

Enzymatic Synthesis of Trimethylolpropane-Bases Biolubricants from Waste Edible Oil Biodiesel Using Different Types of Biocatalysis

Gürkaya Kutluk, Bahar ; Kutluk, Togayhan^{*†}; Kapucu, Nurcan

Department of Chemical Engineering, Kocaeli University, Kocaeli, TURKEY

ABSTRACT: *The synthesis of environmentally friendly biodegradable lubricants has been the focus of the attention of researchers in recent years. As a result of the research, it has been determined that petroleum-based oils can compete with their physical properties. In this study, we examined the synthesis of biolubricant such as trimethylolpropane (TMP) ester from fatty acids methyl esters (FAME) of waste edible oil (WEO) by immobilized lipase Lipozyme TL IM and Novozyme 435. The effects of reaction parameters were investigated. Experimental results, it's indicated that the conversion of FAME to biolubricant was obtained at 83%, and 99% with high diester (86%) and triester (89%) content in the presence of Lipozyme TL IM and Novozyme 435 respectively. As a result of the experimental studies the physical properties of trimethylolpropane triester obtained by Novozyme 435 catalysis showed a high flash point (229 °C), pour point (-18 °C), high viscosity index (170) with physical properties that met the requirements between ISO VG32-37 standards. This study showed that lubricant derived from WEO FAME's has great potential to be used as a base stock regarding favorable biodegradability and physical performance.*

KEYWORDS: *Biolubricant; Fatty acids methyl esters lipase; Trimethylolpropane ester.*

INTRODUCTION

Due to the toxic properties of mineral oils, the damage to the environment is very high. Furthermore, they can also remain in nature for many years without degradation. To protect the environment, especially from pollution caused by mineral-based lubrication and hydraulic oils, it is necessary to reduce the possible energy losses during use and to be able to reuse the oil waste [1, 2]. Lubricants compatible with the environment and do not harm the natural structure of water, soil, and air are called environmentally friendly biolubricants (IENICA, 2004).

Moreover, in one year, biolubricants that are degraded by 95% in nature can be used in any industry.

In recent years, there has been an increase in the use of biolubricants since they are cheaper, renewable, and more biodegradable than hydrocarbons including synthetic lubricants. Esterification reactions can be carried out by chemical or enzymatic catalysis. The product obtained in this way is semi-synthetic and has a biodegradable structure [3]. Different forms of esters can be used on hydraulic fluids, air compressor lubricants, turbine oils,

^{*} To whom correspondence should be addressed.

[†] E-mail: togay71@gmail.com

1021-9986/2023/5/3234-3243

10\$/6.00

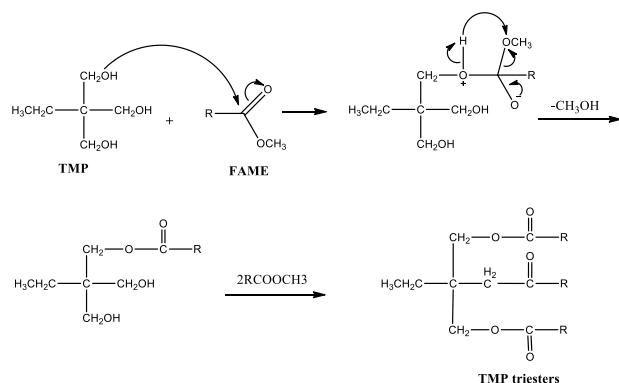


Fig. 1: Reaction mechanism of lubricant synthesis

high-temperature chain oils, metalworking fluids, 4-stroke engine oils, etc. commercially.

While sodium methylate is used as the chemical catalyst, different microorganisms may be preferred as lipase sources in enzyme-catalyzed reactions. According to many researchers, the temperature is very high in the reactions catalyzed by chemical catalysis and the reaction time is short. While lipase-catalyzed reactions with low temperatures and reaction times get longer. Lipases can decrease by-products and unit operations because they follow only a specific reaction mechanism. Besides, fatty acids or fatty acid methyl esters may be used instead of oils as the substrate for transesterification reactions [4]. Fig. 1 shows the reaction of fatty acid methyl esters to obtain TMP esters. The transesterification reaction is a reversible reaction that involves three consecutive mechanisms with the presence of a catalyst. The overall reaction stoichiometry requires 1 mol of TMP and 3 mol of Fatty Acid Methyl Esters (FAME)

