

Comparison of the Tribological Properties of Environmentally Friendly Esters Produced by Different Mechanisms

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ABSTRACT

Environmentally friendly esters are well-known lubrication materials used in pollution sensitive applications. Esters derived from renewable resources have inherent biodegradability, lubricity, an extremely high viscosity index, and non-volatility. However, their energy-intensive synthesis makes them relatively more expensive and less attractive for industry. Comprehensive studies have been conducted related to the lowering of energy requirement for ester synthesis. However, the tribological properties of these esters have not been compared. The current study for the first time is comparing the tribological properties of environmentally friendly trimethylolpropane (TMP) esters having different production paths. It was found that despite physicochemical properties are changing the method of TMP ester synthesis has a marginal effect on its tribological properties. Moreover, all the investigated esters were found to be compatible with the anti-wear additive.

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1. INTRODUCTION

In the past two decades, significant efforts have been made to develop bio-based, non-toxic, environmentally friendly lubricants. To start with, pure vegetable oils were investigated and used without any chemical modification. However, there were a host of issues arising due to poor oxidation and hydrolytic stability, and high pure point temperature [1]. To enhance the properties of vegetable oils, changes were made in their structure. The structure of triglyceride was converted to form a new type of esters, referred to as polyol esters. Trimethylolpropane

(TMP), neopentylglycol (NPG), and pentaerythritol (PE) are well-known representatives of polyols that could be used for the transesterification of triglycerides or fatty acid methyl esters and synthesis of polyol esters. Base-stocks derived from vegetable oils possess better lubricity and superior viscosity index compared to petroleum-based or synthetic lubricants [2,3]. Esters find application in various fields, including hydraulic transmission and metalworking fluids, engine and compressor oils, and refrigeration, aviation, and chain lubricants [4]. Among them, TMP is the most commonly used polyol ester.

The synthesis of polyol esters can be performed via either chemical or enzymatic reactions. Lipase-catalyzed synthesis has a low conversion rate and requires a relatively long duration [5]. Moreover, most of the enzymes cannot withstand the high melting temperature of alcohol [6]. The existing research predominantly focused on the use of alkaline catalysts, particularly sodium methoxide, potassium hydroxide, and potassium carbonate.

Studies have been conducted on the activity of the alkaline catalyst in the transesterification of fatty acid methyl esters (FAME) by TMP. It was found that potassium hydroxide and potassium carbonate exhibit the highest activities [7].

Using alkaline catalysts, esters are synthesized by the transesterification of FAME with the corresponding alcohol. During the reaction, the methanol in FAME is replaced by the corresponding alcohol and released into the mixture. Continuous removal of methanol must be ensured to drive forward the reversible transesterification reaction. Vacuum ranging from 0.1 to 50 mbar is required to remove methanol and push the reaction forward [7,8]. However, decreased vacuum pressure leads to ester hydrolysis followed by irreversible fatty acid saponification [9]. Methanol removal can also be performed using inert gas flow. It requires relatively lesser energy and capital investment [10].

The reaction temperature is critical to get high conversion rates. The temperature of 120–140 °C is reported to be the most effective [6,7,11]. Uosukainen et al. suggested temperature increments in stages [5].

The highest conversion to TMP triesters was observed at a molar ratio of 3.9:1 of FAME-to-TMP [6,9]. However, the final product still contains unreacted FAME that is usually removed by means of vacuum distillation. A high vacuum of <1 mbar must be applied to perform distilling below ester thermal degradation temperature of 210 °C [12].

Polyol esters have tribological properties comparable to that of mineral and synthetic-based lubricants. Zulkifli N.W.M et al. [13] showed that TMP and PE esters possess friction reduction properties similar to that of a fully formulated lubricant. The application of TMP ester as a potential engine lubricant was also investigated. It

was found that small quantities of palm oil-based TMP ester in ordinary engine lubricant can improve both wear and friction reduction properties [14]. It has been suggested that fatty acids present in esters are responsible for their good lubricity [4]. However, lubricity is temperature-dependent and tends to decrease as temperature rises [15].

