

Boundary lubrication properties of lipid-based compounds evaluated using microtribological methods

S. Bhuyan^a, S. Sundararajan^{a,*}, L. Yao^b, E.G. Hammond^b and T. Wang^b

^aDepartment of Mechanical Engineering, Iowa State University, Ames, IA 50011, USA

^bDepartment of Food Science and Human Nutrition, Iowa State University, Ames, IA 50011, USA

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Microscale friction tests were utilized to evaluate the boundary lubrication behavior of three sets of branched compounds and their corresponding linear compounds. The performances of the compounds were compared to that of lipid-based saturated and unsaturated acids, esters and alcohols as well as to that of commercial synthetic lubricant formulations. At low concentrations (~0.5%) in paraffin oil and for the load conditions used, the branched compounds showed minor differences in friction behavior as compared to their linear counterparts. The ester compounds by comparison showed higher friction behavior than alcohols and acids.

KEY WORDS: biodegradable oils, boundary lubrication friction, friction test methods, lubricant degradation, oxidation resistance, pour point, steel, vegetable oils, viscosity

1. Introduction

Due to the poor biodegradability of petroleum based fluids, there is a growing interest in developing and using vegetable oil based lubricants and fluids for industrial applications [1]. In addition, bio-based esters derived from plants and vegetable oils exhibit better performance at lower cost compared to synthetic esters [2]. Typical vegetable oils by their chemical nature are long chain fatty acid tri-esters of glycerol and provide most of the desired lubricant properties such as good boundary lubrication, high viscosity index, high flash point and low volatility [3]. So far a majority of the tribological characterization studies of bio-based products have been on long chain compounds and on the effect of chain length, unsaturation and polarity on boundary lubrication. Predominantly, compounds with longer chains show lower friction and lower wear than those with shorter ones [4–8]. The saturated compounds show better behavior than the unsaturated ones [3,9–11] and acids with a high degree of polarity exhibit improved tribological properties compared to esters whose polarity is less [3]. Lipid-based compounds however have two major disadvantages; their application is limited by poor oxidative stability and poor low temperature fluidity properties. Branching can eliminate the necessity of choosing between oxidative stability and low temperature pourability in bio-based lubricants. However few studies have evaluated the tribological behavior of

branched bio-based lubricants with a branched radical. Weller and Perez [5] have shown that the straight-chain and the branched molecules show comparable friction. In this paper, microscale friction tests are used to study the friction of normal and branched-chained compounds under light boundary lubrication conditions and their behavior is compared to other lipid-based compounds, specifically saturated and unsaturated compounds with various degrees of polarity.

2. Materials

The molecular formulae of all the samples are indicated in Table 1. Three pairs of branched and unbranched compounds were tested for their boundary lubrication behavior. They consisted of saturated methyl ester of stearic (C-18), palmitic (C-16) and myristic acids (C-14). The branched compounds in this case were the methyl-esters of the aforesaid compounds with a single methyl branched to one of the carbon atoms on the fatty acid chain. These compounds were isolated from lanolin (wool wax) by saponification and subsequently methylated [12]. All compounds were available in its nearly pure form with concentrations greater than 95% (w/w). In order to study the effect of polarity and saturation of the bio-lubricant constituents the boundary lubrication behavior of saturated compounds stearic acid, stearyl alcohol, methyl stearate were compared to the unsaturated compounds oleic acid, oleyl alcohol and methyl oleate. These were obtained commercially from Nu-Chek Prep, Inc., Elysian, MN. Two commercial

*To whom correspondence should be addressed.
E-mail: sriram@iastate.edu

Table 1.
Molecular formulae of all the compounds used.