On the other hand, approximately 1.5 million tons of vegetable oil are used in the food industry country every year. Approximately 300 thousand tons of waste edible oil is produced in commercial enterprises such as restaurants, fast food places, cafeterias, ready meal factories, hotels, motels, hospitals, touristic facilities, holiday villages, as well as military facilities and households. The average edible oil consumption per person in the world is 15 kg per year, and in developed countries is 30-38 kg a year. Waste oils cover the surface of the water when they are poured into the sea, ponds, and rivers, preventing the transfer of oxygen from the air to the water and causing the death of fish and other living things. The frying oil poured into the sink constitutes 25% of the domestic wastewater pollution and adheres to the drain system, causing the wastes in the sewage pipe to stick to the pipe wall, which makes the pipe

narrower and the sewer system useless in time. It is becoming increasingly important that useless oils, waste oils, or algae oils are regarded as a more sustainable source of raw materials for these reactions and that they are transformed into high-value-added products instead of edible oils due to the increasing population of the world. Due to the disadvantages of chemical catalysts, the use of lipase catalysts has been steadily increasing in recent years [3, 5]. There are many chemical-catalyzed studies in the literature on the production of biolubricants. Lipase-catalyzed studies are limited in number and have been performed with free or commercial immobilized lipase forms. Limited studies have been reported in the literature about the enzymatic synthesis of trimethylolpropane esters from WEO's FAME and ester analysis by GC. The physical properties of the obtained lubricant were investigated, and its tri-ester content was not determined by any chromatographic method.

In a comparable study in the literature, free Lipozyme TL 100 L lipase was immobilized on a duolite A568 type support material, and tri-esters were produced in the presence of this type of lipase catalyst [26]. The physical properties of the obtained lubricant were investigated, and its tri-ester content was not determined by any chromatographic method. In this study, the performances of the comparative two lipases in the production of lubricants were investigated for the first time in the literature, and it was supported by the chromatographic method that the products obtained were tri esters.

Free lipase (*Candida rugosa*) was immobilized on different inorganic supports and Linko *et al.* investigated the transesterification reaction between low erucic acid rapeseed (canola) oil methyl esters and TMP in terms of chemical and enzymatic catalysis [6]. *Candida rugosa* in free-form lipase was immobilized on different supports in powder form. Vegetable oils and free fatty acids or methyl esters of these oils can be used as raw material. In recent years, there has been an increased interest in studies related to the evaluation of waste oils. Besides, the number of environmentally friendly enzyme-catalyzed studies instead of traditional chemical catalysts to produce biolubricants is increasing [7-10]. A limited number of studies on enzymatic reactions where waste edible oils are used as substrates have been reported in the literature. Some of the studies done on the enzymatic synthesis of biolubricants are summarized in Table 1.

Table 1: Studies on the enzymatic synthesis of biolubricants.

Oil source	Alcohol	Temp.(°C)	Enzyme content (%)	Reaction time (h)	Conv. (%)	Reference
Rapeseed	TMP	58	40	24	75	[6]
Rapeseed	TMP	37	40	24	95	[11]
Caprylic acid	TMP	40	16	24	93	[12]
Oleic acid	TMP	30	1	18	86	[13]
Castor	TMP	40	0.4	-	80	[14]
Castor	TMP/PE/NPG	40	4	96	16/55/0	[15]
Palm kernel	Simulated fuel oil	45	500U/g	48	99	[16]
Waste edible	Octanol	60	5	30	95	[5]
Waste edible	2-ethyl hexanol	50	5	12	98	[17]
Waste filter coffee oil	TMP	55	5	24	88	[2]
Oleic acid	TMP	70	5	60	98	[27]
Fatty acids Methyl Esters	2-ethyl-1-hexanol	60	10	10	100	[28]
Palm oil methyl ester	TMP	70	5	23	92	[29]
Waste edible	TMP	50	5	48	90	This study

According to the authors' knowledge, the effect of critical reaction parameters on the transesterification reaction between WEO's FAME and TMP was investigated for the first time in this study. On the other hand, the mono-di-tri ester content of the product (TMP esters) was determined and clarified the chromatograms.

EXPERIMENTAL SECTION

Materials

WEO with 1.4% Free fatty acids (FFA) content collected from local restaurants in Kocaeli/TURKEY. *Thermomyces lanuginosus* (Lipozyme TL IM) and *Candida antarctica* (Novozyme 435) lipases are gifts from Novozymes Denmark. The chemicals O-Bis (trimethylsilyl) trifluoroacetamide (BSTFA), Trimethylolpropane (TMP), methanol, methyl heptadecanoate, Supelco 37 Component FAME Mix standard, and all other chemicals used in the experimental studies were purchased from Merck and Sigma-Aldrich.

WEO's FAME production

WEO was obtained according to the method we determined in our previous research [2]. The transesterification reaction was kept in 500 mL open flasks with the oil/methanol molar ratio of 1/3, initial water content (% substrate, w/w) 1%, and 5% Lipozyme TL IM lipase content. Reactions were carried out at 250 rpm in a shaking incubator (INNOVA 40 brand) incubator for 24h.

Biolubricant production

Transesterification reactions were implemented in 50 mL open flasks on magnetic stirrers at (200-500) rpm agitation speed with FAME/TMP molar ratio (1/3;1/4;1/6), at (25-35-45) °C temperature, lipase content (0-10 %), for 96 h reaction time.