For a lubricant to be economically valuable, its tribological properties and the method as well cost of synthesis are important. Due to the requirement of energy and reagents in their production, esters are very expensive. Expenses can be reduced by the use of cheaper raw materials as well as through synthesis optimization. Irrespective of the chosen approach, the final product must have specific properties and be fit for the intended use.

The current study aims to compare the tribological properties of environmentally friendly TMP esters produced using different production paths. The impact of the ester's physicochemical properties and antiwear additives on tribological properties was also investigated.

2. MATERIALS AND METHODS

2.1 Materials

Rapeseed oil methyl esters (RME) were supplied by JSC Mestilla (Lithuania) and used as received. Its physicochemical properties and composition are listed in Table 1.

Table 1. Physicochemical properties and fatty acid composition of the RME used for TMP ester synthesis.

Property	Value
TAN (mgKOH/g)	0.05
Viscosity at 40°C, mm ² /s	4.6
Viscosity at 100°C, mm ² /s	1.8
Viscosity index	233
Pour point (°C)	-12
Flashpoint (°C)	182
Density at 40 °C, g/cm ³	0.866
Fatty acid composition (%)	
C16:0 palmitic	4.33
C18:0 stearic	1.98
C18:1 oleic	64.03
C18:2 linoleic	19.54
C18:3 linolenic	6.39
C20:1 gadoleic	1.29

2-Ethyl-2-(hydroxymethyl)-1,3-propanediol, 98 % (TMP) was purchased from Acros Organics. Potassium carbonate, toluene, acetone, n-Heptane, and ethyl acetate were purchased from Sigma-Aldrich. Grade 4.0 nitrogen gas was supplied from AGA (Lithuania). Ashless anti-wear additive was purchased from Lubrizol (Germany).

2.2 Synthesis of TMP ester

Two different methods of synthesis were selected for this study: transesterification in nitrogen gas and transesterification in a vacuum.

The molar ratio of RME-to-TMP was 3.9:1. 0.9 % of potassium carbonate, an alkaline catalyst, based on the total mass of reactants, was chosen for the study because of its activity and non-toxicity. To ensure a higher conversion to triesters, 3 hours was set as the reaction time.

Transesterification in a nitrogen gas environment was performed in a 250 ml round-bottomed glass flask equipped with a thermometer and two pipes for the inlet and outlet of nitrogen gas. The reaction vessel was immersed in an oil bath with temperature control. 100 g of RME, 11.6 g of TMP, and an appropriate volume of potassium carbonate catalyst were placed in the reaction vessel and constantly mixed at a speed of 400 rpm with a magnetic bar. The mixture was heated up to the reaction temperature of 130 °C. To avoid excessive oxidation, nitrogen gas flow was set at 2 l/min from the beginning of the heating process till the point when the temperature dropped to 60 °C.

Transesterification in a vacuum environment. The reaction was performed in a 250 ml round-bottomed glass flask equipped with a thermometer and reflux condenser. The condenser was connected to a vacuum line and an accumulator. The reaction vessel was immersed in an oil bath with temperature control. Amounts of RME, TMP, and catalyst took were the same as in the case of a nitrogen gas environment. They were placed in the reaction vessel and constantly mixed at a speed of 400 rpm with a magnetic bar. The mixture was heated up to a reaction temperature of 130 °C. Once the desired temperature was reached, the vacuum was gradually increased to 20 mbar. To avoid excessive oxidation, a vacuum of 200 mbar was applied from the beginning of the heating process till the point when the temperature reached 60 °C.

