

Leaves Based Lubricant Additive Towards Improving Tribological Properties

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Abstract: Three kinds of crop leaf-surface waxes were extracted from wheat, corn and broomcorn leaves, respectively. The crop leaf-surface waxes as lubricant additives were added to synthetic ester and the friction and wear properties of prepared lubricants for steel-aluminum and steel-copper friction pair were investigated in detail. The scanning electron microscopy (SEM) and secondary ion mass spectrometry (SIMS) were employed to explore the friction mechanisms. The results show that crop leaf-surface waxes could successfully reduce the friction and wear of steel-aluminum and steel-copper sliding friction pairs as compared with pure synthetic ester. For example, when the concentration of wheat leaf-surface wax as additive was 2%, the COFs was decreased by 58%; the four additives can be ranked by the anti-wear capability as follows: Corn > Wheat > Glycerol > Broomcorn to steel-aluminum sliding friction pairs. The SIMS spectra of positive and negative ions on the worn surfaces have reduced the exposure of Al and increased short chain ions counts. The good friction reduction and anti-wear abilities are attributed to the adsorption or reaction films formed by leaf-surface wax on worn surface.

Keywords: Crop leaf-surface wax; green additive; synthetic ester; tribological property

1 Introduction

Lubricants are used mainly to reduce the friction and wear between two moving metallic surfaces in contact. They also facilitate other functions such as heat dissipation, corrosion control, cleanliness, providing seal at moving contact et al. [1]. In order to perform these functions, a lubricating formulation must have specific chemical and physical characteristics. The lubricant base oils obtained either from the conventional petroleum resources or synthetics do not have all these characteristics, therefore different additives are used to achieve the desired application specific characteristics [2]. Now due to depletion of petroleum reserves, increasing crude oil prices and legislation regarding environment protection, emphasis has been shifted to the biodegradable and environmentally friendly lubricant compositions [3,4]. Base oil from vegetable oil has emerged as an alternative in the last two decades [5]. Lawal etc. review of application of vegetable oil-based metalworking fluids in machining ferrous metals [6]. Panchal etc. review of methods of vegetable oil extraction [7]. However, pure vegetable oil cannot meet all the needs because of its poor anti-oxidation or short service life. Modifications to the base oil were carried out by researchers to eliminate these disadvantages [8-9]. Panchal et al modified the Karanja oil with kinds of alcohols and formed fatty acid esters, which performed better properties than pure Karanja oil in tribological test [8]. Also, additives are utilized in vegetable oils to enhance their tribological properties. Rani, Aravind and Talib et al. all found that additives are essential to make the vegetable oil more suitable to practical applications than pure oils [9-11]. For a completely biodegradable lube formulation, other constituents, such as additives and thickeners, should also be biodegradable along with base oil [12]. Dimitratos et al

studied different thickeners in lubricating grease, but both of them were degradable and non-toxic [13]. Vegetable oil can also be used as additives as reported by Shahabuddin et al. [14]. Necessary modifications or derivations sometimes are available to improve the properties of pure oils. Madankar et al. used derivatives from canoli oil as an additive in mineral oil and obtained good lubricity [15]. Saga et al reported good tribological properties of oils with celluloses, which are naturally generated in a lot of plants [16]. Singh et al. has two kinds of modified amino acid, cysteine schiff base ester, to be evaluated as multifunctional additive in polyol base oil for antioxidant, antifriction, antiwear and anticorrosion property [17]. All these plant-derived substances showed good or even excellent tribological properties.

The leaves of the most plants have a lot of leaf-surface wax, which could work as a protective screen to reduce the damages of outside radiation, damages and pollutions, etc. [18]. It has been reported that leaf-surface waxes are mainly composed of alcohols, esters, long-chain fatty acids, alkanes and so forth [19,20]. These degradable compounds of leaf surface wax may be employed as environmentally friendly additives to improve the tribological properties. Recently, a research extracted different leaf-surface waxes as additives and found that the leaf-surface waxes promoted the friction reduction and anti-wear properties of lubricating oil [21-23].