FAME content analysis

The amount of FAME in the mixture was determined by an Agilent 7820 A GC analysis system equipped with a flame ionization detector (FID) and a 30m × 320µm × 0.25µm capillary column (CARBOWAX 20M). The system was calibrated using the internal standard methyl heptadecanoate according to EN 14103.

First, the gas chromatography device was calibrated according to TS 14103 with Supelco 37 Component FAME Mix standard for FAME analysis. Analyzes were repeated 6 times for the quality and accuracy of the analysis results. The accuracy was performed based on three concentrations around the test concentration (80%, 100%, and 120%); three replicates of each concentration were injected. The percentage of recovery and percentage of the Relative Standard Deviation (RSD) were calculated for each of the repeated samples. To evaluate the precision of the assay method, six samples of suppositories were prepared and injected in a replicate. The percentage of RSD must be less than 2.0 and all percentages of accuracy results must be within the specifications.

Fig. 2: Effect of lipase content on transesterification reaction (500 rpm, 45°C, 1:3TMP/FAME, 96h).

These verification processes were repeated for the accuracy of both FAME and lubricant analyses.

The FAME conversion was calculated using Eq. (1)

$$\text{FAME \%} = \frac{(\Sigma A) - A_{MH}}{A_{MH}} * \frac{C_{MH} * V_{MH}}{m} * 100 \quad (1)$$

ΣA : Total peak area from methyl ester (methyl myristate) at C_{14} to methyl ester (methyl carbonate) at $C_{24:1}$.

A_{MH} : Peak area corresponding to methyl heptadecanoate.

C_{MH} : Concentration of methyl heptadecanoate solution (10 mg/mL solution).

V_{MH} : Volume (mL) of methyl heptadecanoate solution.

m : 100 mg

Determination of mono-di-tri ester content in TMP esters by gas chromatography

The ester separation on the gas chromatography (HP Agilent 7820A) system was performed using the capillary column SGE HT5, 12 m \times 0.53 mm, i.d. 0.15 μ m (SGE, Melbourne, Australia). The oven temperature was set initially at 80°C, held for 3 min, then increased at 6°C/min to 340°C and held for another 6 min. The injector and detector temperatures were at 300 and 360°C, respectively. Helium was used as the carrier gas at a flow rate of 26.7 mL/min. The split ratio is 1:1, and the injection sample volume is 1.0 μ L [23].

The TMP-triester content was calculated using Eq. (2)

$$Ts\% = (Ts/St) \times 100 \quad (2)$$

$$St = Ms + Ds + Ts$$

Ms : Total peak area of monoesters

Ds : Total peak area of diesters

Ts : Total peak area of triesters

St : Total peak area of esters

Sample preparation for gas chromatography

0.03 g of sample was measured exactly into a 5-mL vial and diluted with 1.0 mL of ethyl acetate. The sample was vortexed for 1 minute to dissolve the mixture. Then BSTFA (0.5 mL) was then added to the mixture and vortexed. The sample was then transferred to a 2-mL autosampler vial for injection into the chromatography system. Substrate and products' chemical structures were compared and verified by FT-IR analysis.

RESULTS AND DISCUSSION

Effect of lipase content

The effects of lipase content on the transesterification reaction of FAME with TMP in the presence of Lipozyme TL IM and Novozyme 435 is shown in Fig. 2. Lipase amount is the most important economic factor for the enzymatic processes because the industrial enzymes are costly.

The highest FAME conversions (83% and 99%) were achieved when the amount of lipase Lipozyme TL IM and Novozyme 435 were 5% and 1% respectively. The increase in the amount of Lipozyme TL IM caused mixing problems in the reaction medium. For this reason, the mass transfer limitations between the enzyme and substrate were reduced to FAME conversion. On the other hand, when Novozyme 435 was used, a 1% lipase amount was sufficient for the desired conversion of 99%. The most common problem is the aggregation of lipases in the medium with the increase of the enzyme amount [2,3,6]. This effect was eliminated by using Novozyme 435 lipase. It is stated that Novozyme 435 was successful because of the immobilization support Lewatit VP OC 1600, a macroporous acrylic polymer resin [3, 30, 31].

Effect of reaction temperature

An increase in activity is observed with the temperature rising during the enzymatic reactions [3, 18]. However, once an optimum temperature has been exceeded, the enzymes become denatured and lose their activity like other proteins. For each enzyme, there is an optimum temperature at which the substrate quickly forms the Enzyme-Substrate called ES complex at a unit of time. The effect of temperature on the transesterification reaction of FAME with TMP in the presence of Lipozyme TL IM and Novozyme 435 is shown in Fig. 3. By using the optimum enzyme amounts (5% for Lipozyme TL IM and 1% for Novozyme 435), 45 °C was determined as the appropriate

Fig. 3: Effect of temperature on transesterification reaction (500 rpm, 1:3 TMP/FAME, 72h, with optimal lipase contents).

Fig. 4: Effect of molar ratio on transesterification reaction (500 rpm, 45°C, 72h, with optimal lipase contents).

