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STRUCTURE–TRIBOLOGY RELATIONSHIPS OF BIO-BASED ESTERS FOR ENVIRONMENTALLY FRIENDLY HYDRAULIC FLUIDS

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Abstract: Bio-based esters are promising alternatives to mineral oils for environmentally friendly hydraulic fluids owing to their biodegradability, low toxicity and favourable lubricating properties. Their physicochemical and tribological performance is strongly influenced by molecular structure, including hydrocarbon chain length, branching and functional group arrangement. This study investigated the structure–property relationships of synthesised polyol esters, hybrid ether–ester compounds and the commercial diester, focusing on the effects of hydrocarbon chain length on viscosity, low-temperature behaviour, oxidative stability, and tribological performance. The investigated compounds exhibited viscosities ranging from 14.05 to 43.78 mm²/s at 40°C, 3.70 to 7.85 at 100°C, viscosity indices above 140 and pour points as low as −60°C. The study aims to clarify the relationship between molecular structure and friction and wear behaviour, supporting the development of high-performance, environmentally friendly hydraulic fluids.

Keywords: bio-based esters, friction, wear, oxidative stability, hydraulic fluids

1. INTRODUCTION

The increasing demand for sustainable technologies and environmentally responsible industrial processes has stimulated interest in biodegradable lubricants for transportation, agricultural and industrial applications. In particular, bio-based hydraulic fluids offer a promising alternative to conventional mineral-oil-based formulations because of their potential biodegradability, reduced environmental impact and favourable lubricating properties. Vegetable oils, fatty acid derivatives and synthetic esters, including adipate esters and polyol esters, are widely investigated as alternative lubricant basestocks [1, 2].

The basestock typically constitutes approximately 80–100% (w/w) of a lubricant formulation, while the remaining fraction consists of functional additives designed to enhance specific performance characteristics. These additives may improve rheological behaviour, friction and wear reduction, low-temperature fluidity, corrosion protection, elastomer compatibility, oxidative stability and other formulation properties. However, several fundamental characteristics of lubricants, including viscosity, low-temperature fluidity, volatility, oxidative stability and solvency, are predominantly determined by the chemical composition and molecular structure of the basestock [3]. Consequently, the selection and molecular design of suitable base fluids are essential for achieving the required performance of environmentally friendly hydraulic fluids.

Synthetic esters are particularly attractive because their molecular structure can be tailored through the selection of alcohols and carboxylic acids. Structural parameters such as hydrocarbon chain length, molecular branching, functional group arrangement and molecular symmetry influence the physicochemical properties of esters, including viscosity, viscosity index, pour point and oxidative stability. These structural characteristics also affect tribological behaviour, which is critical for reducing

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friction and wear between contacting surfaces in hydraulic systems [4]. Interactions between ester molecules and metallic surfaces, including adsorption and the formation of protective lubricating layers, may determine lubrication effectiveness under operating conditions.

The effects of these structural features are interrelated and depend on the overall molecular architecture. Longer hydrocarbon chains generally increase viscosity and reduce volatility, whereas unsaturation may compromise oxidative stability [1]. Molecular branching can disrupt molecular packing and influence low-temperature fluidity, although its effects on viscosity and tribological performance depend on the specific molecular structure [5, 6]. Recent studies have demonstrated that the arrangement of ester and ether groups, as well as the distinction between linear and branched structures, can affect surface adsorption and wear behaviour [4, 5]. These relationships highlight the need to balance different structural features when designing ester-based basestocks for hydraulic fluids.

Despite the increasing development of bio-based ester lubricants, establishing systematic relationships between molecular structure, physicochemical properties and tribological performance remains important for the design of advanced hydraulic fluids. Therefore, this study investigates the influence of hydrocarbon chain length on the physical and tribological characteristics of synthesised polyol esters and hybrid ether–ester compounds to elucidate the relationship between molecular structure and lubricant performance, supporting the development of environmentally friendly hydraulic fluids.