Corn, wheat and broomcorn are the staple food for human and are planted in the world. The cultivation of wheat has played an important role in sustaining humans. Together with barley, wheat constituted the principal grain stock that founded Neolithic agriculture, allowing the establishment of permanent human settlements; a major milestone in the development of civilisation as we know it [24]. Corn is very suitably planted in many relatively severe environmental, and thus is widely planted all over the world. China is an agricultural country, and broomcorn is common in North China because of its good dry and freezing tolerance. Considering the easiness of massively obtaining, in this work, the waxes extracted from the surface layer of these crops leaves were evaluated as lubricant additives in base oil. Ester oil possesses good viscosity-temperature characteristics, high viscosity index, low solidifying point, good low-temperature fluidity and oxidation resistance and so forth [25]. Therefore, the present research selected the synthetic ester (SE) with a biodegradation rate of almost 100% as base oil. The friction and wear properties of leaf surface wax in synthetic ester for steel-aluminum and steel-copper friction pair were investigated in detail. The possible lubrication mechanisms were also proposed based on the analysis of the worn surfaces.

2 Experiment

2.1 Experiment Material

Synthetic ester as base oil was provided by Zhongcheng Petrochemical Co., Ltd. and Tab. 1 gives the typical properties. Glycerol as contrastive additive and chloroform (analytically pure) as extractant were purchased from Sinopharm Chemical Reagent Co., Ltd. The testing machine used in this research is designed as a ball on block structure, with a steel ball (AISI 52100 steel ball, diameter 5 mm, hardness 710 Hv) pressed against aluminum block (Φ 24 mm, 7.9 mm, aluminum block: 2024 aluminum and hardness 160-170 Hv) and copper block (Φ 24 mm, 7.9 mm, bronze copper and hardness 125 Hv), respectively. All the surface roughness was about 0.05 μ m after polishing process.

Table 1: physical and chemical properties of synthetic ester

Item	Synthetic ester
Appearance	Faint yellow, transparent liquid
Kinematic $\frac{40^{\circ}\text{C}}{100^{\circ}\text{C}}$ viscosity	25 cSt 2 cSt
Viscosity index	136
Condensation point	<60°C
Open cup flash point	252°C

2.2 Extraction of Additives and Preparation of Lubricating Oil

Gathered as its color was still green, crop leaves were cleaned with pure water for several times and then air-dried. After that, clean leaves were soaked in chloroform solution for about 15-20 seconds (See literature 24 for details). The additives were obtained after the natural volatilization of the chloroform from the beaker.

To prepare lubricating oil, different concentrations including 0.5%, 1% and 2% (mass fraction) of extracted waxes was ultrasonically dispersed in SE. SE containing same concentration of glycerol was prepared to be used as contrastive lubricants as the same method.

2.3 Friction and Wear Test Surface Analysis

An MFT-R4000 reciprocating friction and wear tester with a steel ball contacting an aluminum or copper block was employed to investigate the tribological properties. All experiments were carried out at a frequency of 5 Hz, a strokes of 5 mm for 30 min. The testing load increases from 20 N to 40 N for steel-aluminum pair and from 40 N to 60 N for steel-copper pairs, respectively. Each lubricants were tested for 3 times to get more accurate value as the final data. The friction coefficients (COF) were automatically recorded by the computer which was connected with the testing machine. The wear widths were collected by measuring the wear width through an optical microscopy. After friction test, the surface morphology was observed through a scanning electron microscopy (SEM, EVO-18, ZEISS). Meanwhile, the components on the worn surface were detected by a Time of flight mass spectrometer (SIMS).

3 Results and Discussion

3.1 Tribological Properties for Steel-Aluminum Friction Pair

Fig. 1(a) shows the COFs and wear widths of SE containing different concentration of leaf-surface waxes and glycerol. According to the graphs, compared to the friction coefficients of the neat SE base oil, the addition of all additives improved the friction reduction ability to a certain extent, especially in the case of wheat leaf-surface wax, where the COFs decrease by 58% when the additive concentration was 2%. The wheat leaf-surface wax generally performed better than corn and broomcorn at any concentration (0.5%, 1%), although they performed close COFs at 2%. The reduction in COFs indicates leaf-surface wax could significantly enhance the friction reduction ability of SE.