Fig. 5: Effect of agitation speed on transesterification reaction (45°C, 1:3 TMP/FAME, 72h, with optimal lipase contents).

temperature for both enzymes. The FAME conversions obtained at 45 °C were 83% and 98% for Lipozyme TL IM and Novozyme 435, respectively.

Effect of the molar ratio

The stoichiometric molar ratio between TMP and FAME is 1:3, however, the excess amount of TMP promotes the forward reaction. The molar ratio of TMP: FAME was chosen

between 1:3, 1.5:3, 2:3, 2.5:3, and 3:3. The effect of the substrate molar ratio on transesterification in the presence of Lipozyme TL IM and Novozyme 435 is shown in Fig. 4.

TMP has three hydroxyl groups according to its molecular structure, and the excess amount of TMP would alter the reaction equilibrium in a forward direction. Increasing the TMP loading was not affected by the synthesis of TMP esters. Similar results have been reported in the literature [2,19,20]. Maximum FAME conversion at stoichiometric molar ratio 1:3 was achieved as 82.5% and 98.5% for Lipozyme TL IM and Novozyme 435 respectively.

Effect of agitation speed

Low mixing rates were not sufficient to overcome the mass transfer limitations [2, 3]. On the other hand, it was observed during the reaction that the enzymes in the medium adhered to the surface of the vessel at high agitation speeds. The effect of agitation speed on the transesterification reaction in the presence of Lipozyme TL IM and Novozyme 435 is observable in Fig. 5.

Agitation speeds of 200, 300, and 400 rpm are insufficient to attain the inter-phase mass transfer restrictions according to the results obtained for the transesterification reactions. It appears that this barrier has been exceeded at 500 rpm in the presence of Lipozyme TL IM. For the Novozyme 435, even a 200 rpm shaking speed is sufficient for 94% conversion. But at 500 rpm, the conversion increased slightly. Maximum FAME conversion at 500 rpm was achieved as 82.5% and 97.5% for Lipozyme TL IM and Novozyme 435, respectively.

Effect of reaction time

The effect of reaction time on the transesterification of TMP with FAME catalyzed by Lipozyme TL IM and Novozyme 435 is shown in Fig. 6.

This Figs. clarifies that FAME conversions have increased during reaction time since the beginning of the reaction. FAME conversions reach a maximum value at 48-72 h for two lipases and then slightly get constant at further reaction times. Hydrolysis of ester bonds occurs in chemically catalyzed reactions. Therefore, undesirable hydrolysis takes place during the reaction, thus reducing the ester yield. Unwanted hydrolysis does not occur in enzyme-catalyzed reactions. Also, the extended reaction time requires more energy costs. Similar results were discussed by other comparable studies [21, 22].

Fig. 6: Effect of reaction time on transesterification between FAME and TMP (45°C, 1:3 TMP/FAME, 500 rpm, with optimal lipase contents).

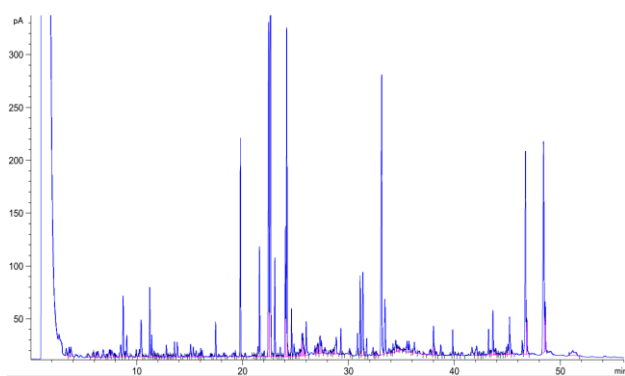


Fig. 7: Gas chromatogram of the polyol esters (Novozyme 435) ME: Monoesters, DE: Diesters, TE: Triester.

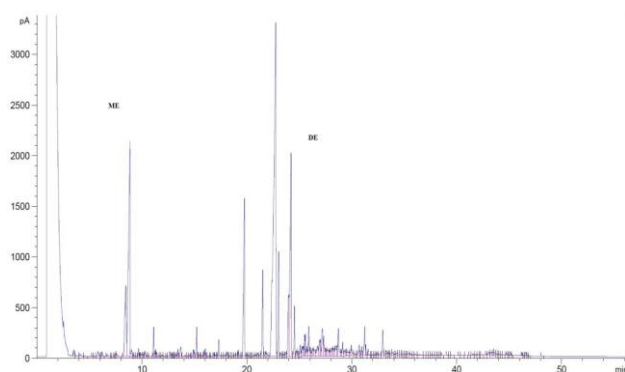


Fig. 8: Gas chromatogram of the polyol esters (Lipozyme TL IM) ME: Monoesters, DE: Diesters, TE: Triester.

Ester Analysis

GC chromatograms of TMP esters were shown in Fig. 7 for Lipozyme TL IM and Fig. 8 for Novozyme 435 with high diester (86%) and triester (89%) content respectively.

