

Ester Oils Prepared from Fully Renewable Resources and Their Lubricant Base Oil Properties

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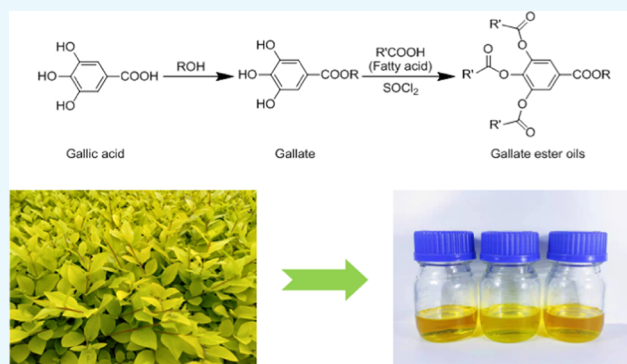


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ABSTRACT: The work reports on the physicochemical and tribological properties of gallate ester oils prepared from fully renewable resources, such as gallic acid and fatty acids. The ester structures were identified by proton nuclear magnetic resonance spectroscopy (^1H NMR), carbon nuclear magnetic resonance spectroscopy (^{13}C NMR) and high-resolution mass spectra (HRMS) data. The density at 20 °C (d_{20}), kinematic viscosity (KV), viscosity index (VI), pour point (PP), flash point (FP), thermal and oxidative stabilities, friction-reducing and antiwear properties of gallate ester oils were evaluated. The tribological properties of gallate ester oils as lubricants for steel, copper, and aluminum tribo-pairs can be compared with those of the commercially available lubricating oil tris(2-ethylhexyl) trimellitate (Phe-3C₁₈), but their viscosity-temperature characteristics, thermal and oxidative stabilities are better than those of Phe-3C₁₈. More importantly, they have much higher biodegradabilities than Phe-3C₁₈. The study of the lubrication mechanism shows that the physical and/or chemical adsorption film formed by gallate ester molecules between friction pairs is the key factor for them to obtain friction-reducing and antiwear properties.



1. INTRODUCTION

At present, global lubricant consumption is increasing year by year due to the rapid development of modern industry. Notably, most of the currently used lubricants are based on petroleum resources. It is well known that petroleum reserves in the world are diminishing. Meanwhile, degradation resistance of petroleum-based oils leads to serious environmental pollution.^{1–5} Because abandoned oil destroys the physical structure of soil, decreasing soil porosity, permeability and aeration. The oil moves from soil into surrounding reservoirs and affects the exchange of oxygen between water and the atmosphere, resulting in insufficient oxygen supply in the reservoirs. Finally, it threatens the life of aquatic organisms and destructs aquatic ecosystems.⁶ It is reported that in the European Community, about 585 000 tons of lubricants are directly discharged into the environment annually. In Germany, about 5000 tons of chain saw lubricant seeps into forest soil every year. In Malaysia, more than 150 million liters of waste lubricants are produced by transportation annually.⁷ Therefore, to prevent environmental pollution and preserve petroleum reserves, the use of bio-based and environmentally friendly lubricants is gaining immense attention.^{8,9} With respect to the development of sustainable biolubricants, vegetable oils such as soybean oil, rapeseed oil, sunflower oil, olive oil, castor oil, and palm oil are fully investigated due to their high biodegradability and renewability.^{1,10–18} However, as the operating environment of lubricating oil is becoming

more and more severe, lubricants based on vegetable oils can no longer meet the need of industrial lubricants due to their drawbacks of low thermal and oxidative stabilities, poor low temperature fluidity and small range of available viscosity.^{19–21} In this case, synthetic ester oils have received wide acceptance due to their improved performances. In a synthetic ester, the ester molecule is composed of at least one carbonyl moiety and one alcoholic moiety, which is prepared from carboxylic acid and alcohol by means of chemical synthesis.²² At present, the most widely used synthetic esters in lubrication engineering can be divided into four categories, monoester, diester, polyol ester, and aromatic carboxylic ester according to the number and position of ester groups in synthetic ester molecules.^{23,24} Compared with vegetable oils, synthetic ester oils have advantages such as good low-temperature and viscosity-temperature performances and excellent friction-reducing and antiwear properties.^{25–28} Due to these remarkable advantages, they have been widely used in aerospace and automobile industries, food processing, etc. Synthetic ester oils are

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supposed to be one of the most valuable and promising lubricants for future lubrication engineering.^{29,30} With the rapid development of modern industry, the design of high-performance synthetic esters is highly desired. Moreover, worldwide concern about environmental pollution and energy-saving issues is encouraging the development of high-quality synthetic esters based on renewable resources.^{31,32} At present, most of the raw materials used to synthesize commercially available synthetic esters still come from petroleum resources. We are committed to develop new synthetic esters based on renewable resources in the past few years.^{33,34} In our former work, high-quality synthetic esters were developed through chemical modification of naturally available 3,4,5-trihydroxybenzoic acid.³⁵ Although they were found to have high thermal and oxidative stabilities, excellent friction-reducing and antiwear properties at high temperatures. In view of environmental pollution and energy-saving issues, the developed esters still have defects of dependency on nonrenewable petroleum resources and inadequate biodegradability due to the presence of long alkoxy chains. To overcome these problems, herein, a novel synthetic ester based on completely naturally available compounds, gallic acid and fatty acids, was developed.

2. RESULTS AND DISCUSSION

2.1. Density at 20 °C, Kinematic Viscosity and Viscosity Index. Kinematic viscosity (KV) represents the flow resistance of a liquid under gravity and its value is the ratio of dynamic viscosity to density at a given temperature. KV is an important parameter of lubricants, which is related to the film thickness of the lubricant on the sliding surface. Lubricating oil must have suitable viscosity to form a good lubricant film between tribo-pairs. The Viscosity index (VI) of lubricating oil indicates its KV variation with temperature. A higher VI reveals less change in KV with increasing or decreasing temperature, which can ensure the lubricating oil to form an effective lubricating film on the sliding surface in a wide range of temperatures.³⁶ As listed in Table 1, the KVs of

Table 1. Density at 20 °C (d_{20}), Kinematic Viscosity at 40 °C (KV₄₀), at 100 °C (KV₁₀₀) and Viscosity Index (VI) of the Gallate Ester Oils and Phe-3C₁₈

lubricants	d_{20} (g/cm ³)	KV (mm ² /s)		VI
		KV ₄₀	KV ₁₀₀	
Phe-3C ₁₈	0.99	90.2	9.4	74
3C ₈ -C ₃	1.02	58.6	8.3	112
3C ₈ -C ₁₅	1.01	69.0	9.5	116
3C ₈ -C ₁₈	0.99	56.7	8.4	119
3C ₁₈ -C ₁₈	1.00	149.4	13.4	81
3C ₄ -C ₁₈	1.07	95.7	10.0	81
3C ₁₂ -C ₁₈	0.96	73.9	10.8	135

the gallate ester oils are in the range of 56.7–149.4 mm²/s at 40 °C and 8.3–13.4 mm²/s at 100 °C. Most of the gallate ester oils have lower KVs than the reference sample (tris(2-ethylhexyl) trimellitate (Phe-3C₁₈)) at 40 °C, but higher KVs at 100 °C. The KVs of the gallate ester oils are found to decrease as the ester chain increases within a certain range both at 40 and 100 °C, for example, KV₄₀ (3C₈-C₁₅, 69.0 mm²/s) > KV₄₀ (3C₈-C₁₈, 56.7 mm²/s), KV₄₀ (3C₄-C₁₈, 95.7 mm²/s) > KV₄₀ (3C₈-C₁₈, 56.7 mm²/s), KV₁₀₀ (3C₈-C₁₅, 9.5 mm²/s) > KV₁₀₀ (3C₈-C₁₈, 8.4 mm²/s), and KV₁₀₀ (3C₄-C₁₈, 10.0 mm²/s) > KV₁₀₀ (3C₈-C₁₈, 8.4 mm²/s). Similar

observations are observed in our previous work, which is also in accordance with the studies reported by other researchers.^{2,13,32} However, if the increase of the ester chain goes beyond a certain range, an increase in KV is observed, e.g., KV₄₀ (3C₈-C₁₈, 56.7 mm²/s) < KV₄₀ (3C₁₂-C₁₈, 73.9 mm²/s) and KV₁₀₀ (3C₈-C₁₈, 8.4 mm²/s) < KV₁₀₀ (3C₁₂-C₁₈, 10.8 mm²/s). For ester oils, increasing the branched chain leads to higher dependence of viscosity on temperature.^{35,37} Besides, the introduction of branched chains can increase KVs, e.g., KV₄₀ (3C₈-C₁₈, 56.7 mm²/s) < KV₄₀ (3C₁₈-C₁₈, 149.4 mm²/s) and KV₁₀₀ (3C₈-C₁₈, 8.4 mm²/s) < KV₁₀₀ (3C₁₈-C₁₈, 13.4 mm²/s). The VIs of the gallate ester oils vary from 81 to 135, which are all higher than that of Phe-3C₁₈ (74). It indicates that less KV change with temperature is observed for the gallate ester oils during lubrication. With an increase in the length of the ester chain, an increasing trend in the VIs is observed, e.g., VI (3C₈-C₃, 112) < VI (3C₈-C₁₅, 116) < VI (3C₈-C₁₈, 119) and VI (3C₄-C₁₈, 81) < VI (3C₈-C₁₈, 119) < VI (3C₁₂-C₁₈, 135).^{23,38} In addition, the introduction of branched chains decreases the VI of the gallate esters, e.g., VI (3C₁₈-C₁₈, 81) < VI (3C₈-C₁₈, 119).^{35,37} From Table 1, it is observed that the densities at 20 °C (d_{20}) of the gallate ester oils vary from 0.96 to 1.07. As the ester chain decreases, the d_{20} of the gallate ester oils increase due to the closer packing of the gallate ester molecules, e.g., d_{20} (3C₁₂-C₁₈, 0.96 g/cm³) < d_{20} (3C₈-C₁₈, 0.99 g/cm³) < d_{20} (3C₁₈-C₁₈, 1.00 g/cm³) < d_{20} (3C₄-C₁₈, 1.07 g/cm³) and d_{20} (3C₈-C₁₈, 0.99 g/cm³) < d_{20} (3C₁₈-C₁₈, 1.00 g/cm³) < d_{20} (3C₈-C₁₅, 1.01 g/cm³) < d_{20} (3C₈-C₃, 1.02 g/cm³). The results are consistent with the reported data of Barnhill.³⁹