After the above-explained reaction processes, the obtained products were filtered using an 8 µm filter paper. A clear yellowish viscous liquid was obtained. The obtained products from the nitrogen gas and vacuum environments are referred to as TMPE G and TMPE V, respectively. These products still contained unreacted (excess) RME. Further purification was done using vacuum distillation in a 250 ml round-bottomed glass flask equipped with a thermometer and reflux condenser. The condenser was connected to a vacuum line and an accumulator. The distillation flask was immersed in an oil bath with temperature control. The distillation was carried out under a vacuum of 0.6 mbar and a temperature of 180 °C for 3 h. Mixing was constantly carried out at 400 rpm. To avoid excessive oxidation, the vacuum was applied from the beginning of the heating process till the point when the temperature dropped down to 60 °C. After distillation, two products were obtained: TMPE GD from TMPE G, and TMPE VD from TMPE V. In the present case, the final products contained a mixture of mono-, di- and tri-esters of TMP and fatty acids. Transesterification reaction of RME in the presence of trifunctional alcohol TMP proceeds stepwise: In the first step, one hydroxyl group reacts with acyl group and a monoester is formed (ME); subsequently, the second hydroxyl group is reacted and a diester is formed (DE); the final product of transesterification in optimal process conditions is a triester.

2.3 Analysis of the ester composition

The composition of the as-synthesized ester was evaluated using thin-layer chromatography (TLC). TLC analysis was performed according to the procedure developed by Yunus et al. [16]. For separation of mono- (or di-esters) and RME (or triesters), n-Heptane/ethyl acetate in different ratios (83:17 and 95:5, respectively) was used as the eluent. Boron-impregnated silica gel G-25 plates (layer thickness of 0.25 mm) were employed for the analysis. These plates were developed in an iodine vapor chamber. The location, brightness, and area of spots were compared with reference sample spots. To determine the positions of tri-, di- and monoesters, triglycerides and a mixture of mono- and diglycerides were used as references.

2.4 Physicochemical properties

Physicochemical properties having close association with on tribological properties were investigated. Kinematic viscosity was determined according to ISO 3104. Standards used for other properties are, as follows - viscosity index (VI) - ISO 2909, total acid number (TAN) - ISO 6618, density - ISO 12185, pure point temperature (PPT) - ASTM D97, flash point temperature - ASTM D92.

2.5 Tribological properties

The tribological properties of pure and anti-wear additive loaded esters were investigated. To evaluate the compatibility with anti-wear additives, all the prepared esters were loaded with 1% of an ashless anti-wear additive (AW). Tribological experiments were carried out using a four-ball tribotester. The balls of 12.7 mm diameter were made of chrome bearing steel, SAE 52100. A load of 150 N was applied that corresponds to an average Hertzian pressure of 1053 MPa which was calculated based on eq. (1), (2), and (3). The load distribution in the four-ball contact can be mathematically described as follows:

$$F_n = \frac{\sqrt{6}}{6} \cdot F = 0.408 \cdot F, [N] \quad (1)$$

where F is the total load applied to the tribosystem.

Under the applied load F_n the balls deform elastically. The contact diameter, which forms under the stationary load between the balls can be calculated:

$$d = 2 \cdot \sqrt[3]{\frac{1.5(1-\nu^2)F_n \cdot r}{E}}, [mm^2] \quad (2)$$

where ν is Poisson ratio; r is the ball radius; E is the modulus of elasticity.

This allows calculating average Hertzian pressures in the contacts:

$$p = \frac{4F_n}{\pi d^2}, [MPa] \quad (3)$$

The duration of the tests was set to one hour. At least two repetitions were done for each sample. Before each experiment, all relevant parts of the machine and the balls were rinsed in toluene and heptane. The diameters of the wear scars on three stationary balls were measured using an optical microscope Nikon Eclipse MA 100 and

the average diameter of three balls was reported as WSD (Wear Scar Diameter).

3. RESULTS AND DISCUSSION

3.1 Evaluation of energy consumption

The schemes of energy consumption during the production of esters are presented in Fig. 1. Energy is consumed for heating, maintaining the vacuum, and mixing. The proportion of energy consumed in mixing was negligible in comparison to that required in other processes, and further, since it is included in all the processes, it was not considered in the study. The three main processes where energy is consumed are, as follows:

1. Transesterification in the gas environment requires energy E_1 where the main constituent is the energy required for heating, EHT;
2. Transesterification in vacuum environment requires energy, E_2 that comprises energy required for heating, EHT and for maintaining the vacuum, EVT;
3. Distillation requires energy, E_3 that comprises energy for heating, EHD and for maintaining the vacuum, EVD.