After the esterification process, three types of polyol esters were present when Novozyme 435 biocatalyst was used, which are monoester (ME), diester (DE) -OH groups were partially

esterified and triester (TE) when -OH groups in TMP were fully esterified. All the -OH groups in polar compounds (monoesters and diesters) switched with the trimethylsilyl (-SiMe₃), and silanization increases the separation of the peaks. The peaks were described based on the number of the alkyl carbon group attached to the TMP backbones. The esters formed were identified by comparing the obtained chromatograms with studies [3, 23, 24].

Fourier Transform InfraRed (FT-IR) spectrophotometry analysis

From the esterification reaction in the presence of different lipases between waste oil biodiesel (FAME) and alcohol (TMP), FT-IR analyses were carried out to determine the characteristic bonds of products Fig. 9 and Fig. 10. From the FT-IR spectra, there are characteristic peaks of ester carbonyl functional groups (C = O) in the band 1742 cm⁻¹ and CH₂ and CH₃ vibrations between 2920 cm⁻¹ and 2860 cm⁻¹ respectively. Characteristic aliphatic C = C double bonds around 3003 cm⁻¹ are visible. The light bulging characteristic is -OH vibrations as seen in the spectrum from 3400 cm⁻¹ to 3600 cm⁻¹. Sharp peaks at 164 cm⁻¹ are characteristic peaks due to C-O vibration. Finally, the presence of C-H groups in the structure is evident from the 722 cm⁻¹ absorber bands [2-4].

Physical properties of TMP-triester

Hydraulic system oils are classified as ISO (International Organization for Standardization) VG (Viscosity Grade) according to international standards. The higher the VG number, the more viscous the liquid. The VG number indicates which hydraulic oil is thicker. WEO-based TMP-ester and ISO SAE (Society of Automotive Engineers) classifications for hydraulic system oils are given in Table 2. As shown in Table 2, the WEO-based TMP-ester by Novozyme 435 catalysis physical properties, involving viscosity, viscosity index, flash point, and pour point, meet the requirements which are between ISO VG32 and ISO VG37 [19]. Also, in terms of kinematic viscosity values (33.6 mm²/s at 40 °C, and 6.9 mm²/s at 100 °C), close to two-stroke engine oil (40.6 mm²/s at 40 °C, and 6.6 mm²/s at 100 °C) were obtained. Flashpoint is the lowest temperature at which a liquid will form a vapor in the air near its surface that will "flash," or briefly ignite, on exposure to an open flame. The flash point is a general indication of the flammability or

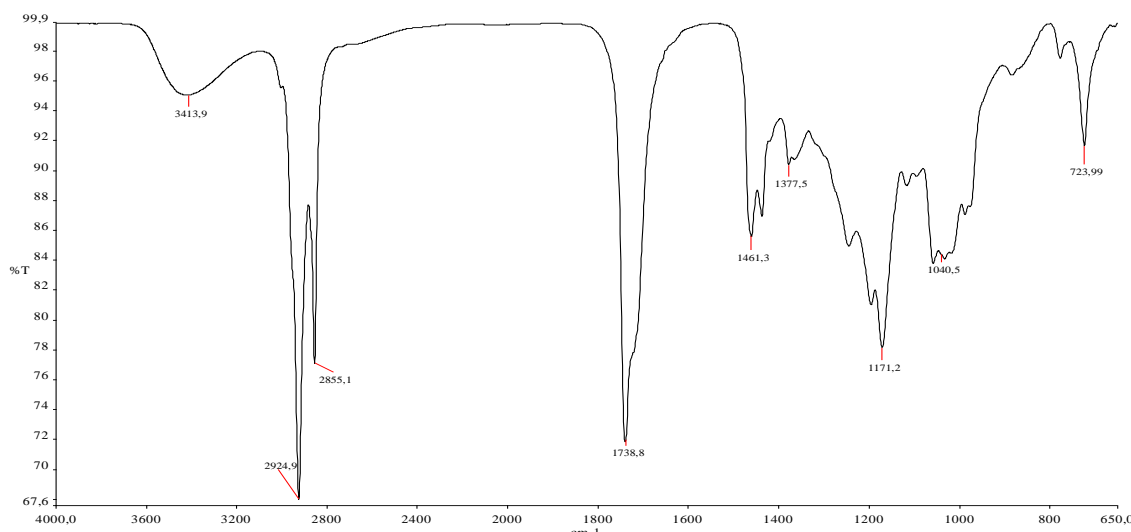


Fig. 9: FTIR spectra of the TMP ester (catalyst: Lipozyme TL IM).