2.2. Pour Point and Flash Point. Pour point (PP) refers to the lowest temperature at which the cooled lubricating oil can flow under the specified test conditions. It can be observed that the gallate ester oils exhibited PP in the range of 16 to -58 °C (Table 2). Among them, the PP of 3C₁₈-C₁₈ (-58 °C)

Table 2. Pour Point (PP), Flash Point (FP), Oxidation Induction Time (OIT) and Initial Decomposition Temperature (T_d) of the Gallate Ester Oils and Phe-3C₁₈

lubricants	PP (°C)	FP (°C)	OIT (min)	T_d (°C)
Phe-3C ₁₈	-48	213	45	272
3C ₈ -C ₃	16	210	225	300
3C ₈ -C ₁₅	19	201	146	304
3C ₈ -C ₁₈	-39	219	114	329
3C ₁₈ -C ₁₈	-58	188	148	305
3C ₄ -C ₁₈	-46	189	75	274
3C ₁₂ -C ₁₈	-4	196	87	365

is the lowest, which means that it has the best low-temperature fluidity among the gallate ester oils. At the same time, lower PP is observed with increasing the length of the ester chain attached to the carboxyl group at 1-position of the aromatic ring, for example, PP (3C₈-C₁₅, 19 °C) > PP (3C₈-C₁₈, -39 °C), whereas in the case of substituents on 3,4,5-positions, the PPs of the gallate ester oils increase as the chain length increases from butyl to octyl and from octyl to dodecyl, e.g., PP (3C₄-C₁₈, -46 °C) < PP (3C₈-C₁₈, -39 °C) < PP (3C₁₂-C₁₈, -4 °C). In addition, the PP could be increased by introducing branched chains, e.g., PP (3C₁₈-C₁₈, -58 °C) < PP (3C₈-C₁₈, -39 °C). It is attributed to the increasing steric hindrance caused by the branched chain. As a result, it is difficult for individual molecules to come close for easy stacking.^{23,35,40,41}

With the increase of heating temperature, vapor forms on the surface of lubricating oil. Flash point (FP) is the minimum temperature at which the mixture of the vapor and the surrounding air flashes once it comes in contact with the flame. In general, lubricating oils with high FPs are desired, which can ensure safe operation and minimum volatilization. The FPs of the gallate ester oils are presented in Table 2 and observed in the range of 188–219 °C. As the ester chain increases within a certain range, higher FPs are observed, for example, FP (3C₈-C₁₅, 201 °C) < FP (3C₈-C₁₈, 219 °C) and FP (3C₄-C₁₈, 189 °C) < FP (3C₈-C₁₈, 219 °C). Similar observations are found in our previous work, which is also in accordance with the studies reported by other researchers.^{11,27,32,42,43} However, if the increase of the ester chain goes beyond a certain range, a decrease in FP is observed, for example, FP (3C₈-C₁₈, 219 °C) > FP (3C₁₂-C₁₈, 196 °C). In addition, the introduction of branched chains decreases the FP, e.g., FP (3C₈-C₁₈, 219 °C) > FP (3C₁₈-C₁₈, 188 °C).

2.3. Oxidative Stability. Oxidative stability refers to the ability of the lubricating oil to maintain its properties without oxidative decomposition in the atmosphere or oxygen environment. The rotating oxygen bomb (ROB) test is an effective way to measure the oxidative stability of the lubricating oil. Oxidation induction time (OIT) is usually reported for evaluating the oxidative stability.⁴⁴ The OITs of the gallate ester oils are shown in Table 2. It can be found that the gallate ester oils exhibit longer OIT than Phe-3C₁₈ (45 min), which are observed in the range from 75 to 225 min, which means that the gallate ester oils have obviously higher oxidative stability than Phe-3C₁₈. In the gallate ester oils, as the ester chain length increases, a decreasing tendency is found in OITs, e.g., OIT (3C₈-C₃, 225 min) > OIT (3C₈-C₁₅, 146 min) > OIT (3C₈-C₁₈, 114 min) > OIT (3C₁₂-C₁₈, 87 min). However, if the chain length of the ester groups on 3,4,5-positions decreases beyond a certain range, a decrease in OIT is observed, e.g., OIT (3C₄-C₁₈, 75 min) < OIT (3C₈-C₁₈, 114 min). In addition, the introduction of side chains can increase the OIT, e.g., OIT (3C₁₈-C₁₈, 148 min) > OIT (3C₈-C₁₈, 114 min).

2.4. Thermal Stability. The thermal stability of a lubricant is its ability to resist decomposition at high temperatures. Increasing-temperature thermogravimetric (TG) analysis and constant-temperature TG analysis are used to evaluate this property.

During the increasing-temperature TG analysis, T_d TG, and derivative thermogravimetric (DTG) curves are used to evaluate the thermal stability of the lubricating oil. The TG and DTG curves of the gallate ester oils and Phe-3C₁₈ are presented in Figures 1 and 2. The corresponding T_d values are summarized in Table 2. From Figures 1 and 2, it is observed that all of the samples just show rapid weight loss after 250 °C and completely decompose at about 450 °C. All of the gallate ester oils except 3C₄-C₁₈ possess better thermal stability than Phe-3C₁₈. The T_d values of the samples displayed in Table 2 also show the same results. All of the gallate ester oils exhibit higher T_d than Phe-3C₁₈. Particularly, 3C₁₂-C₁₈ shows T_d up to 365 °C, indicating its extremely high thermal stability and suitability for high-temperature applications. In addition, the T_d of the synthesized esters increases with the increase of the carbon chain length, which is attributed to the increasing molecular weight,⁴⁵ e.g., T_d (3C₈-C₃, 300 °C) < T_d (3C₈-C₁₅, 304 °C) < T_d (3C₈-C₁₈, 329 °C) and T_d (3C₄-C₁₈, 274 °C) < T_d (3C₈-C₁₈, 329 °C) < T_d (3C₁₂-C₁₈, 365 °C). In addition,

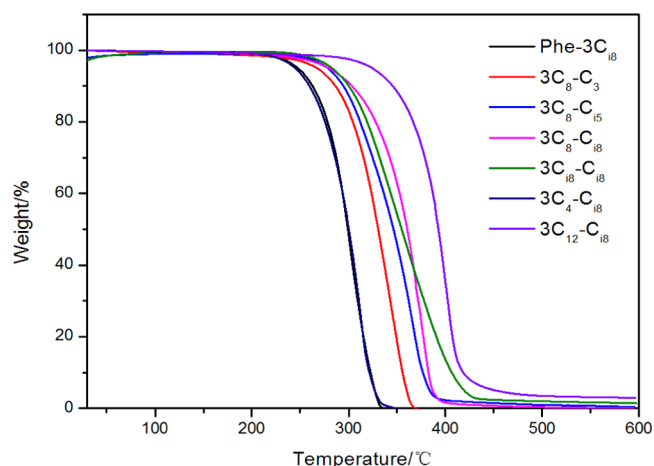


Figure 1. Increasing thermogravimetric (TG) curves of the gallate ester oils and Phe-3C₁₈.

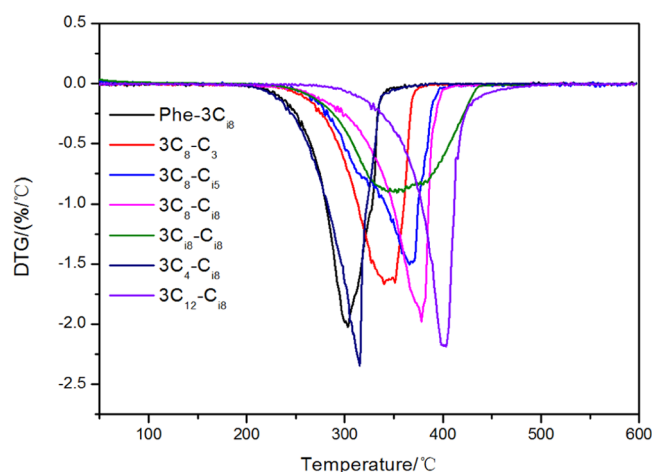


Figure 2. Increasing derivative thermogravimetric (DTG) curves of the gallate ester oils and Phe-3C₁₈.

the introduction of branched chains can decrease the T_d, which can be attributed to the increased steric hindrance caused by the branches, which reduces the intermolecular force, e.g., T_d (3C₈-C₁₈, 329 °C) > T_d (3C₁₈-C₁₈, 305 °C).