Fig. 1(b) shows wear scar widths of SE base oil containing different concentration of additives. The widths were greatly reduced in the presence of additives. Among them, leaf-surface wax, especially the waxes from corn at the concentration of 2% has the best wear resistance property, while broomcorn leaf-surface wax and glycerol resisting abrasion by a certain degree. Compared comprehensively, the four additives can be ranked by the anti-wear capability as follows: Corn > Wheat > Glycerol > Broomcorn.

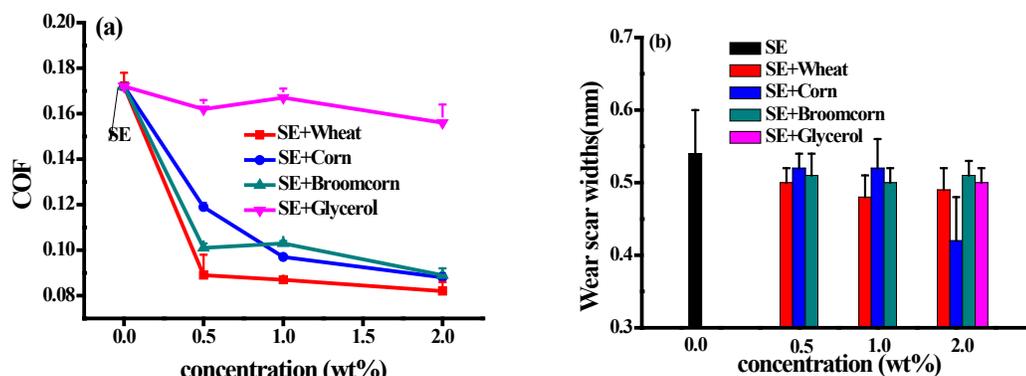


Figure 1: average COFs (a) and wear scar widths (b) for the lubricants for steel-aluminum pair at different additive concentration at 20 N, 5 Hz and RT

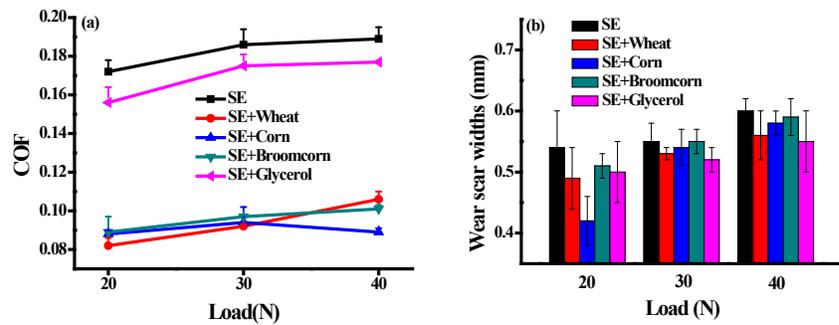


Figure 2: average COFs (a) and wear scar widths (b) for the lubricants for steel-aluminum pair at different loads at 5 Hz and RT

The tribological properties of SE containing 2% additives were further investigated under different loads, and Fig. 2 gives the results. As shown in Fig. 2(a), it is clearly illustrated that the improvement of different crop leaf-surface wax was close, by which the largest reduction in COF is up to 53%. By contrast, at the high load of 40 N, the improvement obtained using wheat and broomcron leaf-surface wax is not as good as corn leaf-surface wax, but the reduction in COF can still reach to 49%. As for glycerol, its COF is almost as high as that of SE. The results confirmed that leaf-surface wax as additive in SE could greatly improve the friction reduction ability of SE under different loads for steel-aluminum pair.

Fig. 2(b) gives the wear scar widths under different loads for the four additives. At the low load of 20 N, the crop leaf-surface wax all have some certain improvement effect on anti-wear ability. The corn leaf-surface wax performed good anti-wear ability. With the increasing load, the improvement of wear scar widths become poor, even worse than the glycerol.

3.2 Tribological Properties for Steel-Copper Friction Pair

Fig. 3(a) shows the tribological properties of SE containing different concentrations of additives for steel-copper friction pair under 40 N. As shown in Fig. 3(a), all the additives at all the concentration greatly enhance the friction reduction ability. Compared with the COFs of the pure SE base oil as 0.142, the addition of broomcorn leaf-surface wax improved the best, where the COF was decreased by 42% when the additive concentration was 2%. The broomcorn leaf-surface wax generally performed better than corn and wheat at any concentration.

