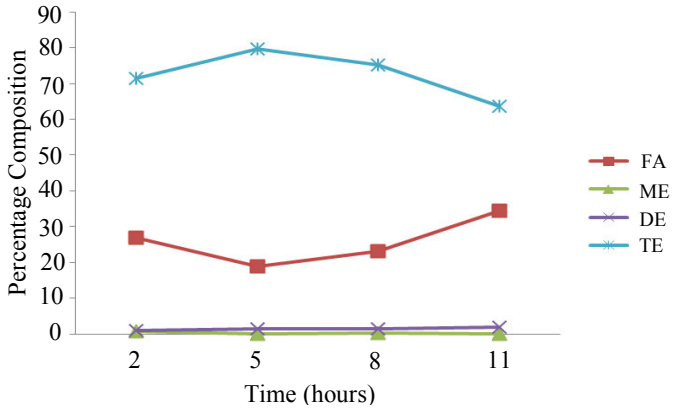

Figure 3: Effect of time on esterification at 150°C using 2% (w/w) of sulphuric acid.

3.3 Effect of Catalyst

The weight of catalyst used in the reaction is based on the weight of RSO fatty acid. For the esterification process, sulphuric acid is used because it is suitable for high temperature reaction (more than 100°C). The concentration of catalyst impacts the esterification process as it influences the percentage composition of the end product. According to Figure 4, the formation of TE is low (62.34%) at 1% (w/w) of sulphuric acid but increases up to 79% at 2% (w/w). The formation of TE decreases as percentage concentration of sulphuric acid increases up to 4%. However, TE formation rises when sulphuric acid is at 5% (w/w). High concentration of sulphuric acid leads to the additional amount of water in the reaction even though water had been removed in the early stage of the process as sulphuric acid is an aqueous. The

use of high concentration of sulphuric acid has affected the end product, which became more viscous with much darker colour.

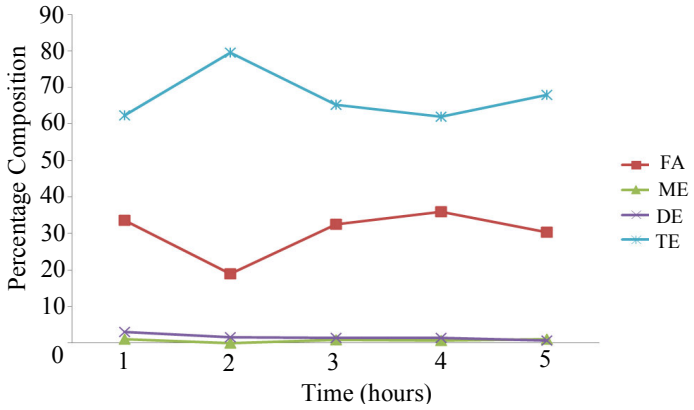

Figure 4: Effect of catalyst concentration on esterification at 150°C and 5 hours of reaction.

The end product of fully optimized ester was washed with methanol to remove the ME and excess of FA. The composition of the product contains 0.9% DE and 99.1% TE with the percentage yield of 66.8%. Figure 4 shows the GC-FID chromatogram of fully optimized TMP ester based on rubber seed oil at 5 hours of reaction using 2% (w/w) of sulphuric acid at 150°C of reaction temperature. The GC chromatogram peaks refer to the number of carbon contained in the TMP ester formed. Ester of the same carbon number will merge and appears as one peak in the chromatogram. In reference to Figure 5, TE 54 is the combination of C18:0, C18:1, C18:2 and C18:3 as it contained the same number of carbon.

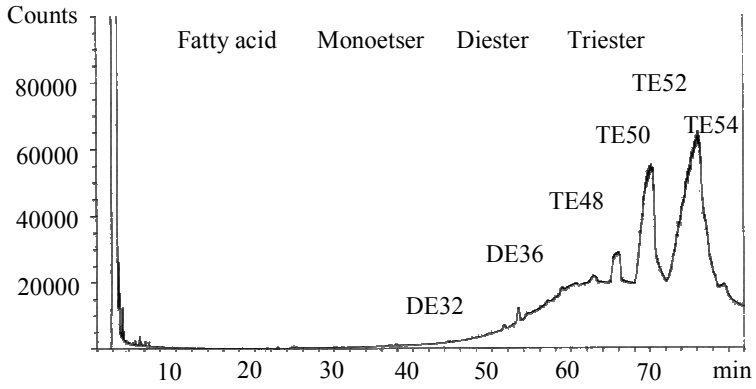

Figure 5: GC-FID chromatogram of rubber seed oil based TMP ester after removing ME and excess FA.

Ester formation is also shown on the comparison result of IR analysis of fatty acid and ester TMP formed. According to Figure 6, the comparison between the two results, show a chemical shift at a wavelength of 1713.26 cm^{-1} which refers to C=O group of carboxylic acid in fatty acid to a wavelength of 1744.19 cm^{-1} of C=O group in ester. This shows that both TMP and fatty acid have reacted with each other to form TMP ester.

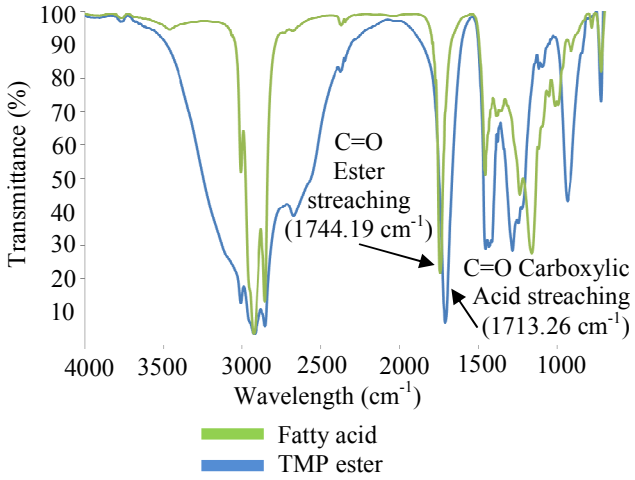

Figure 6. IR spectra comparison between fatty acid and optimized TMP ester (after removing ME and FA).

4. CONCLUSION

The esterification of RSO with TMP has successfully formed TMP ester with the percentage yield of 66.8% containing high content of TE (99.1%) and low DE (0.9%). Results of optimization test showed complete formation of TMP ester with high TE content is in the following circumstances; reaction duration: 5 hours, temperature: 150^{o}C and catalyst concentration: 2%. The high content of TE makes ester TMP plausible to be as biolubricant base stock.

Acknowledgement

The authors would like to thank the Faculty of Science and Technology and Universiti Kebangsaan Malaysia (UKM) for funding the project.

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