Constant-temperature TG analysis is used to measure the weight loss of the lubricating oil due to vaporization. The weight loss of the gallate ester oils and Phe-3C₁₈ are presented in Figure 3. The gallate ester oils except 3C₄-C₁₈ have lower volatility than Phe-3C₁₈. Meanwhile, the volatility of the gallate ester oils reduces as the ester chain length increases. Particularly, 3C₁₂-C₁₈ only has less than 10% weight loss during the whole testing process. These results are partially attributed to the high molecular weight of the lubricating oils, resulting in a stronger intermolecular force among the molecules. It is also seen that the introduction of branched chains can increase the volatility because it increases the distance and weakens the interaction between the molecules, thereby increasing the volatility of the lubricant.³⁷

2.5. Tribological Properties. Figure 4 shows the tribological properties of the gallate ester oils and Phe-3C₁₈ as lubricants for steel tribo-pairs. It can be found in Figure 4(a, c) that the gallate ester oils showed slightly lower coefficients of friction (COFs) than Phe-3C₁₈, but their wear volumes (WVs) are similar to that of Phe-3C₁₈, which means that the

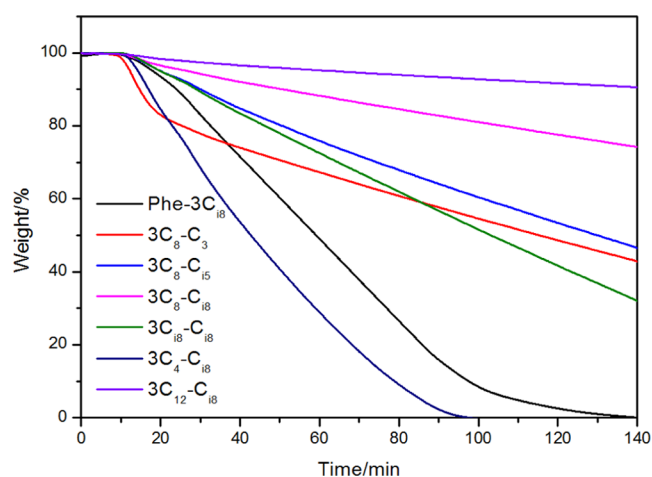


Figure 3. Constant TG curves of the gallate ester oils and Phe-3C₁₈.

gallate ester oils have better friction-reducing and comparable antiwear properties than Phe-3C₁₈. It can also be found that the COFs of the gallate ester oils increase with the increase of KV₄₀, e.g., COF (3C₈-C₃, 0.085) < COF (3C₈-C₁₈, 0.088) < COF (3C₈-C₁₅, 0.092) and COF (3C₈-C₁₈, 0.088) ≈ COF (3C₁₂-C₁₈, 0.086) < COF (3C₄-C₁₈, 0.090) < COF (3C₁₈-C₁₈, 0.094). This can be attributed to the high internal friction in the lubricating molecules, which can increase the shearing force of the lubricant, resulting in the increase of the COF.⁴⁶ From Figure 4(b, d), it is observed that varying the chain

length of the ester group attached at 1-position of the aromatic ring has no obvious influence on the antiwear properties of the gallate ester oils, while varying the chain length of the ester groups attached at 3,4,5-positions of the aromatic ring influences their antiwear properties obviously. The antiwear properties of the corresponding ester oil increase gradually with the increase of the ester chain length, which may be attributed to the film formation of the lubricating oil on the friction surface because the ester oil with a longer carbon chain can form more effective protecting films during the lubricating process.

The tribological properties of the gallate ester oils as lubricants for copper tribo-pairs are also evaluated, and the results are shown in Figure 5. Similar to the results obtained on steel tribo-pairs, the gallate ester oils have better friction-reducing properties than Phe-3C₁₈, but their antiwear properties are comparable to those of Phe-3C₁₈ when they are used as lubricants for copper tribo-pairs (Figure 5). The COFs of the gallate ester oils increase with the increase of KV₄₀, e.g., COF (3C₈-C₃, 0.069) < COF (3C₈-C₁₈, 0.074) < COF (3C₈-C₁₅, 0.081) and COF (3C₈-C₁₈, 0.074) ≈ COF (3C₁₂-C₁₈, 0.075) < COF (3C₄-C₁₈, 0.086) < COF (3C₁₈-C₁₈, 0.091), but the change rule of WVs is not obvious in the gallate ester oils. The reason may be that WVs are impacted not only by KV but also by other characteristics such as the VI and molecular structure of the lubricating oil. As lubricants for aluminum tribo-pairs (Figure 6), the friction-reducing properties of the gallate ester oils are comparable to those of Phe-

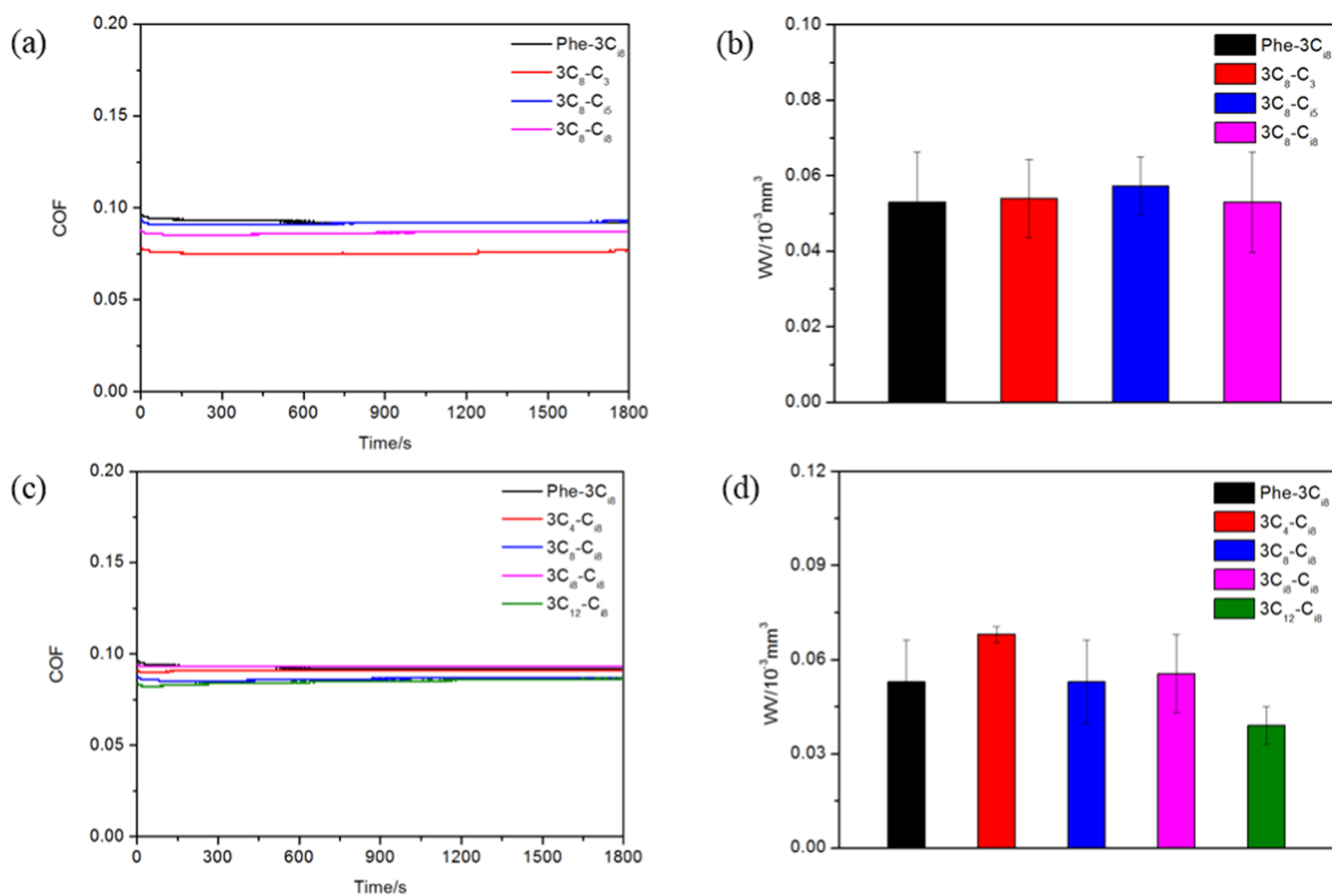


Figure 4. Evolution of coefficient of friction (COF)/time (a, c) and wear volume (WV) (b, d) of lower steel plates lubricated with the gallate ester oils and Phe-3C₁₈ at room temperature (RT).