2. EXPERIMENTAL

Bio-based oils and their fatty acid derivatives, along with polyhydric alcohols (polyols) such as glycerol, trimethylolpropane (TMP), pentaerythritol, or dipentaerythritol, were utilized for the synthesis of ester and hybrid ether–ester base oils. The hydroxyl groups of the polyol can be partially etherified to form a modified polyol, while the remaining hydroxyl groups are subsequently esterified with fatty acids. This approach yields polyol esters or hybrid ether–ester compounds, whose molecular structure can be tailored by adjusting the ratio of ether to ester groups and the nature of the fatty acid chains [7, 8]. The polyol esters and hybrid ether–ester compounds investigated in this study were previously described in published patent applications [7, 8]. The present work focuses on the characterisation of their physicochemical, tribological and oxidative properties. The analytical-grade reagents and fatty acids with a purity of >90% used for the synthesis were acquired from Sigma-Aldrich. The commercial diester, >90% diethylhexyl dodecanedioate, was purchased from TCI (Tokyo Chemical Industry Co., Ltd., Japan) and used as received.

Bio-based ester testing in this study involved three main methodologies: 1) viscosity and fluidity measurements 2) tribology measurements 3) esters film oxidation. The respective tests are presented accordingly below.

2.1. Fluidity measurements

The fluidity of the synthesised fluids was evaluated based on their kinematic viscosity and low-temperature flow behaviour. Kinematic viscosity was determined in accordance with ASTM D445, Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids.

Low-temperature fluidity was assessed by measuring the pour point using an in-house, low-volume procedure rather than the standard ASTM D97, Standard Test Method for Pour Point of Petroleum Products. The samples were progressively cooled in an ultrafreezer, and their flow behaviour was periodically assessed by inverting the sample containers and observing meniscus movement. The pour point was defined as the temperature at which the sample ceased to flow. The measurement procedure was based on the method reported by BaltTrib 2017 [9].

2.2. Friction and wear measurements

Pin-on-Disc Tribometer TR-20 M63 (Ducom Instruments, India) was used for friction tests in a ball-on-disc reciprocating oscillatory configuration. The test procedure was adapted from the standard high-frequency oscillatory test protocol ASTM D6425. A 6 mm diameter 100Cr6 bearing steel ball (RGP International Srl, Italy) with 96.5% Fe and a hardness of 780 ± 120 HV was used as the stationary part. The ball was fixed into the holder and pressed under a 100 ± 0.5 N load by a pneumatic piston against

the polished EN31 steel alloy with a hardness of 973 ± 146 HV and a surface roughness Ra of 0.15 ± 0.05 μm, mounted on a rotary part. The average roughness and hardness, along with their respective standard deviations (SD), were determined by taking five random measurements in different directions on an 80 mm diameter EN31 steel disc. The maximum wear track diameter of 60 mm was selected by using the graduated scale to adjust the sliding plate with a lever arm. Before tribotesting, the steel disc was cleaned with acetone and 0.1 mL of lubricant was added directly to the contact interface to ensure continuous wetting and avoid fluid starvation during testing. Under the applied normal load of 100 N and an oscillation frequency of 5 Hz, the contact operated predominantly in the boundary-to-mixed lubrication regime. Oscillatory reciprocal motion of 10° angle and 5 Hz frequency was maintained, resulting in a track length of 5.23 mm and a total distance of 10.46 mm for one reciprocal friction cycle. Tribotests were performed at a temperature of 20–23 °C and a relative humidity of 15–50%. The results were presented as a coefficient of friction (COF) curve dependence on sliding distance over a total length of 200 m. Each lubricant was tested in duplicate to ensure that the results were reproducible.

Tangential friction force was acquired continuously using a strain-gauge force transducer at a sampling rate of 1 kHz. Raw force signals were post-processed using a digital low-pass filter to remove mechanical vibration and electrical noise. To eliminate transient spikes and force-sign directional reversals occurring at stroke turning points, data within the inner 80% of each stroke segment were isolated. The steady-state COF was calculated as the absolute average kinetic friction force divided by the applied normal load over the mid-stroke segment for each cycle.

A contact profilometer Surtronic 25 (Taylor Hobson Ltd, UK) was used to determine surface roughness (Ra) and wear scars. The contact needle with a 2 μm tip radius scanned the surfaces horizontally within 1.5 mm of the path and transferred the data into the Image Plus software for visualization. The average Ra and its SD were calculated from five measurements taken at different locations on the EN31 steel disc. In order to obtain wear scar profiles, the surface was scanned perpendicular to the centre region of the wear track. The average cross-sectional area of the wear track and its SD were calculated from 2–3 measurements taken on two wear scars. The average wear volume was calculated on the assumption that wear is uniform over a track length of 5.23 mm.