The ranking based on energy requirements in different processes for maintaining heat and vacuum is as follows: $E_1 < E_2 < E_3$. Therefore, based on energy consumption, esters can be ranked, as follows: TMPE G < TMPE V < TMPE GD < TMPE VD. As can be seen, ester produced in a vacuum and distilled requires the highest amount of energy.

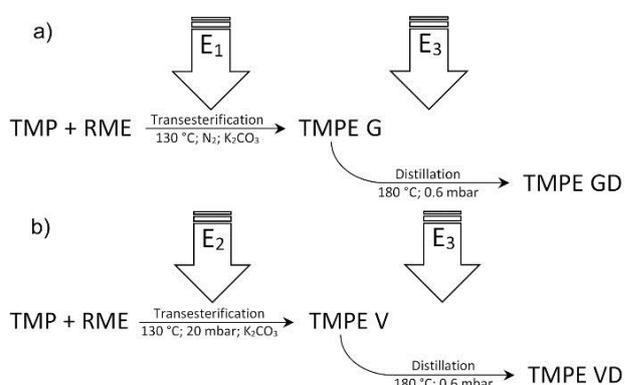


Fig. 1. Schemes of the energy consumed during TMP ester production: a) - nitrogen gas environment and b) - vacuum environment.

3.2 Composition of the as-synthesized esters

The results of TLC analysis are presented in Fig. 2. According to results on the plate (A), in synthesized samples, no monoesters and a marginal amount of diesters were found. The non-distilled samples had lesser diesters as compared to the distilled ones. It can be attributed to the degradation of triesters during distillation. There was a separation of triesters and RME on the plate (B). While the main part of the product was triester, the separation implies that the transesterification reaction was performed effectively, i.e., every molecule of alcohol reacted with two or three acyl radicals. However, some amount of RME remained in the distilled samples.

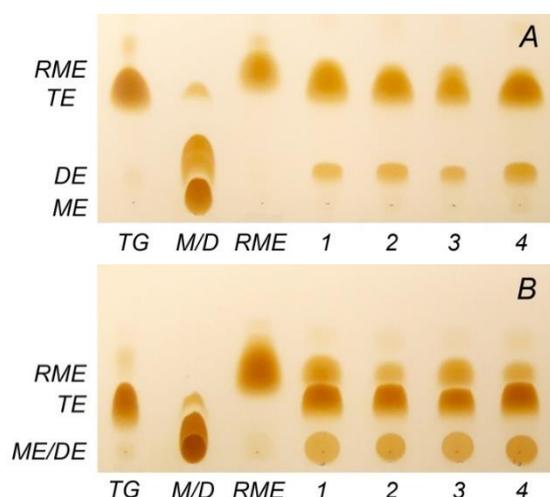


Fig. 2. TLC images of the as-synthesized esters. (A) n-Heptane/ethyl acetate, 83:17; (B) n-Heptane/ethyl acetate, 95:5. RME - reference of rapeseed oil methyl esters; TG - reference of triglyceride; M/D - joint reference of mono-, diglyceride. 1 - TMPE G; 2 - TMPE GD; 3 - TMPE V; 4 - TMPE VD.

3.3 Physicochemical properties and their impact on tribological properties

The physicochemical properties of the prepared esters are listed in Table 2. Transesterification

and distillation resulted in a slight increase in TAN. However, it was still within the appropriate limits (< 2 mgKOH/g) for bio-based lubricants. There were no significant differences in the viscosities of esters synthesized using different methods. However, due to residual RME, the difference between distilled and non-distilled esters is clear. Non-distilled esters, TMPE G and TMPE V met ISO VG 22 viscosity grades, while the distilled samples, TMPE GD and TMPE VD met ISO VG 32. These grades are most popular in the production of hydraulic fluids and engine oils. The viscosities of distilled esters recorded in our study are similar to those reported in other published studies. Synthesized esters are characterized by a high viscosity index. While no differences could be attributed to the synthesis method, the elimination of RME reduced VI. In general, a higher VI is desirable for high-quality base oil. The pour point determines the lowest temperature at which the lubricant can flow. In general, an ester's PPT depends on its structure and fatty acid composition. It was determined in our study that pour point temperature differs slightly between methods of synthesis (Table 2). Vacuum synthesized esters have a lower PPT. The PPT was also shown to improve with distillation. RME, having a higher pure point temperature, initiates crystallization centers in the volume which leads to a faster sample solidification. To further decrease PPT, appropriate pour point depressants or diluents should be used.