Compounds	Molecular Formula
Methyl stearate	$\text{CH}_3(\text{CH}_2)_{16}\text{COOCH}_3$
Methyl 17-methylstearate	$(\text{CH}_3)_2\text{CH}(\text{CH}_2)_{15}\text{COOCH}_3$
Methyl palmitate	$\text{CH}_3(\text{CH}_2)_{14}\text{COOCH}_3$
Methyl 15-methylpalmitate	$(\text{CH}_3)_2\text{CH}(\text{CH}_2)_{13}\text{COOCH}_3$
Methyl myristate	$\text{CH}_3(\text{CH}_2)_{12}\text{COOCH}_3$
Methyl 13-methylmyristate	$(\text{CH}_3)_2\text{CH}(\text{CH}_2)_{11}\text{COOCH}_3$
Stearic acid	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$
Steryl alcohol	$\text{CH}_3(\text{CH}_2)_{17}\text{OH}$
Oleic acid	$\text{CH}_3(\text{CH}_2)_7 \text{CH} = \text{CH}(\text{CH}_2)_7\text{COOH}$
Methyl oleate	$\text{CH}_3(\text{CH}_2)_7 \text{CH} = \text{CH}(\text{CH}_2)_7\text{COOCH}_3$
Oleyl alcohol	$\text{CH}_3(\text{CH}_2)_7 \text{CH} = \text{CH}(\text{CH}_2)_8\text{OH}$

grade synthetic lubricants, i.e. multigrade engine oil of grade SAE 5 W20 (brands Amsoil and Castrol), were used as a benchmark for the boundary lubrication response of the bio-based compounds. This grade of oil particularly shows better high temperature viscosity and hence reduces friction while maintaining a full fluid film separation between the lubricating surfaces [13]. The compounds were tested as 60% (w/w) blend in paraffin oil except the branched compounds which were available in limited amounts, were tested as a 0.5% (C-18), 0.63% (C-16) and 0.75% (C-18) (w/w) blend in paraffin oil.

3. Methods

3.1. Microscale friction tests

Contact between engineering surfaces occurs at multiple discrete locations (asperities) and the tribological performance of the interface is dictated by the behavior at these asperity contacts. By understanding the mechanisms responsible for tribological behavior at these contacts, the behavior of the macroscopic interface can be predicted. For the experiments described in this paper, a custom-built reciprocating ball-on-flat microtribometer that can produce a microscale (apparent area ~ 1000 square microns) multi-asperity contact [14] was used. Microscale tests are also beneficial when only a limited quantity of the test material is available. A schematic of its major components is shown in figure 1. A spherical probe is placed at the end of a crossed I-beam structure, which is lowered using a linear stage to apply a desired normal load to the sample. The normal and friction (lateral) forces are measured using semiconductor strain gages on the cantilevers. Friction forces can be resolved to approximately $\pm 5 \mu\text{N}$ and normal forces to approximately $\pm 15 \mu\text{N}$. The signal from the normal load is monitored and used in a feedback loop to maintain the desired normal force regardless of any slope or waviness in the surface of the sample. A flat sample (substrate) of desired material is affixed to another stage set perpendicular to the beam, which provides linear motion. For this study a substrate

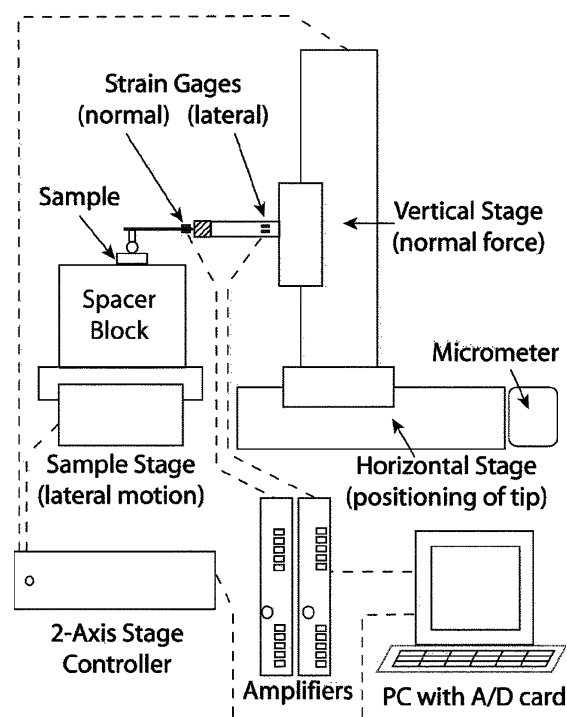


Figure 1. Schematic of the custom built microtribometer setup used in this study.

material of steel (AISI 52100, hardness 848 VHN and elastic modulus 210 GPa) was used. The steel was fabricated into 10 mm-thick sample discs with a diameter of 50 mm. They were grinded to yield a finer polish with an RMS roughness of 128 ± 22 nm. Surface roughness characterizations of the steel surfaces indicated that they are Gaussian in nature. All samples were cleaned with acetone in an ultrasonic bath for 15 min and dried using dry air prior to tests.