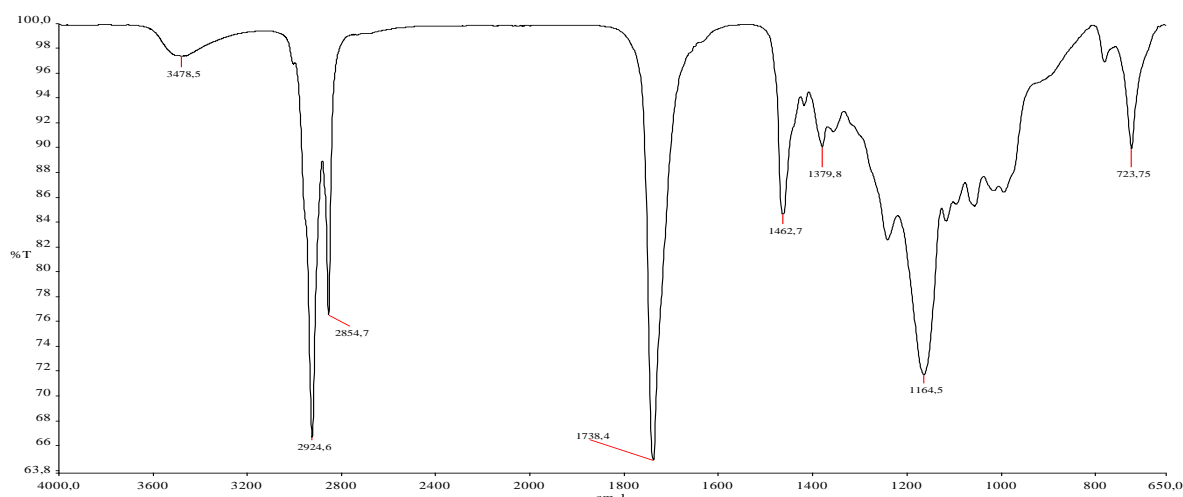


Fig. 10: FT-IR spectra of the TMP ester (catalyst: Novozyme 435).

combustibility of a liquid. For hydraulic system applications, this value is around 200-250°C. The flash point of the WEO-based TMP ester obtained gave the best result at 229°C compared to all these lubricants. It is envisaged that it can be used in piston systems, which are widely used in construction machinery and agricultural machinery.

Especially, the WEO TMP triester's viscosity (6.9, 100 °C) slightly passes over the requirements of ISO VG46 (6.4, 100 C). The flash point (229 °C) of the WEO TMP triester is also the requirement of ISO VG46 with 229°C [24].

The pour point of oil for the lubrication of mechanical equipment and surfaces is another important parameter. The pour point can also be expressed as the lowest temperature at which the oil can be worked. It is not appropriate to use biolubricant obtained at temperatures

below this value. A significantly lower pour point ensures the lubricant's operational stability over a wider range of temperatures [22]. WEO TMP triester's pour point value is -18 °C. For some diesel engines, this pour point value may be appropriate, but it is usually important to be able to lower temperatures. By adding appropriate additives to the base oil, the desired level of decrease at the pour point of lubricant can also be achieved. When compared in terms of viscosity index values, it is seen that the WEO TMP triester has the best result with an index value of 170. Therefore, it can be said that it will be least affected by temperature changes compared to other samples. The great lubricant has the same viscosity at the wide temperature range studied. Thus, the biolubricant obtained is operable to be used over a wider range of temperatures.

Table 2: ISO specifications and properties of WEO-based TMP-triester

Pour point (°C)	ASTM D-97	-18	-27	-24	-24	-24	-30	-20
Flashpoint (°C)	ASTM D-92	229	216	222	228	236	215	220
Viscosity 40 °C (mm ² /s)	ASTM D-445	33.6	32	37	46	68	40.6	76.5
Viscosity 100 °C (mm ² /s)	ASTM D-445	6.9	5.4	5.7	6.4	8.5	6.6	10.6
Viscosity index	ASTM D-2270	170	100	99	98	97	140	85
Density at 15°C	ASTM D-4052	0.92	0.877	0.874	0.884	0.887	0.863	0.915

CONCLUSION

Biolubricant (TMP ester) was successfully synthesized from Waste Edible Oil (WEO) Fatty Acids Methyl Esters (FAME) by immobilized lipase Lipozyme TL IM and Novozyme 435. Based on the experimental study, the following observations were derived:

- The production yield in the presence of Lipozyme TL IM and Novozyme 435 is 86% and 89%, respectively with high diester (86%) and triester (89%) yields.
- For both enzymes used in this study, a stirring speed of 500 rpm, a temperature of 45°C, and a stoichiometric ratio of 1:3 TMP: FAME are common. However, when 5% Lipozyme TL IM and 1% Novozyme 435 were used, the highest conversions were obtained.
- The physical properties of WEO-based TMP-ester synthesized using Novozyme 435 catalysis are according to ISO VG32 and ISO VG37.
- The Novozyme 435 showed strong activation in the transesterification reaction of triglycerides structure in FAME of WEO due to its good hydrophobicity.
- A higher amount of tri-ester conversion was achieved in the presence of Novozyme 435 catalyst with a lower amount of catalyst. In the presence of Novozyme 435 lipase, it is understood that the activation energy of the reaction required to produce triesters is exceeded.