2.3. Ester film oxidation test

The methodology and main principles of the ester film oxidation test have been described previously [10, 11]. The oxidative stability of the bio-based esters was evaluated using a film oxidation test conducted on low-carbon steel coupons. Prior to each test, the coupons were polished with 2000-grit SiC abrasive paper to obtain clean and uniform surfaces. The specimens were subsequently cleaned with acetone, dried and weighed using an ALJ-160-4NM analytical balance (Kern Analytical Instruments GmbH, Germany), with a weighing accuracy of ±0.1 mg.

The lubricant samples were applied uniformly to the steel surfaces using a pipette, forming films with a nominal thickness of 500 μm and an accuracy of ±2%. The coated coupons were placed in a 120 °C HCP-108 forced-draft oven with humidity control (Memmert GmbH, Germany) and exposed to a predetermined temperature for a specified duration. Following the oxidation treatment, the specimens were removed from the oven, cooled to room temperature and reweighed for further evaluation.

3. RESULTS AND DISCUSSION

3.1. Fluidity properties

The codes and systematic names of the studied compounds, along with their structural formulas, are presented in Table 1 and Figure 1, respectively.

Table 1. Effect of molecular properties on fluidity of tested esters and derivatized polyol esters.

Code mol wt	IUPAC, colloquial or trade name	Alcohol moiety	Acid moiety	Pour point, °C	Viscosity, mm^2/s at 40 °C	Viscosity, mm^2/s at 100 °C	Viscosity Index
8PG 831.40	2-ethylhexyl ether of TMP digondoate	dimethylol 2EHoxy propane	C20:1	-11	36.80	7.85	192
63U 564.92	3,5,5-trimethyl hexyl ester of C18:1 diacid	isononanol	C18:1 α,ω-COOH	-33	28.80	6.70	202
8C1 711.00	2EH ester of methoxy C18:0 diacid acylated with caprylate	2-ethylhexanol	methoxy C18 α,ω-COOH 9-C8	-60	43.78	7.74	147
6GM 639.04	hexyl ether of TMP dimyristate HexG-14,14	dimethylol hexoxy propane	C14:0	-9	27.00	5.67	157
D26 512.90	2-ethyl hexyl ether of glycerol didecanoate	2EH glycerol	C10:0	-54	14.05	3.70	160
6G9 526.83	hexyl ether of TMP pelargonate undecanoate EtOHex-9,11	dimethylol hexoxy propane	C9:0 C11:0 1 mol each	-60	15.19	3.75	141
12E 454.74	diethylhexyl dodecanedioate	2-ethylhexanol	C12:0 α,ω-COOH	-48	14.72	3.72	147