To obtain the coefficient of friction, a ramped load tests were performed in which the load was increased linearly with the sliding distance. An AISI 52100 steel ball of radius 1.2 mm and RMS roughness of 4 nm was used to probe the test steel samples. The load was increased from 0.2 to 180 mN as the probe was moved across a stroke distance of 45 mm at 10 mm/s. Preliminary tests showed that, for our load conditions, sliding speed has only a small effect on friction and wear relative to other factors. All tests for the acids, esters and alcohols were performed at 70 °C (melting point of stearic acid = 67 °C). The exception was for the low concentration straight and branched compounds which were heated slightly (40 °C) to blend in paraffin but were tested at room temperature environment of 25 °C. The tests were performed at room humidity of 50%. Tests on unlubricated surfaces were conducted at RH 20% to avoid water meniscus based effects. Four sets of friction measurements were performed for each sample. For the loading condition used, the Hertzian contact pressures were in the range of 0–710 MPa. Hertzian contact theory predicts an elastic response [15]. However, evaluation of

the plasticity index, based on Onion and Archard's definition, yields a value greater than 1 for the interfaces, which is the local plastic deformation limit. This suggests that local plastic deformation at the asperity levels may be occurring.

3.2. Viscosity measurements

Sample viscosities were measured with a cone and plate-system of a computer-controlled RS150 Rheo-Stress rheometer (Haake, NJ). A Ti cone with 60-mm diameter and 2° angle was used. The temperature was controlled with TC81 Peltier (Haake, NJ) and a water bath. The measurements were performed by raising temperature gradually step by step, and keeping all other measurement conditions constant. Each sample was held at each measuring temperature for one minute to equilibrate before data was taken. Viscosities of liquid samples were measured from 40 to 100°C. Viscosity of samples that were solid at room temperature were measured from temperatures above each sample's melting point and within a 50 degree range. Shear rate was controlled at 1000 revolution/s. Triplicate measurements were done for each sample.

4. Results and discussion

4.1. Friction test

Figure 2 shows representative friction data for several of the samples tested. The unlubricated system exhibits typical stick-slip type of behavior associated with the dry sliding of like mating surfaces (steel-steel). It can be seen that the base oil by itself does not provide any significant form of lubrication to the interface. This is in agreement with past studies on pure paraffin oil [16]. The long chained alkane monomers of paraffin do not form strong hydrogen bonding amongst themselves thereby becoming vulnerable to breakdown. All the test compounds, however, resulted in improved friction behavior, although in varying degrees as indicated in tables 2 and 3. Some oscillatory effects were seen in the friction response, typical of confined molecular films [17]. Figure 3 shows the percentage reduction in the coefficient of friction for all the compounds tested with respect to the coefficient of friction of the base oil.

4.2. Effect of branching

All sets of linear and branched compounds demonstrated lower friction force response (8–28%) compared to the base oil. The friction force observed increased with a decrease in carbon chain length of the linear compounds, which is consistent with previous reports [4–8]. There were very minor differences in friction response of the branched compounds and their linear