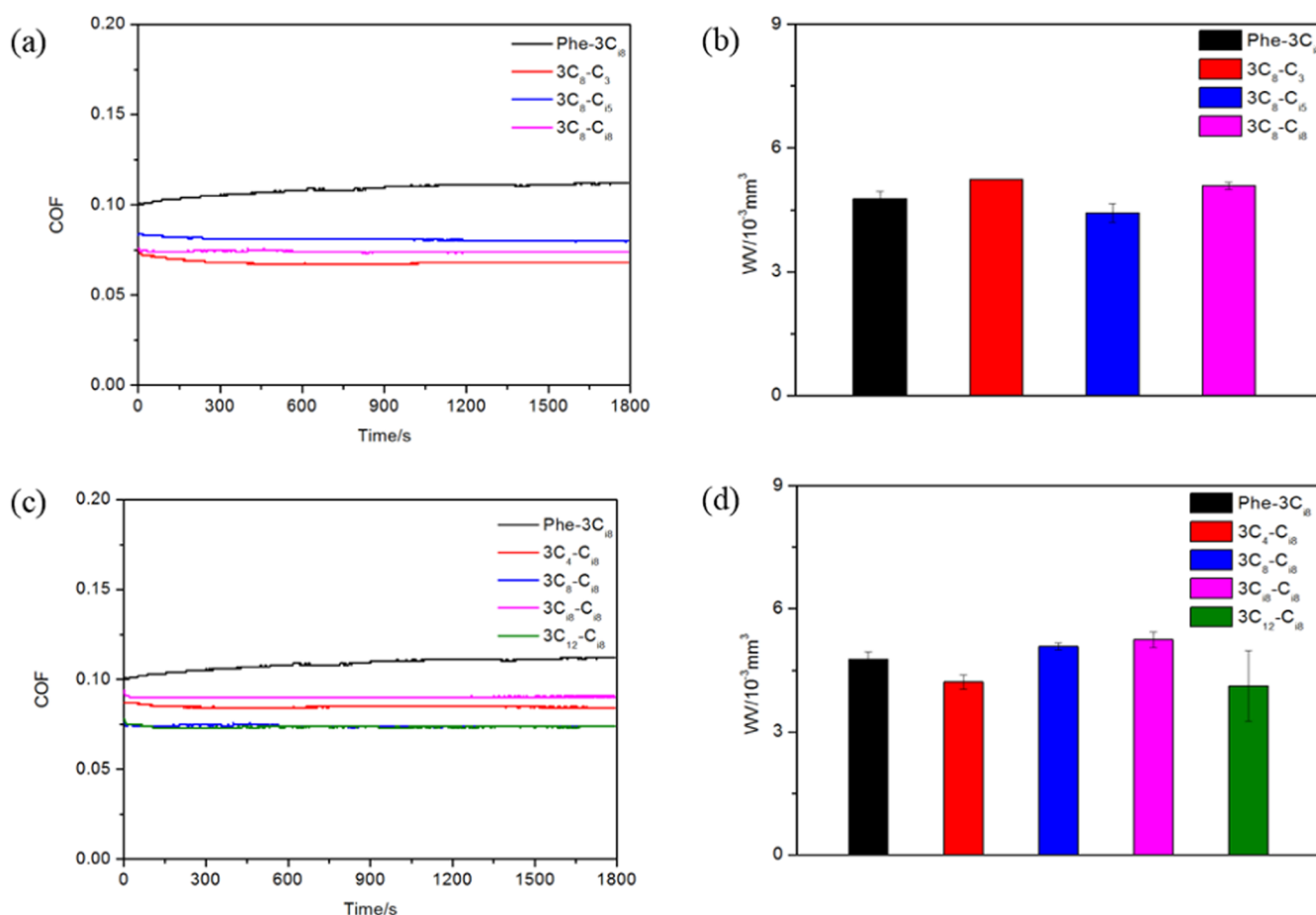


Figure 5. Evolution of COF/time (a, c) and WV (b, d) of lower copper plates lubricated with the gallate ester oils and Phe-3C₁₈ at RT.

3C₁₈, but their antiwear properties are slightly worse than those of Phe-3C₁₈.

In general, the gallate ester oils have comparable friction-reducing and antiwear properties to those of Phe-3C₁₈. Their friction-reducing and antiwear properties are speculated to be attributed to the multiple polar groups, which can effectively adsorb on metal surfaces and form good physical and/or chemical adsorption films or chemical reaction films on the surfaces. There are benzene rings in the structures of the gallate ester oils; the aromatic π - π conjugation promotes the adsorption of the lubricant molecules on the metal surface. In addition, aromatic π - π stacking can make the ester molecules adsorb more orderly on the surfaces, thereby forming more stable lubricating films.⁴⁷⁻⁴⁹

To further analyze the friction mechanism, X-ray photoelectron spectroscopy (XPS) was used for the elemental analysis of the wear scar surfaces after lubricating with the gallate ester oils and Phe-3C₁₈. From Figure 7 and Table S4 (Supporting Information), it is observed that a characteristic peak of Fe2p appears at about 710.4 eV and a characteristic peak of O1s appears at about 530.2 eV, which are attributed to the formation of Fe₂O₃ or Fe₃O₄. A characteristic peak of O1s also appears at about 531.9 eV, which is attributed to C-O and C=O.⁵⁰⁻⁵³ From these data, it can be inferred that oxide layers are formed on the surface of the friction pairs. Subsequently, the Ar ion sputtering technique was further used to obtain the in-depth characterization of the tribo-layer formed on the steel surfaces. On the top surface of the worn steel plate lubricated with Phe-3C₁₈ and the gallate ester oils

(Figure 8), the detected binding energy peak of Fe2p at about 706.7 eV increases gradually along with Ar ion sputtering, which means that Fe is exposed. Meanwhile, the detected binding energy peak of Fe2p at about 710.4 eV and the detected binding energy peaks at about 530.2 and 531.9 eV decrease along with Ar ion sputtering, which means the oxide layer decreases gradually. It is found that the binding energy peak shape and its change are very similar in all of the corresponding spectra, which are consistent with the results detected on the surface of a new polished steel plate. So it can be concluded that the oxide layer is not the main reason for the gallate ester oils and Phe-3C₁₈ to exhibit good lubricating properties. It is conjectured that the molecular structures of the gallate ester oils and Phe-3C₁₈ contain polar ester groups, which can make them easily adsorb on the metal surface. In addition, owing to the intermolecular stacking interaction among the aromatic rings, the lubricant molecules can be arranged more orderly and firmly between the friction pairs resulting in the formation of effective physical and/or chemical adsorption films on the sliding surfaces. These physical and/or chemical adsorption films play a key role in the friction-reducing and antiwear properties of the lubricating oils. However, these physical and/or chemical adsorption films were cleaned by ultrasonic waves before XPS testing.^{35,54} The same results are also found on the copper plate surface (Figures S1 and S2 and Table S5) and the aluminum plate surface (Figures S3 and S4 and Table S6 in the Supporting Information).

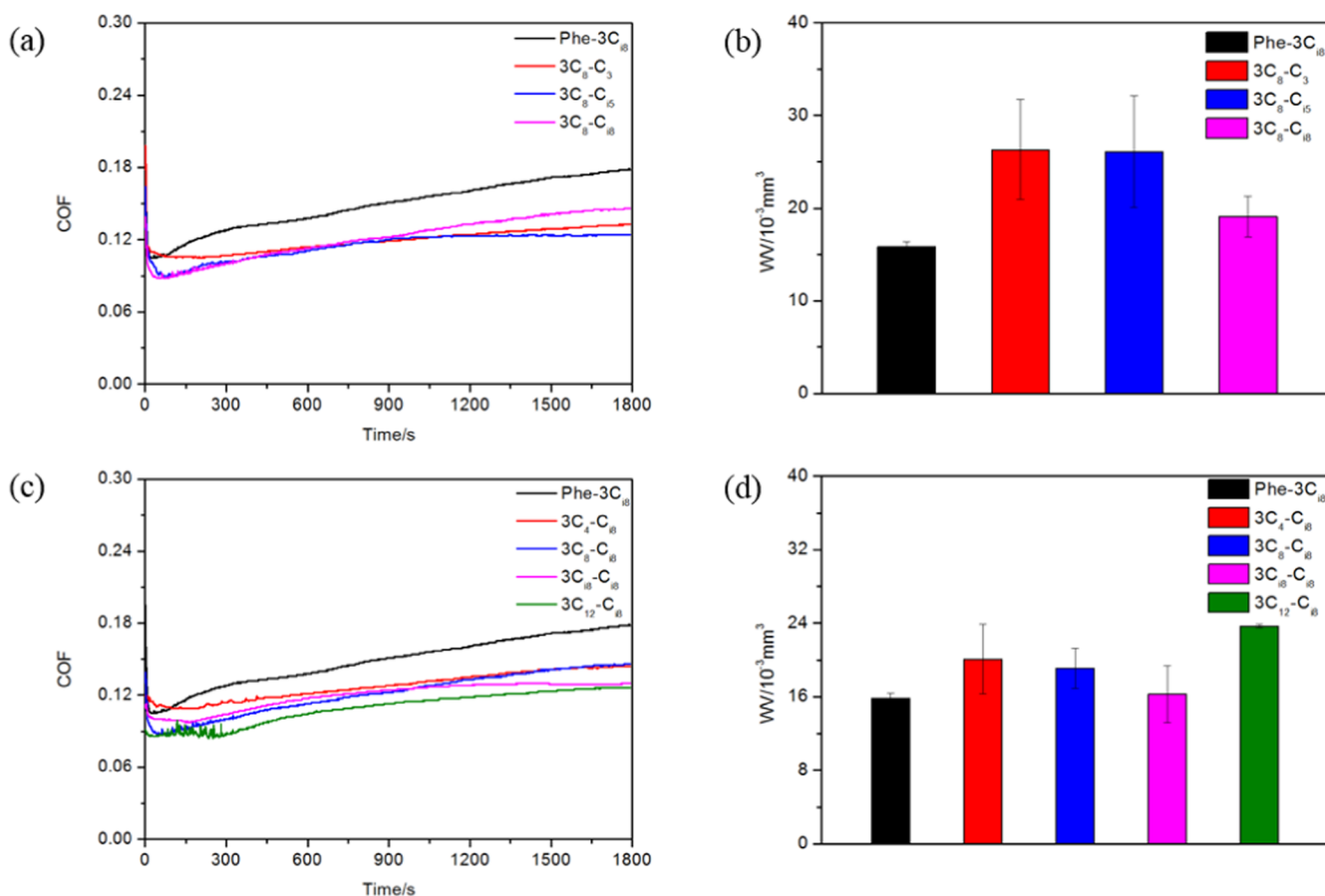


Figure 6. Evolution of COF/time (a, c) and WV (b, d) of lower aluminum plates lubricated with the gallate ester oils and Phe-3C₁₈ at RT.

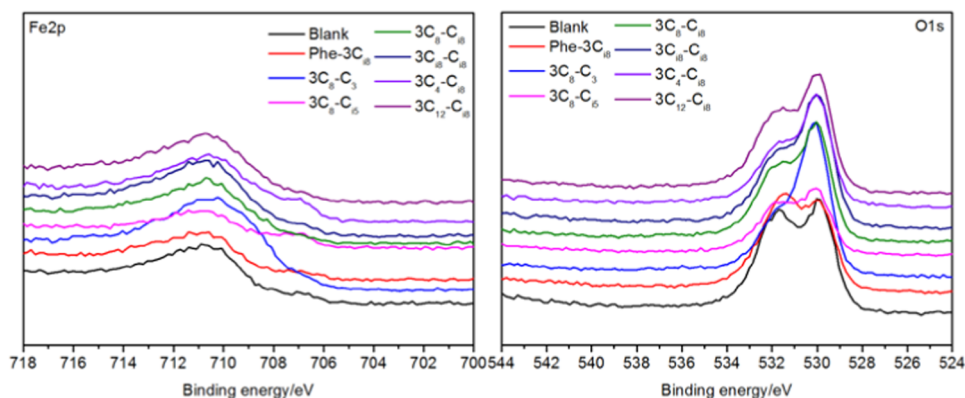


Figure 7. X-ray photoelectron spectroscopy (XPS) spectra of the wear spots lubricated with the samples on steel plates.