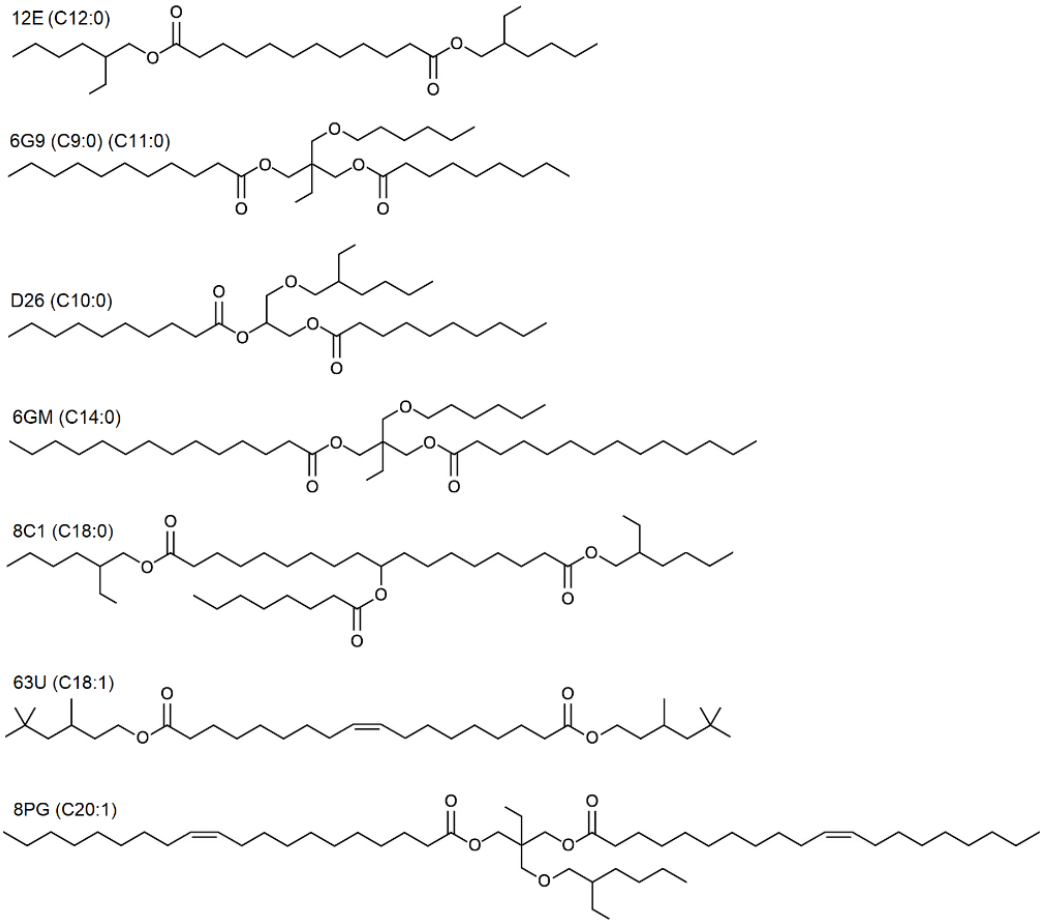

Figure 1. Structural formulas of the studied compounds.

The physicochemical properties presented in Table 1 show considerable differences among the investigated esters. The kinematic viscosity, viscosity index and pour point varied depending on the alcohol and acid moieties as well as the overall molecular structure. The relatively high viscosity indices (>140) indicate a limited temperature dependence of viscosity for most compounds, while the low pour points demonstrate favourable low-temperature fluidity. These results suggest that the physicochemical behaviour of the investigated esters is governed by the combined effects of chain length, branching and functional-group arrangement rather than by fatty-acid chain length alone.

3.2. Tribological properties

The tribological behaviour of the polyol esters was evaluated based on the evolution of COF during sliding and the diameter of the steel ball. All investigated esters provided relatively stable tribological contact. However, noticeable differences in friction and wear performance were observed depending on their molecular structure (Figure 2).