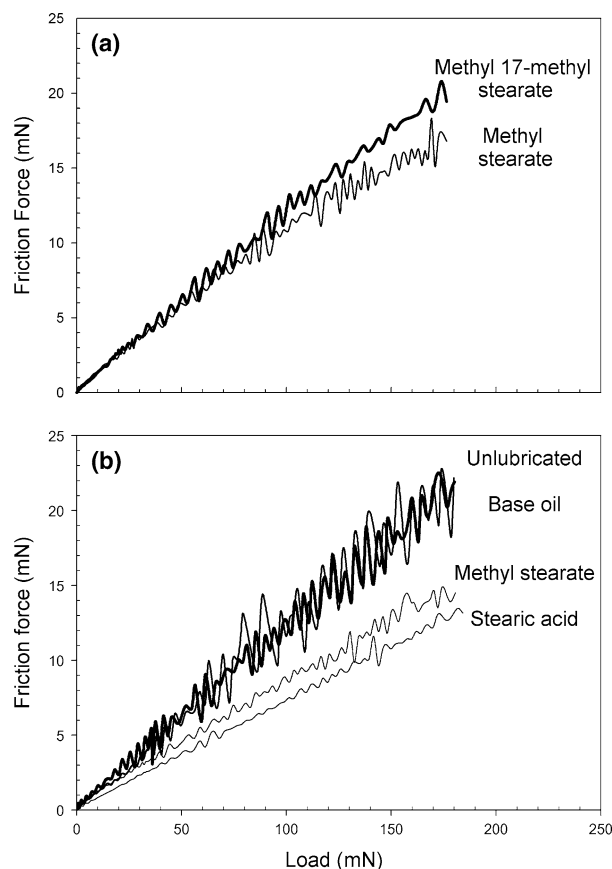


Figure 2. Representative friction vs. normal load plots obtained from ramped-load friction tests for (a) straight and branched chain esters at 0.5% (w/w) and (b) selected acids and esters at 60% (w/w) concentration in base oil.

counterparts. As shown in figure 3(a) and Table 2, at 0.5% concentration the branched C-18 methyl ester shows slightly higher friction than the straight chain ester. But, the straight methyl esters of other compounds (C-16 and C-14) have slightly lower frictions than their branched counterpart. This suggests that there is a combined effect of base chain length and branching. Pooley and Tabor have argued that side groups may hinder translational motion and result in increased friction [18], whereas other results indicate that branched compounds retain better fluid-like performance at higher pressures as compared to linear compounds [19]. The small magnitude of the differences in friction observed between the branched and straight compounds could be due to the small branch length (single methyl group).

4.3. Effect of polarity

It was found that, relative to the base oil, stearic acid demonstrates a 38.3% reduction in friction coefficient whereas methyl stearate shows 30.8% reduction in friction coefficient as shown in figure 3(b) and table 3. Oleic acid and methyl oleate reduces the friction coeffi-

Table 2.
Coefficient of friction and standard deviation values of steel against steel with different linear and branched chained compounds.

Coefficient of friction \pm Standard Deviation			
Unlubricated surface	Base oil	Series	$\sim 0.5\%$ (w/w) solution in base oil
0.140 \pm 0.001	0.139 \pm 0.001	Straight C-18 methyl-ester	0.099 \pm 0.001
		Branched C-18 methyl-ester	0.112 \pm 0.001
		Straight C-16 methyl-ester	0.115 \pm 0.004
		Branched C-16 methyl-ester	0.104 \pm 0.001
		Straight C-14 methyl-ester	0.124 \pm 0.003
		Branched C-14 methyl-ester	0.097 \pm 0.001

Average and standard deviation values have been taken from four tests on the sample at room temperature.

Table 3.
Coefficient of friction and standard deviation values of steel against steel with different compounds.

Coefficient of friction \pm Standard Deviation							
Unlubri-cated	Base oil	Amsoil	Castrol	Series	Acids	Ester	Alcohol
0.122 \pm 0.001	0.120 \pm 0.001	0.080 \pm 0.001	0.092 \pm 0.001	Saturated	0.074 \pm 0.001	0.083 \pm 0.002	0.076 \pm 0.003
				Unsaturated	0.079 \pm 0.001	0.088 \pm 0.001	0.081 \pm 0.003

Average and standard deviation values have been taken from four tests on the sample at 70 °C.

cient by 34.2% and 26.7%, respectively, when compared with the base oil. In general the results show that acids exhibit lower friction performance than esters. These significant reductions can be attributed to the fact that the thin surface film that develops in boundary lubrication is formed by the adsorption of polar compounds at the metal surface of the mating pair or by chemical reaction of the lubricant at the surface [20]. Since boundary lubrication by fatty acids is associated with the adsorption of the acid by dipolar attraction at the surface, they are capable of reducing the friction between the surfaces. Esters have a much lower polarity compared to acids and hence cannot form a strong protective boundary layer. In fact, a larger concentration of esters would be necessary to reduce friction as effectively as acid. The studies herein suggest that acids can indeed form a much better protective layer compared to esters.

The samples consisting of saturated steryl alcohol and unsaturated oleyl alcohol are more polar in nature than their esters. The alcohols were therefore expected to form a stronger lubricating film and show lower friction compared to esters. The conclusion from friction tests, indicated in figure 3(b) and table 3, is that this is generally true—alcohols exhibit higher friction than esters, with the difference being higher for saturated compounds. A considerable difference was noticed in the friction levels of saturated and unsaturated alcohols. Stearyl alcohol displays a 36.7% reduction of friction coefficient but oleyl alcohol shows 32.5%. The polar groups in alcohol compounds form a strong bond with the surface material thereby rendering strong boundary lubrication. However, results from the friction tests

suggest that this protective film may not be as strong as those formed by free fatty acids.