Based on flash point temperature, lubricant volatility and safety against fire can be determined. Residual RME plays an important role in ascertaining the flashpoint of investigated esters. Because of the presence of relatively volatile RME, the non-distilled samples had a lower flash point temperature.

Table 2. Physicochemical properties of synthesized esters.

Property	TMP G	TMP GD	TMP V	TMP VD
TAN (mgKOH/g)	0.08	0.1	0.07	0.1
Viscosity at 40°C, mm ² /s	20.4	30.0	19.8	31.3
Viscosity at 100°C, mm ² /s	5.4	7.0	5.3	7.2
Viscosity index	223	208	221	205
Pour point (°C)	-13	-15	-14	-17
Flash point (°C)	215	236	206	241
Density at 40 °C, g/cm ³	0.894	0.901	0.894	0.902

3.4 Tribological properties

Based on the friction results presented in Fig. 3, tests were performed in a mixed lubrication regime ($\mu = 0.08...0.1$); the two interacting surfaces were partly separated by a lubricating film. Pure lubrication and/or increased contact temperature can lead to more severe lubrication conditions. Scuffing or even seizure can occur. Viscosity plays an important role in this regime. The more viscous a lubricant is, the lesser is the expected direct metal-to-metal contact in the same loading and sliding speed regime. In the present case, distilled ester samples having a higher viscosity in both pure and additive loaded cases displayed lower average friction. However, the environment of synthesis had no significant impact in terms of friction. The higher friction of additive loaded samples is caused by contact tribo-chemistry.

Though the average friction in the case of pure synthesized esters was lesser than that of additive loaded ones, it displayed more fluctuations during the test (Fig. 4). Moreover, lubrication with pure esters led to higher friction at the onset of the test, caused by the running-in of contacting surfaces. The presence of AW additive stabilized the friction and mitigated the running-in process in the case of all the investigated esters.

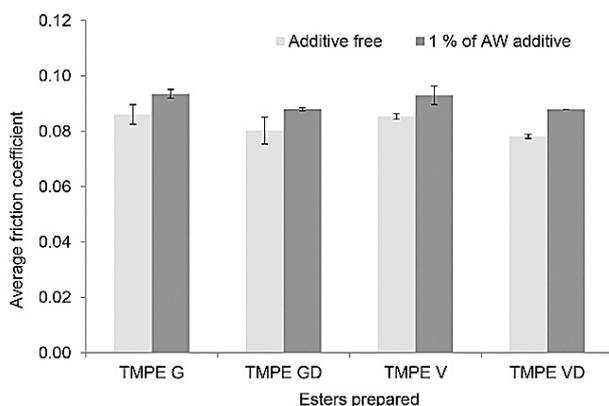


Fig 3. Average friction coefficient observed during the tribological test of the as-synthesized esters. The measured LSD (Least Significant Difference) R.05 additive-free = 0.006, R.05 additive loaded = 0.004.

Vacuum synthesized esters recorded relatively higher friction fluctuations and longer running-in periods (Fig. 4 c and d). Moreover, the friction of TMPE VD sample after 2000 s test time showed indications of the seizure (Fig. 4 d). It was a sharp jump-up of friction followed by a slower recovery.