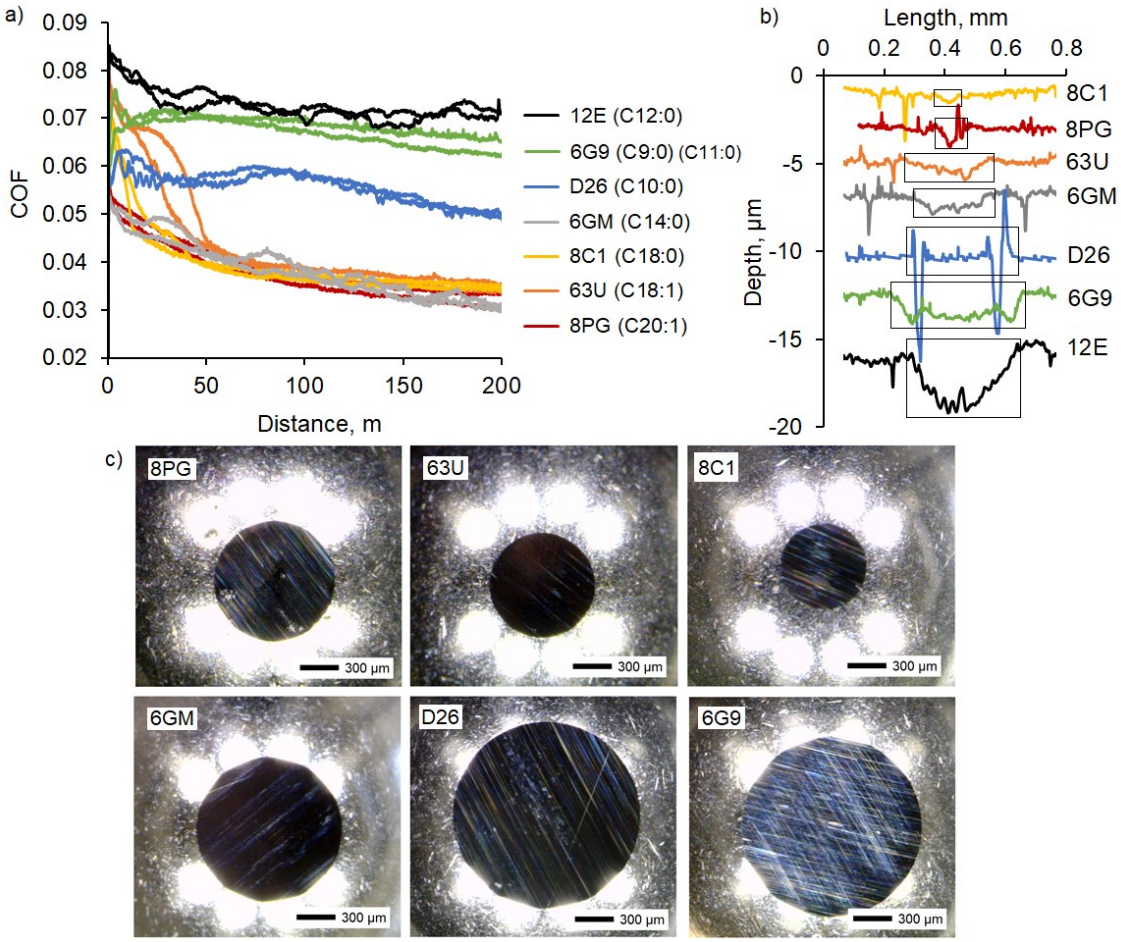

Figure 2. Friction behaviour of ester films (a), wear profiles (b) and wear scar diameter of steel balls (c).

During the initial stage of the tests, the COF was relatively high for most samples and gradually decreased with increasing sliding distance. Following the initial running-in period, the COF generally stabilised, with the steady-state values depending on the chemical structure of the ester. The lowest final COF values, approximately 0.03–0.04, were observed for 6GM, 8PG, 8C1 and 63U, whereas 6G9 and D26 exhibited higher stabilised COF values of approximately 0.06–0.07. Statistical data from two sets of measurements of overlapping curves showed that the average COF values were slightly higher for 8C1 and 63U (both 0.035 ± 0.001), and lower for 8PG (0.032 ± 0.002) and 6GM (0.030 ± 0.001) after a sliding distance of 200 m. However, the dynamics of the friction curve showed COF fluctuations for 6GM and relatively high initial friction for 63U, which may result in increased surface wear. For comparison, commercial ester 12E demonstrated relatively high COF exceeding 0.07.

The consistently low COF observed for 6GM, 8PG, 63U and 8C1 indicates that favourable friction behaviour cannot be attributed solely to hydrocarbon chain length. The 6GM molecule contains a C14:0 fatty acid residue, whereas 8PG, 63U and 8C1 contain C20:1, C18:1 and C18:0 chains, respectively. Additional wear analysis showed that esters with long hydrocarbon chains and the highest viscosity values exhibited the lowest wear volumes: $1.23 \pm 0.70 \times 10^{-4}$ mm^3 for 8C1 and $1.65 \pm 0.40 \times 10^{-4}$ mm^3 for 8PG (Table 2). Conversely, esters with the shortest hydrocarbon chains and the lowest viscosity values demonstrated the highest COF and wear volumes: $12.01 \pm 1.66 \times 10^{-4}$ mm^3 for D26 and $22.07 \pm 2.26 \times 10^{-4}$ mm^3 for 6G9.