Fig. 3(b) shows the wear scar widths for different lubricants. Compared with the base oil, crop leaf-surface wax effect has an obvious improvement on the anti-wear ability. The improvement effect achieved by wheat and corn leaf-surface wax is obvious better than the broomcorn leaf-surface wax, especially at the concentration of 1%.

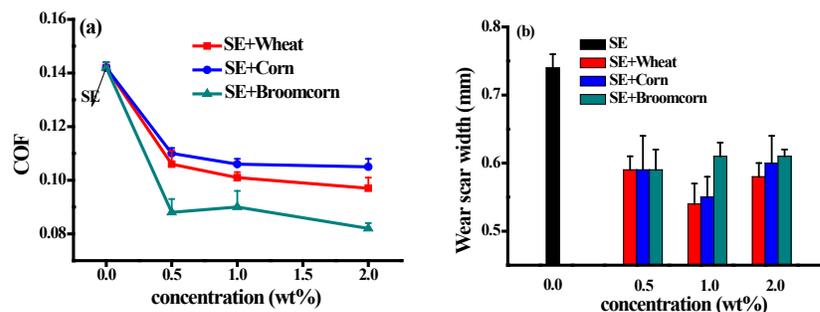


Figure 3: average COFs (a) and wear scar widths (b) for the lubricants for steel-copper pair at different additive concentration at 40 N, 5 Hz and RT

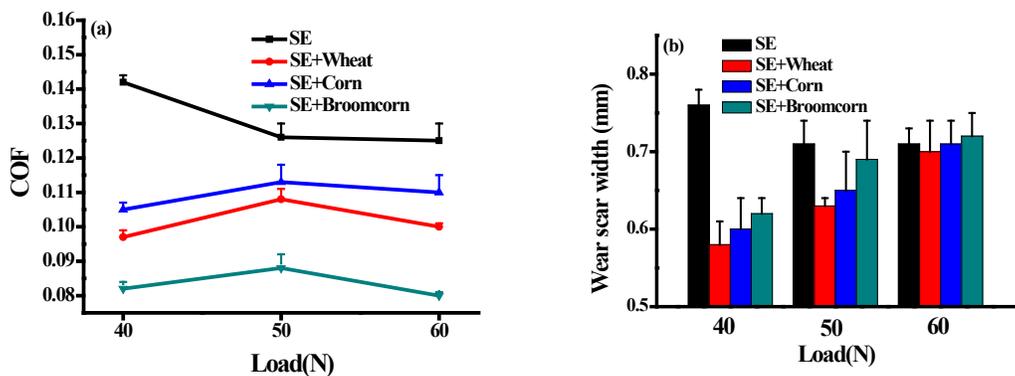


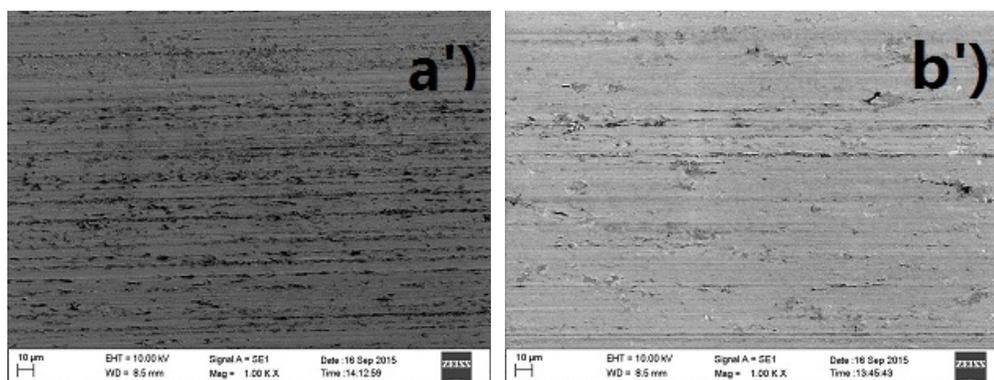
Figure 4: average COFs (a) and wear scar widths (b) for the lubricants for steel-copper pair at different loads at 5 Hz and RT

Fig. 4(a) shows the COF of SE containing 2% additives for steel-copper pair under different loads. Similar to the Fig. 3(a), three kinds of crop leaf-surface wax all exhibit lower COF than neat SE under different loads, and the friction reduction ability can be ranked as follows: broomcorn > wheat > corn.