4.4. Effect of saturation

Figure 3(b) and table 3 indicate that the saturated stearic acid reduces friction coefficient by 38.3% compared to double-bonded oleic acid which reduces by 34.2%. Similarly, in the ester series, methyl stearate and methyl oleate reduces friction coefficient by 30.8% and 26.7% respectively. In general, introduction of a double bond increases friction. This is generally in agreement with previously reported work. The strength of molecular interaction plays a part in boundary lubrication [21]. In saturated acids like stearic acid, which contains no double bond, it is possible for the molecules to align themselves in straight chains and be closely packed on the surface providing a strong protective layer. Addition of a double bond prevents rotation and forces the chain to bend, thereby making it unable to pack closely together and resulting in a weaker protective layer [5].

Oxidation of the lipid molecules leads to polymerization and degradation of the bio-lubricants [2]. The ease of oxidation depends on the fatty acid composition of the vegetable oil. Unsaturated fatty acids are less resistant to oxidation at high temperatures that are generated during boundary lubrication. They react with molecular oxygen to form free radicals that lead to polymerization and fragmentation. The protective film becomes unstable and breaks down over time thereby increasing friction. Greater intermolecular distance between the adsorbed unsaturated molecules results in lower dispersion interaction [10]. The friction test results

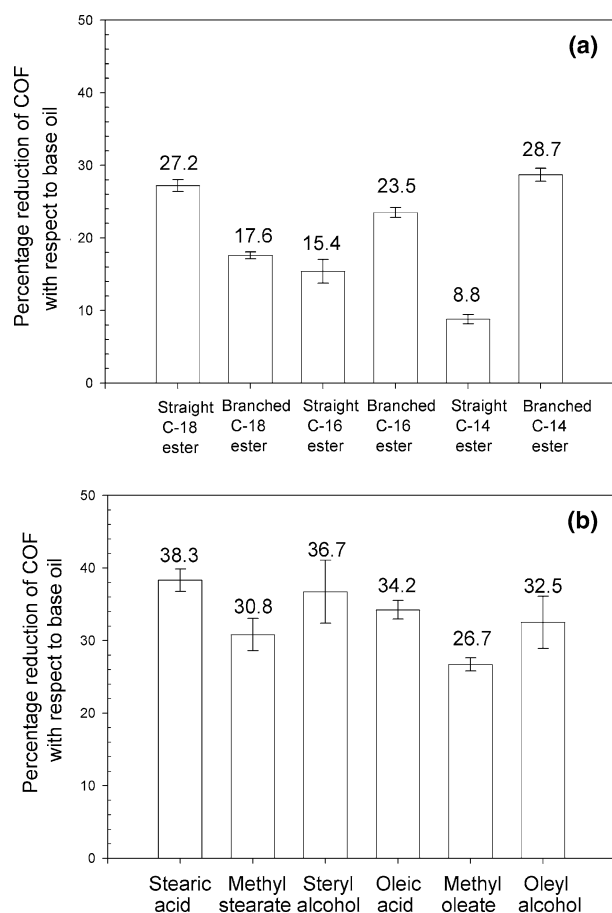


Figure 3. Bar chart indicating the percentage reduction of friction coefficient with respect to the base oil for (a) 0.5% (w/w) concentration of C-18, 0.63% (w/w) of C-16 and 0.15 (w/w) of C-14 straight and branched chained methyl esters and (b) 60% (w/w) concentration of acids, esters and alcohols.

support the idea that among these long lipid molecules, saturated compounds have superior boundary lubrication as opposed to their unsaturated counterparts. It is noted that that all bio-based compounds showed comparable or better friction performance than the synthetic blends as reported in table 3.

4.5. Viscosity

As shown in figure 4, the viscosity of the lipid-based materials decreases when temperature was raised for all samples. The functional group affected the viscosity to various extents. Free carboxyl groups gave the highest viscosity followed by free hydroxyl groups while ester groups gave the lowest viscosity. This trend was observed regardless of the existence of double bonds. The viscosity difference between acids and alcohols was small. Also, in the case of acids and alcohols, double bonds increased viscosity, but not for esters. The viscosity of methyl stearate was higher than that of methyl oleate. There were insufficient samples to evaluate the viscosity of the branched methyl esters.