To confirm the above conjecture and further investigate the physical and/or chemical adsorption film formation on the friction surfaces, the contact resistances between the friction pairs were measured during the friction process. Figure 9 shows the contact resistances formed by the gallate ester oils and Phe-3C₁₈ on steel friction pairs. It can be seen that there are obvious resistances between friction pairs, indicating that adsorption or chemical reaction films do exist between the friction pairs. In general, it can also be observed that the gallate ester oils bearing shorter substituent carbon chains or having lower KVs (such as 3C₈-C₃ and 3C₄-C₁₈) exhibit lower contact resistances, indicating the formation of thinner films on the surfaces during the friction process. On the contrary, the gallate ester oils bearing longer substituent carbon chains or

having higher KVs (such as 3C₁₂-C₁₈ and 3C₁₈-C₁₈) exhibit higher contact resistances, indicating the formation of thicker films on the surfaces during friction process. These results further confirm that effective physical and/or chemical adsorption films are formed on the surfaces during the friction process, which play a major role in the tribological performance of the gallate ester oils.

2.6. Biodegradability. Biodegradability is an important characteristic for lubricating oils to satisfy the requirements of environmental protection. Biodegradability testing represents a way of measuring the risk posed by lubricating oils when they enter the environment. The biodegradation rates (BRs) of the gallate ester oils and the reference sample are illustrated in Figure 10. It could be found that the BRs of the gallate ester

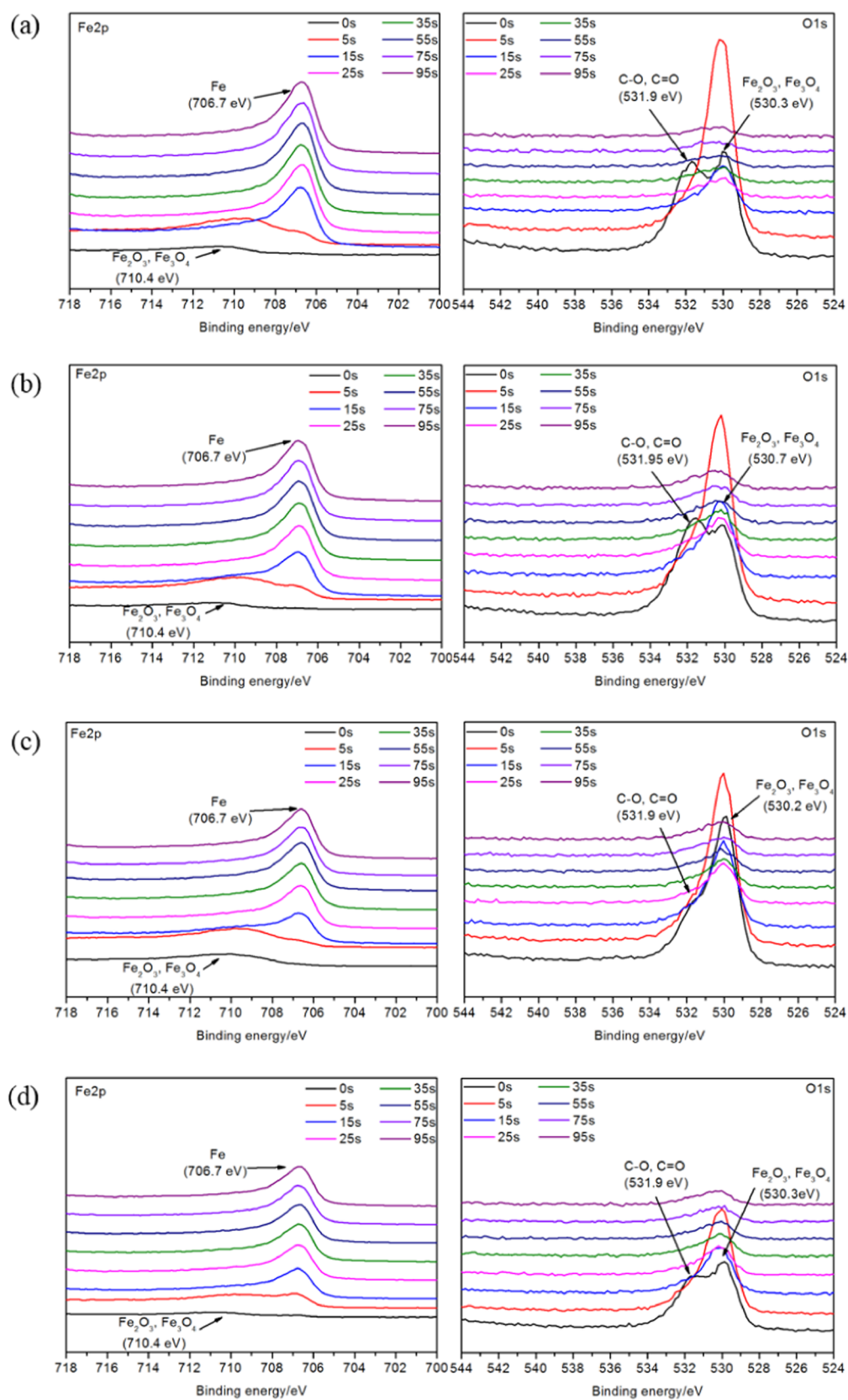


Figure 8. continued

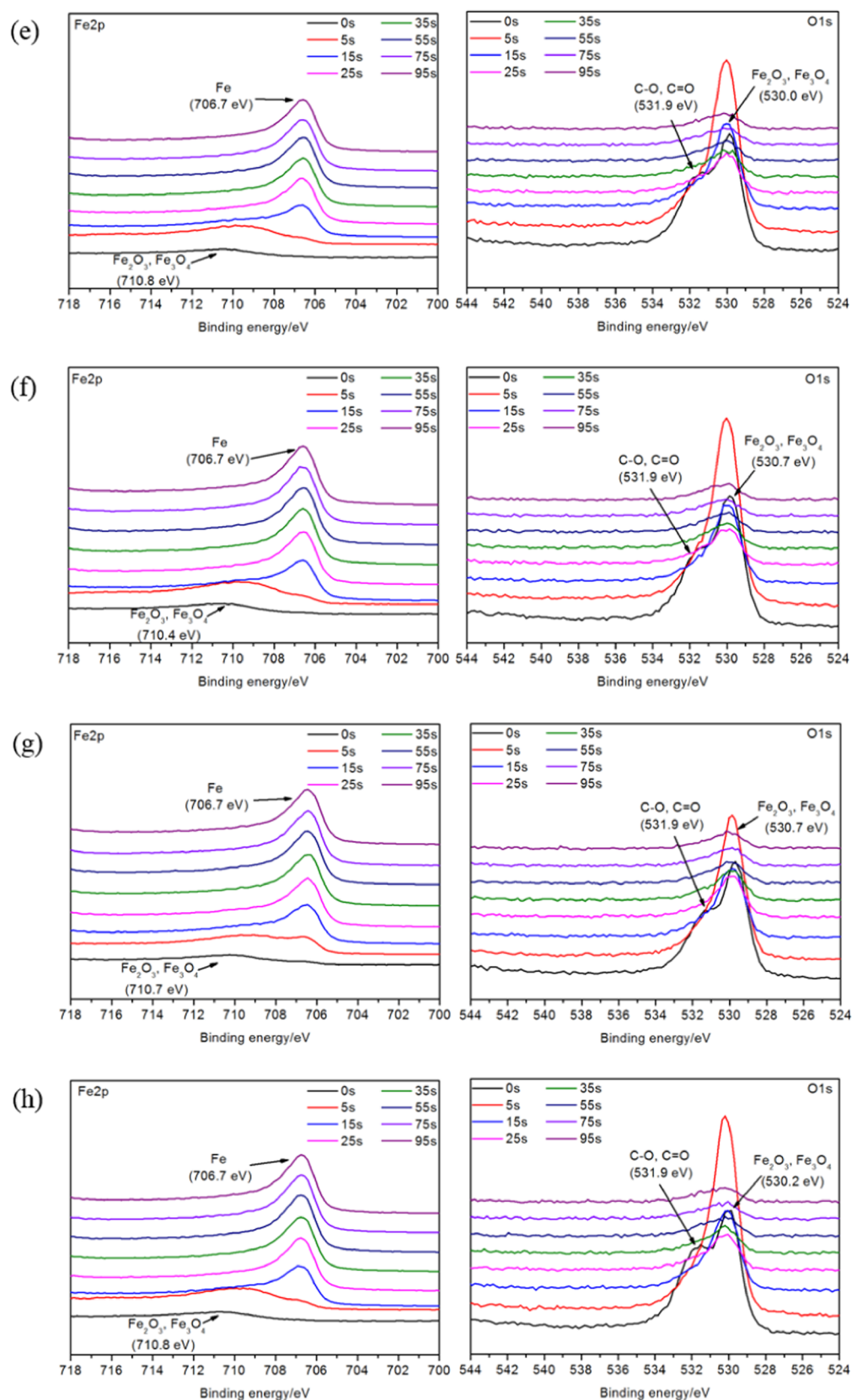


Figure 8. XPS spectra of the wear spots during Ar ion sputtering (a), lubricated with Phe- $3C_{18}$ (b), $3C_8-C_3$ (c), $3C_8-C_{15}$ (d), $3C_8-C_{18}$ (e), $3C_{18}-C_{18}$ (f), $3C_4-C_{18}$ (g), and $3C_{12}-C_{18}$ (h).