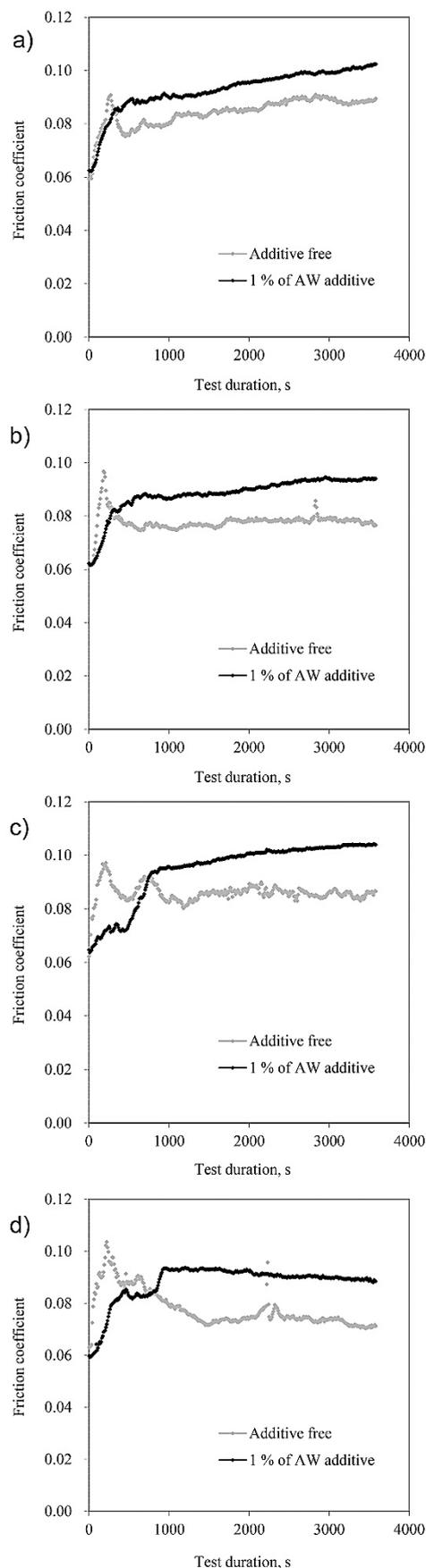


Fig. 4 Friction coefficient variation during the tribological test of as-synthesized esters. a) - TMPE G; b) - TMPE GD; c) - TMPE V; d) - TMPE VD.

A similar but lower impact phenomenon was observed when lubricating with TMPE GD ester (Fig. 4 b). Therefore, it could be concluded that RME improves the lubrication properties of synthesized esters as it has more polar molecules.

More stable friction in the case of samples synthesized in the gas environment can be explained by the presence of nitrogen-containing compounds formed during synthesis. Nitrogen is a heteroatom well known for its role in improving lubricating properties [17]. It is also evident that variation in friction during the test was different in the case of AW loaded gas environment synthesized samples. There was no running-in period at the onset of the test and friction steadily increased throughout the test duration.

It becomes a trade-off between lower viscosity and anti-seizure properties. On one hand, lower viscosity increases friction, while on the other, it saves surfaces from severe wear. It is also possible that the lower friction observed in distilled samples is caused due to scuffing. It is generally known that scuffing is followed by seizure, and friction tends to decrease before a seizure occurs.

The wear behavior results are presented in Fig. 5. The AW additive is very effective and compatible with all the samples. Moreover, based on LSD, there was no significant difference between the samples.

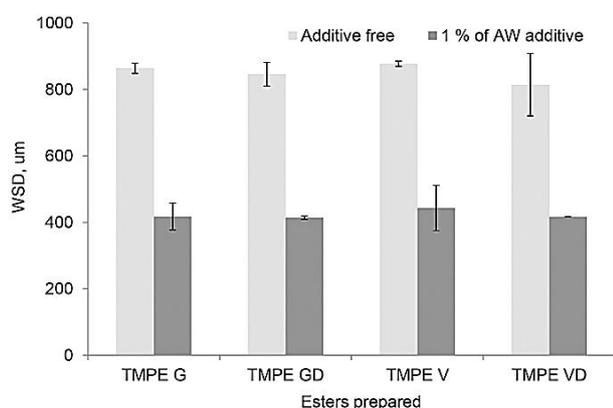


Fig. 5. Average wear observed during the tribological test of synthesized esters. The measured LSD (least significant difference) $R_{0.05}$ additive-free = 102, $R_{0.05}$ additive loaded = 79.