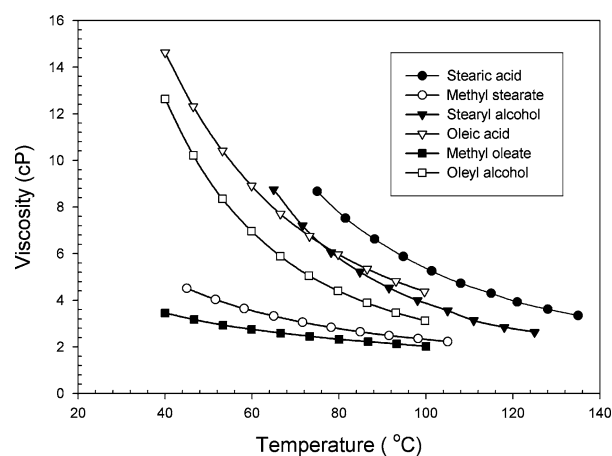


Figure 4. Representative plots of viscosity as a function of temperature for selected acids and esters.

Under boundary lubrication conditions, the friction behavior of the compounds should generally be unaffected by their viscosities. The lubrication regime for the compounds and testing conditions in this study was predicted by evaluating the film parameter λ , defined as follows [22]

$$\lambda = h_{\min} / (R_{q1}^2 + R_{q2}^2)^{1/2} \quad (1)$$

where h_{\min} is the minimum film thickness for the ball-on-flat contact region and R_{q1} and R_{q2} are the RMS roughness of the sample and probe, respectively. A λ value of less than unity generally corresponds to a boundary lubrication regime. Roughness values were obtained from atomic force microscopy scans of the surfaces (15 μm scans). The parameter h_{\min} was estimated for each lubricant using the measured viscosity of the compounds and the analysis of Hamrock and Dowson for elliptical contacts [22]. Table 4 indicates the viscosity values at 70 °C and the range of λ for the lubricants tested for the load ranges used. All the values are lower than unity, thereby corresponding to boundary lubrication. However, on comparing viscosity and friction data for the various lubricants, it was generally observed that compounds with higher viscosity exhibited lower friction. This suggests that the lubrication regime may be in a mixed condition and that hydrody-

Table 4. Viscosities of the test samples at 70 °C and estimation of the λ parameter to verify lubrication regime.

Sample	Viscosity η (cP)	λ parameter ^a
Stearic acid	8.67	0.010–0.017
Methyl stearate	3.05	0.005–0.008
Steryl alcohol	7.20	0.009–0.015
Oleic acid	7.23	0.009–0.015
Methyl oleate	2.52	0.004–0.007
Oleyl alcohol	5.45	0.008–0.012

^a λ reported for load range used: 0.2–200 mN.

namic component (and hence the viscosity) affects the friction behavior. In the case of acids, their hydrogen bonding capability enhances molecular affinity and they exist as weak dimers, which increases their viscosity. They also bind more strongly to the metal surface and hence a larger force is required to overcome the greater resistance of shear forces in order to maintain a smooth flow. This behavior is opposite in esters. Esters have a lower viscosity and for the same reasons have a higher friction. Lack of ability to form hydrogen bonds can separate the molecules easily and much smoother flow is observed. The viscosities and friction reducing capabilities of the hydroxyl group lies somewhere in between acids and esters.

5. Summary and conclusion

In summary, the adhesive friction behavior of a range of lipid-based and synthetic lubricants was evaluated to understand the effect of molecular structure on the boundary lubrication performance. Branch compounds exhibit slightly higher friction than corresponding linear compounds and this trend reverses as the chain length becomes shorter. The studies also showed that, polar compounds exhibit lower friction than non-polar compounds as evident from acids showing lower friction than alcohols and esters. Saturated compounds can reduce friction more efficiently than unsaturated ones. However, the polarity effect is more dominant than the effect of saturation. More studies on branched bio-based compounds are necessary to establish their lubricative effectiveness. It will be particularly interesting to see how the length of the branched radical will affect the boundary lubrication behavior.

Acknowledgments

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