oils are higher than those of Phe- $3C_{18}$ but lower than those of sodium dodecyl sulfate (SDS). It is noteworthy that the ester groups on different positions of the aromatic ring have

different levels of impact on the BRs of the gallate ester oils. An obvious increase in the BR of the oil is found with the decrease of the length of the ester chain attached at 1-position of the

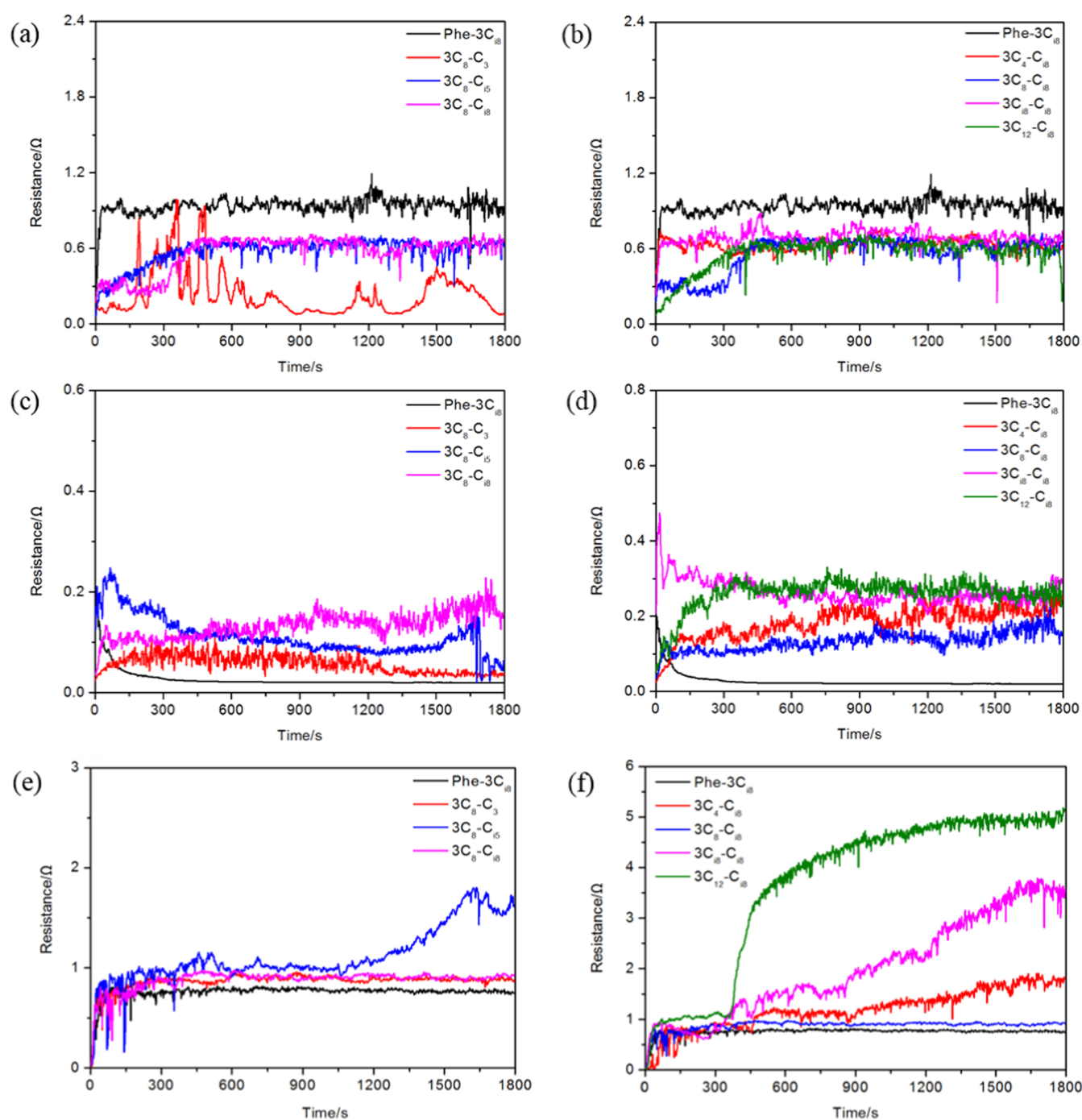


Figure 9. Contact resistances between the steel (a, b), copper (c, d) and aluminum (e, f) plates lubricated with the gallate ester oils and Phe-3C₁₈.

aromatic ring, e.g., BR (3C₈-C₃, 49%) > BR (3C₈-C₁₅, 43%) > BR (3C₈-C₁₈, 26%). The reason is that the longer alkyl chain causes higher lipophilicity of the ester oil, which can make the ester molecule to pass through the cell membrane easily and further destroy its internal structure.^{55–58} However, as the length of ester chains on 3,4,5-positions increases, no significant BR variation can be found. The reason for this phenomenon is still not clear. Anyway, this indicates how to access a high BR while having excellent tribological properties. It can be realized by properly increasing the length of ester chains attached at 3,4,5-positions of the aromatic ring but decreasing the length of the ester chain attached at 1-position.

3. CONCLUSIONS

In this work, new types of gallate ester oils were synthesized, their physicochemical and tribological properties were systematically evaluated.

- (1) Compared with the existing commercially available ester lubricants, the gallate esters oils have the advantage of raw material origin from fully renewable gallic and fatty acids.
- (2) The other prominent advantage of the gallate ester oils is their high biodegradability. The length of the ester chain attached at 1-position of the aromatic ring is proved to have a more obvious effect on the BR of the gallate ester

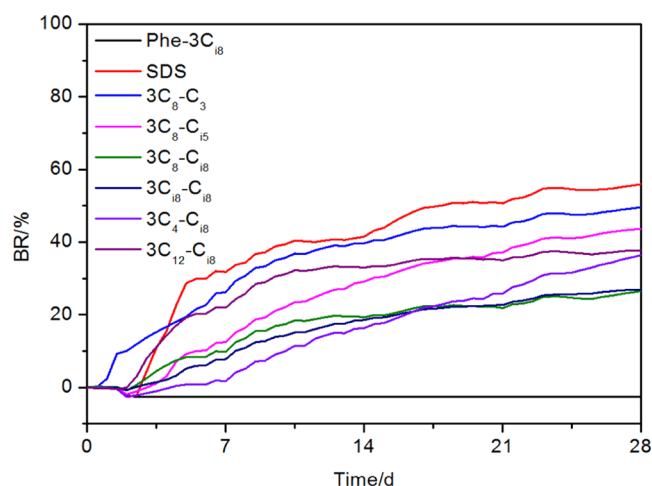


Figure 10. Biodegradation rates (BRs) of the gallate ester oils and Phe-3C₁₈.

oils than the length of the ester chains on 3,4,5-positions of the aromatic ring.

- (3) The viscosity-temperature properties and thermal and oxidative stabilities of the gallate ester oils are also proved to be better than those of Phe-3C₁₈. Their friction-reducing and antiwear properties are found to be comparable to those of Phe-3C₁₈.
- (4) The study of the lubrication mechanism shows that physical and/or chemical adsorption films formed by the gallate ester oils between the friction pairs are the key factors for them to obtain effective friction-reducing and antiwear properties.

The present work is conducive to further research on developing high-performance and environmentally friendly synthetic ester oils from naturally renewable resources.

4. EXPERIMENTAL SECTION

4.1. Materials. Gallic acid, propyl gallate, 2-ethyl-1-hexanol, and thionyl chloride were purchased from Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). *p*-Toluene sulfonic acid, butyric acid, octanoic acid, lauric acid, isooctanoic acid, isoamyl alcohol, and SDS were purchased from 3A Chemicals Co., Ltd. (Shanghai, China). Phe-3C₁₈ was obtained from J&K Scientific Ltd. (Beijing, China).

4.2. Experimental Section. **4.2.1. Synthesis of the Gallate Ester Oils (Synthesis of 3C₈-C₁₈ is Considered as an Example).** During the synthesis process, propyl gallate was

used as purchased without further purification. Isoamyl and isoocetyl gallate were prepared according to the reference reported method.⁵⁹ In the following step, octanoic acid (94 g, 0.65 mol) was added to a 2 L three-neck flask with a constant pressure droplet funnel, a reflux condenser and a thermometer. SOCl₂ was dropped into the flask within 2.5 h under RT. The solution was stirred at 75 °C for 2 h, heated to 90 °C and kept for 2 h. After cooling to RT, excess SOCl₂ was evaporated by vacuum distillation. Subsequently, isoocetyl gallate (28 g, 0.1 mol), K₂CO₃ (96 g, 0.7 mol) and acetone (200 mL) were added into the flask, and the mixture was stirred at RT for 10 h. After the reaction was complete (thin-layer chromatography detection), the mixture was filtered and dropped into a separating funnel. Deionized water was added for removing K₂CO₃ and some byproducts, and ethyl acetate was added to extract the crude product. The collected extract was washed with saturated NaCl and dried with anhydrous Na₂SO₄. The solvent was evaporated and the crude product was purified by column chromatography to give the final product (52.8 g, 80%) (Figure 11).

4.3. Measurements. 4.3.1. Structural Characterization.

The structures of the gallate ester oils were identified with ¹H NMR and ¹³C NMR spectra recorded on an Agilent 400 MHz nuclear magnetic resonance spectrometer (CDCl₃ was used as a solvent and tetramethylsilane was used as an internal standard). The molecular weight of the product was confirmed by high-resolution mass spectra (HRMS) data obtained on a Bruker Dalton micro TOF-Q II instrument.