The additive-free esters displayed similar wear reduction properties. This could be discerned from an analysis of the error bars of the wear data. The wear tests of additive-free distilled samples revealed a relatively higher scatter, which is in the agreement with the unstable friction results. When friction is unstable, different types of wear can be expected. Conversely, for non-distilled samples, higher error bars appear in the presence of AW additive. It is due to the presence of RME polar molecules that compete with AW on the lubricating surface. This process adversely impacts the efficiency of the AW additive, though, fortunately, it does not affect friction.

The characteristic appearance of wear scars on stationary balls is presented in Fig. 6.

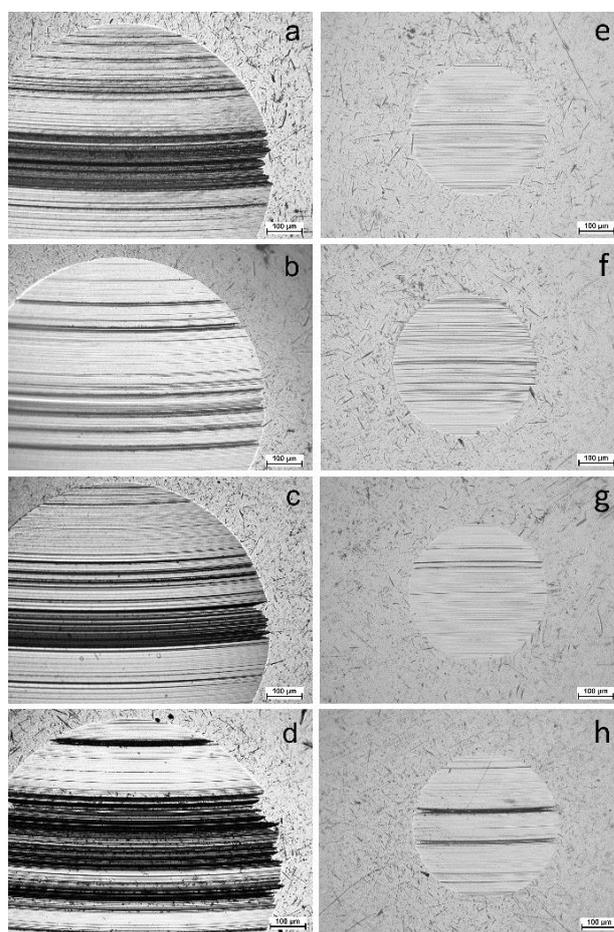


Fig. 6. Wear scars on stationary balls lubricated with: a and e - TMPE G; b and f - TMPE GD; c and g - TMPE V; d and h - TMPE VD additive-free and additive loaded samples respectively.

As for the additive-free samples the most probably, there were fatigue wear and abrasion. The abrasion is dominant in the middle of the

wear scar. It could be the case that severe abrasion occurs at the onset of the test when contact pressure is the highest. This is also supported by high COF in the running-in stage. The most distinct one was the wear scar observed after lubrication with the TMPE VD sample (Fig. 6 d). Deep grooves followed by very smooth regions appeared throughout the scar surface. The severe wear conditions were also reflected in the friction results. After the introduction of AW additives wear scars become relatively smooth, many small scratches are randomly distributed.

4. CONCLUSIONS

The four TMP ester samples were synthesized using different production paths and ranked according to the energy required for production. Ester production involving distillation required the highest amount of energy. Consequently, it exhibited the highest difference in physicochemical properties. The distilled samples show higher viscosity, lower volatility, and lower pure point temperature in comparison to the non-distilled samples. However, distillation reduced the viscosity index.

The method of synthesis has a marginal influence on the tribological properties. Due to the introduction of nitrogen during the transesterification in a nitrogen gas process slightly better tribological response can be discerned. According to the results, non-distilled esters revealed better friction reduction and anti-scuffing properties. However, their wear reduction properties were as poor as that of distilled esters. All the investigated esters were compatible with the anti-wear additive, which improved their wear reduction more than two-fold.

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