In this study, oil obtained from WEO was produced as an alternative to petroleum-based lubricating oil consumed in many sectors. Synthesis of alternative products to traditional petroleum-based oils has been supported with environmentally friendly processes. In addition, high-value-added products were obtained with using of WEO which are wasted around the world in large quantities. In addition, WEO TMP triester shows good physical properties of lubricant and it can be used for environmentally friendly biolubricant applications.

Acknowledgments

This study was financially supported by TUBITAK (Project No: 217M525) and Kocaeli University Scientific

Research Projects Coordination (Project No: 2018/099). Also, the authors thank Novo Nordisk for presenting Lipozyme TL IM and Novozyme 435 lipases.

Received: Jun. 28, 2022 ; Accepted : Oct. 24, 2022

REFERENCES

- [1] Schneider M.P., [Plant-Oil-Based Lubricants and Hydraulic Fluids](#), *J. Sci. Food Agric.*, **86**: 1769–1780 (2006).
- [2] Ünügöl T., Kutluk T., Kutluk B.G., Kapucu N., [Environmentally Friendly Processes From Coffee Wastes to Trimethylolpropane Esters to be Considered Biolubricants](#), *J. Air & Waste Man. Assoc.*, **70(11)**: 1198-1215 (2020).
- [3] Kutluk T., Kutluk B.G., [Lipase Catalysis: an Environmentally Friendly Production for Polyol Esters \(Biolubricant\) from Microalgae Oil](#), *Environ. Tech.*, 1-24 (2022).
- [4] Salimon J., Salih N., Yousif E., [Biolubricants: Raw Materials, Chemical Modifications, and Environmental Benefits](#), *Eur. J. Lipid Sci. Tech.*, **112**: 519–530 (2010).
- [5] Chowdhury A., Mitra D., Biswas D., [Synthesis of Biolubricant Components From Waste Cooking Oil Using a Biocatalytic Route](#), *Environ. P. and Sus. Chem.* **33**: 933-940 (2014).
- [6] Kutluk B.G., Kutluk, T., Kapucu N., [Statistical Analysis of Enzymatic Reaction Parameters for Biolubricant Synthesis via Response Surface Methodology \(RSM\)](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, (2022) [in Press].
- [7] Åkerman C.O., Gaber Y., Ghani N.A., Lamsa M., Kaul R.H., [Clean Synthesis of Biolubricants for Low Temperature Applications Using Heterogeneous Catalysts](#), *J. Mol. Catal. B Enzym.* **72**: 263–269 (2011).
- [8] Bahadi M., Yusoff M.F., Salimon J., Derawi D., [Optimization of Response Surface Methodology by D-Optimal Design for Synthesis of Food-Grade Palm Kernel Based Biolubricant](#), *Ind. Crops Prod.* **139**: 111452 (2019).