4.3.2. *d*₂₀, KV, and VI. The KV and VI of the gallate ester oils and the reference sample (Phe-3C₁₈) were measured using an SVM3000 Stabinger viscometer (Anton Paar GmbH) following the ASTM D 7042-2016 method. Their VIs were automatically calculated. Meanwhile, the *d*₂₀ of the gallate ester oils and Phe-3C₁₈ were determined using the same instrument.

4.3.3. PP. The PPs of the gallate ester oils and Phe-3C₁₈ were measured on a PP apparatus (Lawler DR4-22L) following the ASTM D 97-09 method. To ensure the accuracy of the data, each sample was measured twice.

4.3.4. FP. The FPs of the gallate ester oils and Phe-3C₁₈ were tested on an FP tester (Stanhope-Seta 82000-0) following the ASTM D 3828-09 method. All of the measurements were carried in duplicate.

4.3.5. Oxidative Stability. The oxidative stabilities of the gallate ester oils and Phe-3C₁₈ were determined using a ROB tester (Stanhope-Seta 15200-5) following the ASTM D 2272-09 method. Fifty grams of ester oil, 5 mL of distilled water, and

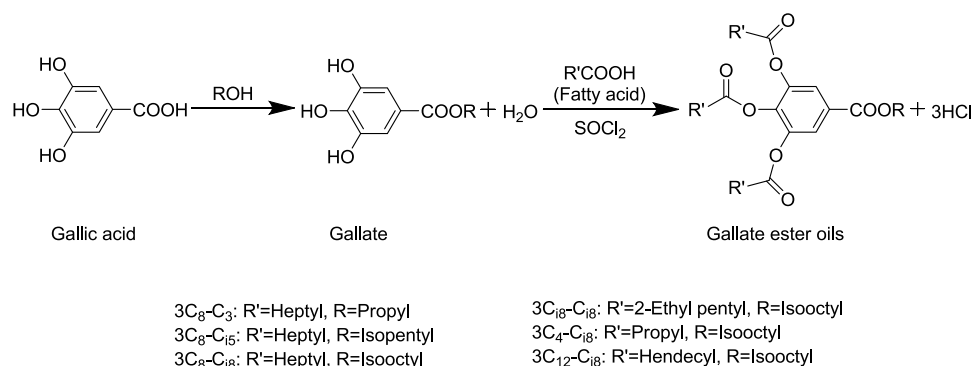


Figure 11. Synthesis of the gallate ester oils.

a copper coil were added to a vessel, which was put into a bomb. The bomb was sealed and charged to about 620 kPa pressure with O₂. Then, it was installed into the tester and kept rotating at 150 °C until the pressure in the bomb dropped by 175 kPa from the original value.

4.3.6. Thermal Stability. The thermal stabilities of the gallate ester oils and Phe-3C₁₈ were evaluated with a synchronous thermal analyzer (Netzsch STA 449 F3) in a nitrogen atmosphere following the SH/T 0731 method. The DTG curves, increasing and constant TG curves were monitored automatically on the analyzer.

4.3.7. Tribological Properties. The friction-reducing and antiwear performances of the gallate ester oils and Phe-3C₁₈ were measured with an oscillating reciprocating friction and wear tester (Optimol SRV-V) at RT. Tests were conducted on steel, copper, and aluminum tribo-pairs. In the tests, an AISI 52100 steel ball was used as the upper ball (diameter = 10 mm, hardness = 59–61 HRC). The lower stationary disks were made of steel (AISI 52100 steel, \varnothing 24 mm \times 7.9 mm, hardness = 59–61 HRC), copper alloy (ZQSn 663, hardness = 130–160 HV) and aluminum alloy (2024, hardness = 140–170 HV). Tests were performed at a frequency of 25 Hz, a stroke length of 1 mm and a load of 100 N for a duration of 30 min. After the tests, the WVs of the lower stationary disks were measured with a surface mapping microscope profile meter (Burker NPFLEX). An X-ray photoelectron spectrometer (Nexsa, Thermo Fisher) was used to perform elemental analysis and in-depth characterization of the tribo-layer formed on the steel, copper, and aluminum surfaces. The used vacuum was 10⁻⁷ Pa and the radiation source was a 150 W Al K α (single) anode.

4.3.8. Biodegradability. The biodegradability of the gallate ester oils and Phe-3C₁₈ were evaluated with an aerobic/anaerobic respirometer system (RSA PF-8000) following the GB/T 21801-2008 method. The activated sludge was taken from Baoji Tongji Water Co., Ltd. To remove the residual organic matter, the sludge needed to be aerated for 5–7 days. The sludge concentration was 3–5 g/L. The solution of the target compound (a theoretical oxygen demand (ThOD) of 50–100 mg/L) was added to the test vessel. SDS was used as positive controls in this experiment. The test lasted at least 28 days. Accordingly, a compound could be defined as “readily biodegradable” if its BR exceeded 60% within 28 days.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c00808>.

The Characterization data; average and standard error data; XPS spectra figures (the copper plate surface and the aluminum plate surface) and XPS deconvolution tables of the gallate ester oils and Phe-3C₁₈ (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Sastry, M. N. P.; Devi, K. D. Experimental investigations on performance of diesel engine with neem oil, cow ghee and NFA blends with atomized diesel. *Int. J. Eng. Res.* **2016**, *5*, 463–467.
- (2) Mondal, P.; Basu, M.; Balasubramanian, N. Direct use of vegetable oil and animal fat as alternative fuel in internal combustion engine. *Biofuels, Bioprod. Biorefin.* **2008**, *2*, 155–174.
- (3) Tandon, A.; Kumar, A.; Mondal, P.; Vijay, P.; Bhangale, U. D.; Tyagi, D. Tribological issues related to the use of biofuels: A new environmental challenge. *Br. J. Environ. Clim. Change* **2011**, *1*, 28–43.
- (4) Gallezot, P. Conversion of biomass to selected chemical products. *Chem. Soc. Rev.* **2012**, *41*, 1538–1558.
- (5) Haus, F.; German, G.; Junter, G. A. Primary biodegradability of mineral base oils in relation to their chemical and physical characteristics. *Chemosphere* **2001**, *45*, 983–990.
- (6) Nowak, P.; Kucharska, K.; Kaminski, M. A. The new test procedure for group-type composition of base oils of lubricating oils, especially emitted into the environment. *Energies* **2020**, *13*, No. 3772.
- (7) Abdullah, N. M. B.; Aluwi, N. S. M. M.; Park, H.; Kamal, N. A. Effect of toxicity concentration of waste lubricating oil (hazardous noxious substances) on aquatic life. *Int. J. Eng. Technol.* **2018**, *7*, 117–120.
- (8) Höfer, R.; Bigorra, J. A sustainable solution for industrial specialties applications. *Green Chem.* **2007**, *9*, 203–212.
- (9) Matthews, N. E.; Cizauskas, C. A.; Layton, D. S.; Stamford, L.; Shapira, P. Collaborating constructively for sustainable biotechnology. *Sci. Rep.* **2019**, *9*, No. 19033.
- (10) Bart, J. C. J.; Gucciardi, E.; Cavallaro, S. Renewable feedstocks for lubricant production. *Biolubricant* **2013**, 121–248.