Fig. 4(b) shows the wear scar widths with the increasing loads. Under the low load of 40 N, three kinds of crop leaf-surface wax have the similar effect on the anti-wear. When the load was increased to 50 N, the wheat and corn leaf-surface wax performed much lower wear scar widths than the broomcorn leaf-surface wax. But at the high load of 60 N, three kinds of crop leaf-surface wax did not significantly improve the anti-wear.

3.3 Morphological Analysis

Fig. 5 shows the SEM images of the worn surfaces on the aluminum blocks at 40 N and 5 Hz. Compared with the SE, the lubricants with leaf-surface waxes still show good lubricity, known from the shallower furrows and smoother worn surfaces. A lot of deep furrows and some corrosion pits can be observed in the image of worn surfaces lubricated by neat SE base oil. It can be concluded that after adding crop leaf-surface wax, anti-wear property of the lubricating oil is improved.



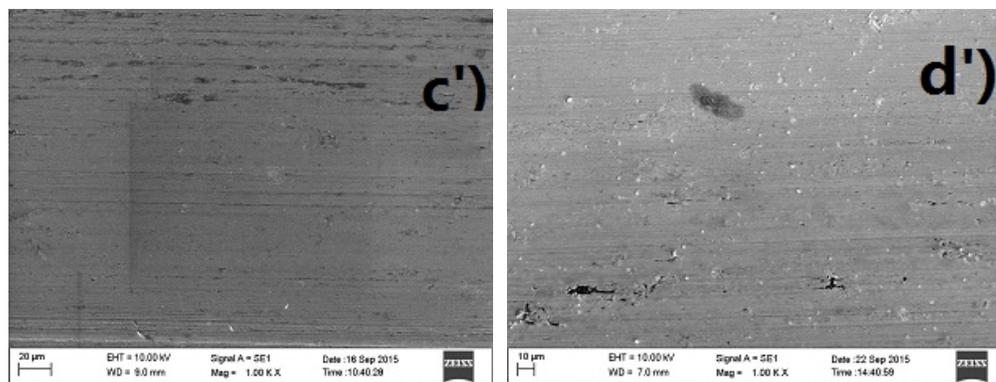


Figure 5: SEM images of the worn surfaces lubricated by (a') SE base oil, (b') broomcorn, (c') corn, and (d') wheat

3.4 Analysis of the Lubrication Mechanisms

In order to analyze the lubricating mechanism, SIMS was used to measure the amount of the ions on the worn surfaces [26,27]. The worn surface of wheat leaf-surface wax was chosen due to its best performances among all three kinds of waxes. Figs. 6(a)-6(b) and Figs. 7(a)-7(b) show the SIMS spectra of positive and negative ions on the worn surfaces lubricated by SE and SE containing wheat leaf-surface wax at room temperature. Fig. 6(a) displays a variety of $C_xH_y^+$ ions coming from pure SE, and the high intensity of Al^+ derived from the aluminum alloy block. It can be observed that the proportion of the Al^+ in Fig. 6(b) is obviously lower than that in Fig. 6(a), which may be due to the dense protective film generated on the worn surfaces reduced the exposure of Al. For the negative ions spectra of pure SE as shown in Fig. 7(a), short chain ions count greatly more than long chain ones, including the AlO_2^- . In Fig. 7(b), not only the long chain ions increased, but also the highest peak altered from C2 to C5, indicating the protective film generated by wheat leaf-surface wax was mainly composed of relatively long chain ions. Fig. 8 shows the chemical images of a selected area of the worn surfaces lubricated by SE and SE with wheat leaf-surface wax using the SIMS analysis at room temperature. Images of negative and positive ions are expressed for comparison. A brighter area means a higher concentration of the objective ions. The chemical images present a good correlation between positive and negative ions products on the worn surface, which can give a direct evidence for the formation of protective film generated by the negative and positive ions on the worn surfaces. The SIMS results show that the enhanced tribological properties of the SE containing wheat leaf-surface wax were dependent on the protective film generated by wheat leaf-surface wax during the friction process.