Table 2. Wear of steel disc and ball wear scar using different esters

Code	Wear track depth, μm	Cross-section area of wear track × 10^{-4}, mm^2	Wear volume × 10^{-4}, mm^3	Steel ball wear scar diameter, μm
8PG	1.15 ± 0.10	0.32 ± 0.08	1.65 ± 0.40	944.9 ± 7.4
63U	1.05 ± 0.06	1.07 ± 0.29	5.62 ± 1.51	824.2 ± 7.4
8C1	0.43 ± 0.06	0.24 ± 0.13	1.23 ± 0.70	650.9 ± 29.7
6GM	1.00 ± 0.08	1.21 ± 0.20	6.34 ± 1.03	1091.9 ± 37.1
D26	6.50 ± 0.35	2.30 ± 0.32	12.01 ± 1.66	1461.9 ± 3.7
6G9	1.93 ± 0.36	4.22 ± 0.43	22.07 ± 2.26	1404.2 ± 3.7
12E	2.63 ± 0.32	4.69 ± 0.70	24.52 ± 3.64	851.0 ± 11.3

The different chain lengths and degrees of unsaturation among these compounds suggest that the overall molecular architecture, including the acid and alcohol fragments, branching and functional-group arrangement, may influence the interactions between ester molecules and the metallic surface. These structural features can affect adsorption at the sliding interface and the formation and stability of a protective lubricating film.

The wear measurements of the steel ball also revealed substantial differences between the investigated esters. The average wear-scar diameter ranged from approximately 650 to 1462 μm. The smallest ball wear scar diameter was measured for 8C1 (650.9 μm), followed by 63U (824.2 μm), 12E (851.0 μm), 8PG (944.9 μm) and 6GM (1091.9 μm). In contrast, the largest wear scars were observed for D26 (1461.9 μm) and 6G9 (1404.2 μm). A strong correlation was observed between the ball scar diameter, friction and wear results. Esters with long hydrocarbon chains and the highest viscosity values effectively reduced COF and inhibited wear on both the steel disc and its counterpart. Conversely, esters with the shortest hydrocarbon chains and the lowest viscosity values increased the COF and caused increased wear to both contacting surfaces. This tendency was not observed for the commercial ester 12E, which caused much greater wear to the disc than to the steel ball. This is probably due to the formation of a more effective boundary film on the ball surface compared to that of the higher molecular weight, more asymmetric compounds D26 and 6G9.

Overall, a lower COF was frequently accompanied by a smaller wear of the EN31 steel and 100Cr6 steel ball, indicating that friction and wear performance may be related. However, the relationship was not absolute. For example, 8C1 produced the smallest wear scar, although its COF was not the lowest among the investigated esters. This indicates that friction reduction and wear resistance represent related but distinct tribological characteristics and may be governed by different aspects of molecular structure, viscosity and surface interactions.

3.3. Thermal exposure and vaporization losses of ester films

The thermal stability and vaporization behaviour of the polyol esters were evaluated gravimetrically by monitoring the mass loss of 500 μm-thick ester films exposed to 120 °C. The mass loss was determined as a function of heating time. Significant differences in vaporization losses were observed among the investigated esters. In all cases, the mass loss increased with increasing exposure time, although the rate of mass loss varied considerably between compounds, indicating differences in their resistance to vaporization during prolonged heating (Figure 3).