- (11) Syahrullail, S.; Zubil, B. M.; Azwadi, C. S. N.; Ridzuan, M. J. M. Experimental evaluation of palm oil as lubricant in cold forward extrusion process. *Int. J. Mech. Sci.* **2011**, *53*, 549–555.
- (12) Borrero-López, A. M.; Santiago-Medina, F. J.; Valencia, C.; Eugenio, M. E.; Sampedro, M.; Franco, J. M. Valorization of kraft lignin as thickener in castor oil for lubricant applications. *J. Renewable Mater.* **2018**, *6*, 347–361.
- (13) Gorla, G.; Kour, S. M.; Padmaja, K. V.; Karuna, M. S. L.; Prasad, R. B. N. Novel acyl derivatives from karanja oil: Alternative renewable lubricant base stocks. *Ind. Eng. Chem. Res.* **2014**, *53*, 8685–8693.
- (14) Hajar, M.; Vahabzadeh, F. Artificial neural network modeling of biolubricant production using Novozym 435 and castor oil substrate. *Ind. Crops Prod.* **2014**, *52*, 430–438.
- (15) Adhvaryu, A.; Erhan, S. Z. Epoxidized soybean oil as a potential source of high-temperature lubricants. *Ind. Crops Prod.* **2002**, *15*, 247–254.
- (16) Lazzeri, L.; Mazzoncini, M.; Rossi, A.; Balducci, E.; Bartolini, G.; Giovannelli, L.; Pedriali, R.; Petroselli, R.; Patalano, G.; Agnoletti, G.; et al. Biolubricants for the textile and tannery industries as an alternative to conventional mineral oils: An application experience in the Tuscany province. *Ind. Crops Prod.* **2006**, *24*, 280–291.
- (17) Aziz, N. A. M.; Yunus, R.; Rashid, U.; Syam, A. M. Application of response surface methodology (RSM) for optimizing the palm-based pentaerythritol ester synthesis. *Ind. Crops Prod.* **2014**, *62*, 305–312.
- (18) Kleinaitė, E.; Jaska, V.; Tvaska, B.; Matijosyte, I. A cleaner approach for biolubricant production using biodiesel as a starting material. *J. Cleaner Prod.* **2014**, *75*, 40–44.
- (19) Fox, N. J.; Stachowiak, G. W. Vegetable oil-based lubricants—A review of oxidation. *Tribol. Int.* **2007**, *40*, 1035–1046.
- (20) Zainal, N. A.; Zulkifli, N. W. M.; Gulzar, M.; Masjuki, H. H. A review on the chemistry, production, and technological potential of bio-based lubricants. *Renewable Sustainable Energy Rev.* **2018**, *82*, 80–102.
- (21) Borugadda, V. B.; Goud, V. V. Improved thermo-oxidative stability of structurally modified waste cooking oil methyl esters for bio-lubricant application. *J. Cleaner Prod.* **2016**, *112*, 4515–4524.
- (22) Murry, P. R. S. *Principles of Organic Chemistry*; Heinemann Educational Books: London, 1987.
- (23) Salimon, J.; Salih, N.; Yousif, E. Improvement of pour point and oxidative stability of synthetic ester basestocks for biolubricant applications. *Arabian J. Chem.* **2012**, *5*, 193–200.
- (24) Brown, M.; Fotheringham, J. D.; Hoyes, T. J.; Mortier, R. M.; Orszulik, S. T.; Randles, S. J.; Stroud, P. M. Synthetic base fluids. *Chem. Technol. Lubr.* **1997**, *2*, 34–74.
- (25) Rizvi, S. Q. A. *A Comprehensive Review of Lubricant Chemistry, Technology, Selection, and Design*; ASTM International: Baltimore, MD, 2009.
- (26) Rudnick, L. R.; Bartz, W. J. Comparison of synthetics, mineral oils, and bio-based lubricant fluids. *Chem. Ind.* **2013**, *135*, 347–365.
- (27) Murphy, C. M.; Zisman, W. A. Structural guides for synthetic lubricant development. *Ind. Eng. Chem.* **1950**, *42*, 2415–2420.
- (28) White, D.; Podolak, K.; Kraus, G. A.; Sundararajan, S. Tribological analysis of a novel lubricant additive: Pyrone esters. *Wear* **2020**, *442–443*, No. 203115.
- (29) Wang, J.; Ren, S.; Yang, S. Study on PFPE lubricants and their tribological characteristics. *Lubr. Eng.* **2002**, 18–21.
- (30) Liu, W.; Xu, J.; Feng, D.; Wang, X. The research status and prospect of synthetic lubricating oils. *Tribology* **2013**, *33*, 91–104.
- (31) Hu, K.; Zhao, D.; Wu, G.; Ma, J. Polyesters derived from bio-based eugenol and 10-undecenoic acid: synthesis, characterization, and structure-property relationships. *RSC Adv.* **2015**, *5*, 85996–86005.
- (32) Kamalakar, K.; Manoj, G. N. V. T. S.; Prasad, R. B. N.; Karuna, M. S. L. Novel acyloxy derivatives of branched mono- and polyol esters of sal fat: multiviscosity grade lubricant base stocks. *J. Agric. Food. Chem.* **2014**, *62*, 11980–11987.
- (33) Fan, M.; Ai, J.; Hu, C.; Du, X.; Zhou, F.; Liu, W. Naphthoate based lubricating oil with high oxidation stability and lubricity. *Tribol. Int.* **2019**, *138*, 204–210.
- (34) Fan, M.; Ai, J.; Zhang, S.; Yang, C.; Du, X.; Wen, P.; Ye, X.; Zhou, F.; Liu, W. Lubricating properties of ester oil prepared from bio-based 2,5-furandicarboxylic acid. *Friction* **2020**, *8*, 360–369.
- (35) Fan, M.; Zhang, C.; Wen, P.; Sun, W.; Dong, R.; Yang, D.; Li, W.; Zhou, F.; Liu, W. High-performance lubricant base stocks from biorenewable gallic acid: Systematic study on their physicochemical and tribological properties. *Ind. Eng. Chem. Res.* **2017**, *56*, 9513–9523.
- (36) Tantratian, S.; Kaepfen, K. Shelf-life of shucked oyster in epigallocatechin-3-gallate with slightly acidic electrolyzed water washing under refrigeration temperature. *LWT* **2019**, *118*, No. 108733.
- (37) Balakrishnan, M.; Arab, G. E.; Kunbargi, O. B.; Gokhale, A. A.; Grippo, A. M.; Toste, F. D.; Bell, A. T. Production of renewable lubricants via self-condensation of methyl ketones. *Green Chem.* **2016**, *18*, 3577–3581.
- (38) Geethanjali, G.; Padmaja, K. V.; Prasad, R. B. N. Synthesis, characterization, and evaluation of castor oil based acylated derivatives as potential lubricant base stocks. *Ind. Eng. Chem. Res.* **2016**, *55*, 9109–9117.
- (39) Barnhill, W. C.; Qu, J.; Luo, H.; Meyer, H. M.; Ma, C.; Chi, M.; Papke, B. L. Phosphonium-organophosphate ionic liquids as lubricant additives: Effects of cation structure on physicochemical and tribological characteristics. *ACS Appl. Mater. Interfaces* **2014**, *6*, 22585–22593.
- (40) Sharma, R. V.; Somidi, A. K. R.; Dalai, A. K. Preparation and properties evaluation of biolubricants derived from canola oil and canola biodiesel. *J. Agric. Food. Chem.* **2015**, *63*, 3235–3242.
- (41) Biresaw, G.; Laszlo, J. A.; Evans, K. O.; Compton, D. L.; Bantchev, G. B. Synthesis and tribological investigation of lipoyl glycerides. *J. Agric. Food. Chem.* **2014**, *62*, 2233–2243.
- (42) Sammaiah, A.; Padmaja, K. V.; Prasad, R. B. N. Synthesis and evaluation of novel acyl derivatives from jatropa oil as potential lubricant basestocks. *J. Agric. Food. Chem.* **2014**, *62*, 4652–4660.
- (43) Gorla, G.; Kour, S. M.; Padmaja, K. V.; Karuna, M. S. L.; Prasad, R. B. N. Preparation and properties of lubricant base stocks from epoxidized karanja oil and its alkyl esters. *Ind. Eng. Chem. Res.* **2013**, *52*, 16598–16605.
- (44) Weng, L.; Liu, X.; Liang, Y.; Xue, Q. Effect of tetraalkylphosphonium based ionic liquids as lubricants on the tribological performance of a steel-on-steel system. *Tribol. Lett.* **2007**, *26*, 11–17.
- (45) Wang, T. L.; Hsieh, T. H. Effect of polyol structure and molecular weight on the thermal stability of segmented poly-(urethaneureas). *Polym. Degrad. Stab.* **1997**, *55*, 95–102.
- (46) Wang, Y. S.; Cao, J. W.; Li, H.; Li, P. Study of frictional and viscosity-temperature characteristics of a space lubricating oil No.4129 in rolling/sliding contact. *Acta Armamentarii* **2014**, *35*, 1515–1520.
- (47) Lin, B.; Zhu, H.; Tieu, A. K.; Hirayama, T.; Kosasih, B.; Novareza, O. Adsorbed film structure and tribological performance of aqueous copolymer lubricants with phosphate ester additive on Ti coated surface. *Wear* **2015**, *332–333*, 1262–1272.
- (48) Hamdan, S. H.; Chong, W. W. F.; Ng, J. H.; Chong, C. T.; Zhang, H. Nano-tribological characterisation of palm oil-based trimethylolpropane ester for application as boundary lubricant. *Tribol. Int.* **2018**, *127*, 1–9.
- (49) Kitakami, O.; Ichijo, M.; Daimon, H. Lubrication of surface oxidized Co-Cr thin films by phosphoric and phosphorous acid esters. *J. Magn. Mater.* **2001**, *235*, 179–182.
- (50) Zou, C.; Meng, Z.; Ji, W.; Liu, S.; Shen, Z.; Zhang, Y.; Jiang, N. Preparation of a fullerene [60]-iron oxide complex for the photo-fenton degradation of organic contaminants under visible-light irradiation. *Chin. J. Catal.* **2018**, *39*, 1051–1059.
- (51) Tauson, V. L.; Babkin, D. N.; Lustenberg, E. E.; Lipko, S. V.; Parkhomen, I. Y. Surface typoschemistry of hydrothermal pyrite:

Electron spectroscopic and scanning probe microscopic data. I. Synthetic pyrite. *Geochem. Int.* **2008**, *46*, 565–577.

(52) Cao, Z.; Qin, M.; Jia, B.; Gu, Y.; Chen, P.; Volinsky, A. A.; Qu, X. One pot solution combustion synthesis of highly mesoporous hematite for photocatalysis. *Ceram. Int.* **2015**, *41*, 2806–2812.

(53) Schultz, J.; Colmenares, C. A.; Naegele, J.; Spirlet, J. C. Surface studies of UFe_2 and evaluation of its catalytic properties with a 2H_2 :CO mixture. *Inorg. Chim. Acta* **1987**, *140*, 37–38.

(54) Minami, I.; Mori, S. Concept of molecular design towards additive technology for advanced lubricants. *Lubr. Sci.* **2007**, *19*, 127–149.

(55) Wu, S.; Li, F.; Zeng, L.; Wang, C.; Yang, Y.; Tan, Z. Assessment of the toxicity and biodegradation of amino acid-based ionic liquids. *RSC Adv.* **2019**, *9*, 10100–10108.

(56) Matzke, M.; Arning, J.; Ranke, J.; Jastorff, B.; Stolte, S. Design of Inherently Safer Ionic Liquids: Toxicology and Biodegradation. *Handbook of Green Chemistry*; John Wiley & Sons, Inc., 2010.

(57) Cornellias, A.; Perez, L.; Comelles, F.; et al. Self-aggregation and antimicrobial activity of imidazolium and pyridinium based ionic liquids in aqueous solution. *J. Colloid Interface Sci.* **2011**, *355*, 164–171.

(58) Liwarska-Bizukojc, E.; Maton, C.; Stevens, C. V.; Gendaszewska, D. Biodegradability and kinetics of the removal of new peralkylated imidazolium ionic liquids. *J. Chem. Technol. Biotechnol.* **2014**, *89*, 763–768.

(59) Chen, Q.; Gu, W. Research on synthesis of n-octyl gallate without water-carrying agent. *Chem. Ind. For. Prod.* **2010**, *30*, 57–60.