The tribological tests demonstrate that the crop leaf-surface waxes have some certain friction reduction and anti-wear abilities for steel/aluminum and steel/copper friction pairs. Based on the SEM and TOF-SIMS analysis, the lubrication can be explained by following aspects. During the process of friction, the rubbing surfaces may be in a state of carrying positive charge because of the emission of the low-energy electrons on the rubbing surfaces [22,28]. At the same time, the high temperature and applied load of the friction zone could promote the long-chain compounds to be broken into short chains which could be a state of carrying negative charge. Thus, the broken short-chain ions could adsorb on the rubbing surfaces to form a lubricating protective film [22,23]. The results shown in Figs. 6-8 may support this lubrication mechanisms. In addition to the physical adsorption film, the tribochemical reaction also occurred. In general, as the friction continues and the temperature rises, a tribochemical reaction film can be formed by the chemical interactions between crop leaf-surface wax and the fresh metal to enhance the friction reduction and anti-wear abilities. This lubrication mechanisms has been reported in our previous research [21]. In a word, based on the tribological data, SEM and SIMS analysis of the worn surfaces, it suggests that crop leaf-surface wax as additives in SE could form a protective lubricating film to improve the friction reduction and anti-wear abilities for steel/ aluminum and steel/copper friction pairs during the friction process.

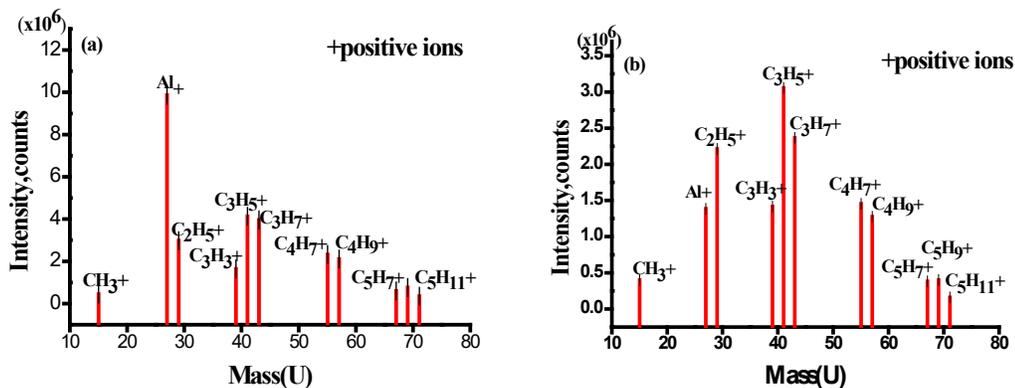


Figure 6: TOF-SIMS spectra of positive ions in the worn surfaces lubricated by (a) neat SE base oil and (b) SE with wheat leaf-surface wax at room temperature