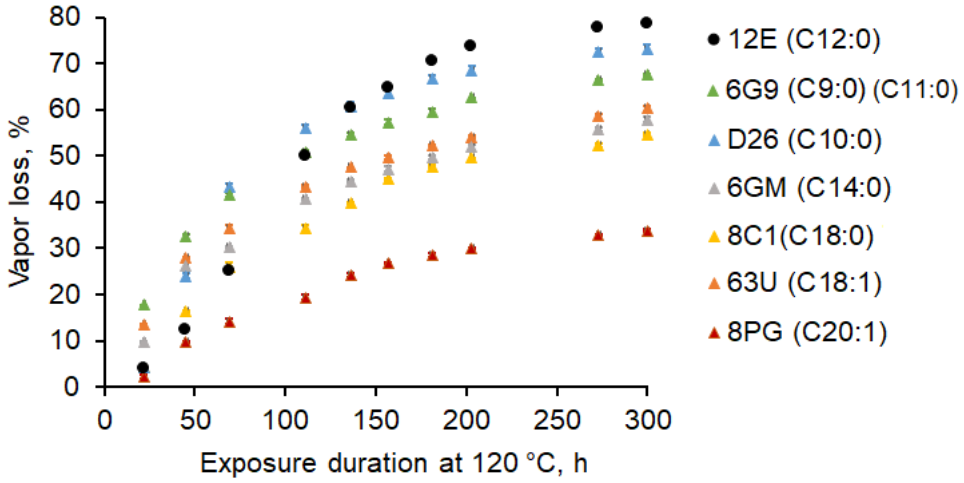

Figure 3. The effect of exposure duration on the evaporation losses of ester films at a constant temperature of 120 °C. Error bars indicate the SD of the mean based on two measurements.

Among the esters containing longer hydrocarbon chains, 8PG (C20:1) exhibited the lowest mass loss, approximately 32% after 300 h. In comparison, the mass losses of 8C1 (C18:0), 6GM (C14:0), 63U (C18:1) and D26 (C10:0) were above 50%, approximately 57%, approximately 60% and approximately 73%, respectively. Commercial ester 12E exhibited mass loss over 78%. The relatively low mass loss observed for 8PG indicates favourable resistance to vaporization under the applied conditions.

The results demonstrate that vaporization losses cannot be directly correlated with fatty acid chain length alone. Although molecular mass and hydrocarbon chain length can influence volatility, the differences between the investigated compounds indicate that other structural parameters also contribute to thermal mass loss. In particular, the alcohol moiety, molecular branching, degree of unsaturation and overall molecular architecture may affect intermolecular interactions and the resistance of the ester film to vaporization and thermal degradation.

3.4. Relationship between structure, tribology and thermal stability

Comparison of the tribological and thermal-stability results indicates that favourable performance in one property does not necessarily correspond to favourable performance in another. For example, 8C1 exhibited the smallest wear volume (1.23×10^{-4} mm^3) and ball scar diameter (approximately 651 µm), indicating favourable wear resistance, but showed a relatively high mass loss during prolonged heating. In contrast, 8PG exhibited a larger wear scar diameter (approximately 945 µm) but showed the lowest mass loss, approximately 32% after 300 h at 120 °C.

These differences demonstrate that wear resistance and resistance to vaporization are related to different aspects of molecular structure and cannot be evaluated using a single structural parameter. The results further emphasise the importance of considering the ester molecular architecture when developing bio-based hydraulic fluids. In particular, the alcohol and fatty-acid fragments, chain length, branching and unsaturation may affect different performance characteristics in different ways. Therefore, the suitability of bio-based esters as hydraulic-fluid basestocks should be assessed through a combined evaluation of viscosity, low-temperature fluidity, tribological behaviour and thermal stability, rather than on the basis of a single performance parameter.

4. CONCLUSIONS

The investigated bio-based esters exhibited distinct physicochemical, tribological and vaporization behaviours, demonstrating the importance of molecular architecture in determining their performance.

• The tribological behaviour depended on the overall molecular structure rather than on fatty-acid chain length alone. Esters with long hydrocarbon chains and highest viscosity values exhibited the lowest wear volumes. The smallest wear volume (1.23×10^{-4} mm^3) and ball scar diameter (650.9 µm) were observed

for 8C1, while the lowest stabilised COF (approximately 0.03–0.04) was measured for 6GM, 8PG, 8C1 and 63U.

• Vaporization losses varied considerably among the investigated esters. After 300 h at 120 °C, the mass losses of the synthesized esters ranged from approximately 32% for 8PG to 73% for D26, whereas that of the commercial ester 12E reached 78%. These results indicate that vaporization behaviour was influenced not only by fatty-acid chain length, but also by other structural features of the esters.

• The results showed that favourable wear resistance did not necessarily coincide with low vaporization losses, demonstrating that different molecular characteristics govern different performance properties.

• Overall, the alcohol and fatty-acid moieties, molecular branching, chain length and degree of unsaturation collectively influence the performance of bio-based ester basestocks. Their suitability for hydraulic-fluid applications should therefore be evaluated using a combination of physicochemical, tribological and thermal-exposure characteristics.

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