- [9] Bassi J.J., Todero L.M., Lage F.A.P Gabrielly I., Ducas J.D., Custodio A.P., Pinto M.A., Mendes A.A., [Interfacial Activation of Lipases on Hydrophobic Support and Application in the Synthesis of a Lubricant Ester](#), *Int. J. Biol. Macromol.* **92**:900–909 (2016).
- [10] Bolina, I.C.A., Gomes, R.A.B., Mendes, A.A., [Biolubricant Production from Several Oleaginous Feedstocks Using Lipases as Catalysts: Current Scenario and Future Perspectives](#), *Bioenerg. Res.* **14**: 1039–1057 (2021).
- [11] Linko Y.Y., Lämsä M., Wu X., Uosukainen E., Seppälä J., Linko P., [Biodegradable products by lipase biocatalysis](#), *J. Biotech.* **66**: 41–50 (1998).
- [12] Tao Y., Chen G., Pavlidis I.V., Jiang Y., Qie L., Cui C., Liu L., Chen B., Tan T., [A Water-Dependent Kinetics Guide for Complex Lipase-Mediated Synthesis of Biolubricants in a Water Activity Control Reactor](#), *Catal. Sci. Technol.*, **5**: 5120-5128 (2015).
- [13] Trivedi J., Aila M., Sharma C.D., Gupta P., Kaul S., [Clean Synthesis of Biolubricant Range Esters Using Novel Liquid Lipase Enzyme in Solvent Free Medium](#), *Springerplus*, **4**: 165 (2015).
- [14] Diaz P.A.B., Kronemberger F.A., Habert A.C., [A Pervaporation-Assisted Bioreactor to Enhance Efficiency in the Synthesis of a Novel Biolubricant Based on the Enzymatic Transesterification of a Castor Oil Based Biodiesel](#), *Fuel*, **204**: 98-105 (2017).
- [15] Duarte J.G., Oliveira E.D.C., Da Silva J.A.C., Lafuente R.F., Freire, D.M.G., [Two-Step Enzymatic Production of Environmentally Friendly Biolubricants Using Castor Oil: Enzyme Selection and Product Characterization](#), *Fuel*, **202**: 196–205 (2017).
- [16] Cerón A.A., Boas R.N.V., Biaggio C.F., Castro H.F., [Synthesis of Biolubricant by Transesterification of Palm Kernel Oil with Simulated Fusel Oil: Batch and Continuous Processes](#), *Bio. and Bioen.*, **119**: 166–172 (2018).
- [17] Zhang W., Ji H., Song Y., Ma S., Xiong W., Chen C., Chen B., Zhang Z., [Green Preparation Of Branched Biolubricant By Chemically Modifying Waste Cooking Oil With Lipase And Ionic Liquid](#), *J. Clean. Prod.*, **274**: 122918 (2020).
- [18] Érika C.G., Aguiéiras Elisa D.C., Cavalcanti P.R., Valéria F. S., Lafuente R.F., Assunção .L.B., Silva J.A.C., Denise M.G., [Enzymatic Synthesis of Neopentyl Glycol-Bases Biolubricants Using Biodiesel from Soybean and Castor Bean as Raw Materials](#), *Ren. Eng.*, **148**: 689-696 (2020).
- [19] Wang E., Ma X., Tang Z., Yan R., Wang Y., Riley W.W., Reaney M.J.T., [Synthesis and Oxidative Stability of Trimethylolpropane Fatty Acid Triester as a Biolubricant Base Oil from Waste Cooking Oil](#), *Biomass and Bioenergy*, **66**: 371-378 (2014).
- [20] Chang T., Masood H., Yunus R., Rashid U., Choong T.S.Y., Biak D.Y.A., [Activity of Calcium Methoxide Catalyst for Synthesis of High Oleic Palm Oil Based Trimethylolpropane Triesters as Lubricant Base Stock](#), *Ind. Eng. Chem. Res.*, **51**: 5438–5442 (2012).
- [21] Chowdhury A., Chakraborty R., Mitra D., Biswas D., [Optimization of The Production Parameters of Octyl Ester Biolubricant Using Taguchi's Design Method and Physico-Chemical Characterization of the Product](#), *Ind. Crops and Prod.*, **52**: 783–789 (2014).
- [22] Appiah G., Tulashie S.K., Akpari E.E.A., Rene E.R., Dodoo D., [Biolubricant Production via Esterification and Transesterification Processes: Current Updates and Perspectives](#), *Int. J. En. Res.*, 1-31. (2021).
- [23] Yunus R., Lye O.T., Fakhru'l-Razi A., Basri S., [A simple capillary column GC method for analysis of palm oil-based polyol esters](#), *J. Amer. Oil Chem. Soc.*, **79**: 1075–1080 (2002).
- [24] Salih N., Salimon J., Jantan F.N., [Synthesis and Characterization of Palm Kernel Oil Based Trimethylolpropane Ester](#), *Asian J. Chem.* **25** (17): 9751-9754 (2013).
- [25] Afifah A.N.S., Syahrullail S., Azlee N.I.W., Sidik N.A.C., Yahya W.J., [Rahim E.A., Biolubricant Production from Palm Stearin Through Enzymatic Transesterification Method](#), *Biochem. Eng. J.*, **148**: 178-184 (2019).
- [26] Kim H., Choi N., Kim Y., Kim H.R., Lee J., Kim I.H., [Immobilized Lipase-Catalyzed Esterification for Synthesis of Trimethylolpropane Triester as a Biolubricant](#), *Ren. Eng.*, **130**: 489-494 (2019).
- [27] Åkerman C.O., Hagströma A.E.V., Mollaahmad M.A., Karlsson S., Kaul R.H., [Biolubricant Synthesis Using Immobilised Lipase: Process Optimisation of Trimethylolpropane Oleate Production](#), *Pro. Bio.*, **46(12)**: 2225-2231 (2011).
- [28] Kleinaitė E., Jaška V., Tvaska B., Matijošytė I., [A Cleaner Approach for Biolubricant Production Using Biodiesel as a Starting Material](#), *J. Clean. Prod.*, **75**: 40-44 (2014).

- [29] Wafti N.S.A., Yunus R., Lau, H.L.N., Yaw T.C.S., Aziz S.A., [Immobilized Lipase-Catalyzed Transesterification for Synthesis of Biolubricant From Palm Oil Methyl Ester and Trimethylolpropane](#), *Bioprocess Biosyst. Eng.*, **44**: 2429–2444 (2021).
- [30] Ortiz C., Ferreira M.L., Barbosa O., Dos Santos J.C.S., Rodrigues R.C., Murcia A.B., Briand L.E., Lafuente R.F., [Novozym 435: The “Perfect” Lipase Immobilized Biocatalyst?](#) *Cat. Sci. and Tech.*, **9**: 2380-2420 (2019).
- [31] Aydoğdu S., Kapucu N., [A Review on the Achievement of Enzymatic Glycerol Carbonate Production](#), *Turkish J. Chem.*, **46**: 1376-1396 (2022).