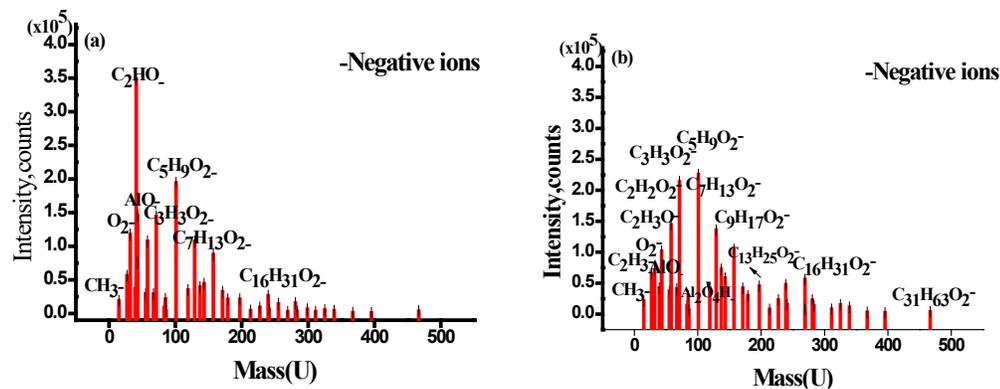
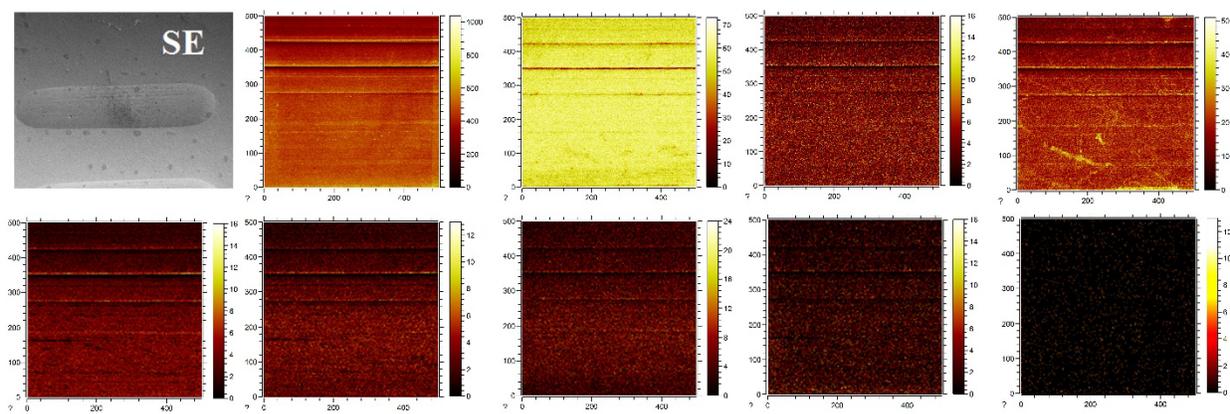


Figure 7: TOF-SIMS spectra of negative ions in the worn surfaces lubricated by (a) neat SE base oil and (b) SE with wheat leaf-surface wax at room temperature



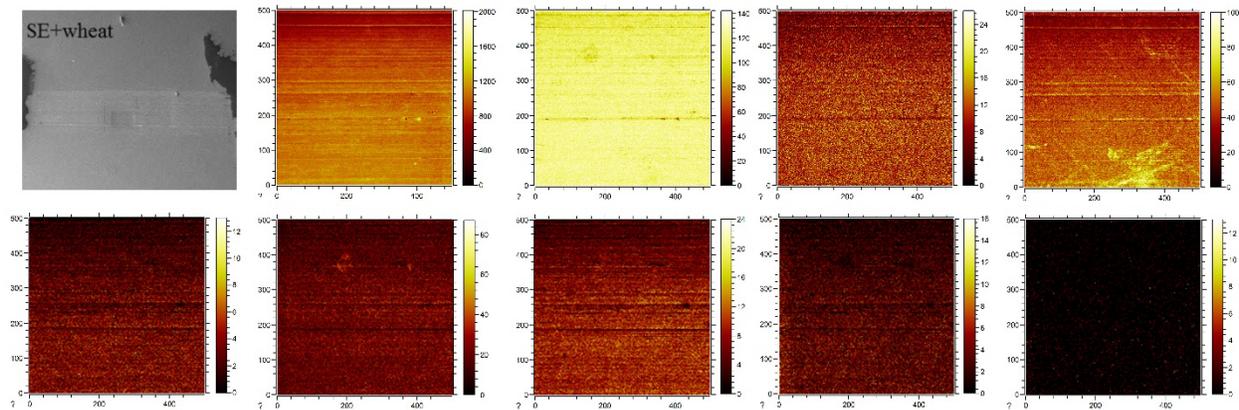


Figure 8: SIMS images of positive and negative ions from a selected area lubricated by the neat SE and SE with wheat leaf-surface wax at room temperature

4 Conclusion

Three kinds of crop leaf-surface waxes including wheat, corn and broomcorn were extracted and explored as environmentally friendly additives in synthetic ester for steel/aluminum and steel/copper friction pairs. The tribological results show that three kinds of crop leaf-surface waxes as additives could not only enhance the friction reduction ability, but also improve the wear resistance for the steel-aluminum pairs as well as steel-copper pairs under different loads. On the basis of analysis of the worn surfaces, such good tribological properties of crop leaf-surface waxes were attributed to the protective lubricating film on the worn surfaces during the friction process. Given the good degradability and tribological properties of crop leaf-surface waxes, it holds a great potential as additives for a range of applications.

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