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Influence of Microalgal Bio-Oil on the Lubrication Properties of Engine Oil

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Abstract — *In order to accelerate and expand the application of bio-energy, two kinds of microalgal bio-oils, prepared* via *co-liquefaction of Chlorella and Spirulina under sub- and supercritical ethanol conditions, were used as partial substitutes for the engine oil CD SAE 15W-40. The friction and wear behaviors of the oils were tested on a four-ball tribometer, referring to the ASTM D4172 standard conditions. The micro-morphology, profiles, roughness and chemical valences of typical elements on the rubbed surfaces were characterized by Scanning Electron Microscopy (SEM), surface profiler and X-ray Photoelectron Spectroscopy (XPS), respectively. The results showed that both of the bio-oils had good lubrication properties. The suitable weight content of the bio-oils in the engine oil was 10%. The lubrication properties of the Bio-Oil (BO_{sup}) prepared in supercritical ethanol were a little better than those of the Bio-Oil (BO_{sub}) prepared in subcritical ethanol. The lubricating mechanisms were ascribed to the combined actions of various lubricating films, including boundary lubrication, and deposited films and tribological chemical reaction films. The stronger tribological chemical effects of BO_{sup} from higher contents of N-containing compounds contributed to its better lubrication properties than those of BO_{sub}.*

Résumé — **Influence de bio-huiles issues d'algues sur les propriétés de lubrification d'une huile moteur** — Afin d'accélérer et d'étendre l'application des bioénergies, deux types de bio-huiles issues d'algues, préparées par co-liquéfaction de *Chlorella* et *Spirulina* dans de l'éthanol à l'état sous- et supercritiques, ont été utilisés comme substituts partiels de l'huile moteur CD SAE 15W-40. Les comportements d'usure et de frottement avec ces huiles ont été testés sur un tribomètre à quatre billes, en se référant aux conditions de la norme ASTM D4172. La micromorphologie, les profils et la rugosité de surface ainsi que les valences chimiques des éléments typiques sur les surfaces frottées ont été respectivement caractérisés par une microscopie à balayage électronique (SEM, *Scanning Electron Microscopy*), par un profilomètre de surface et par spectroscopie photo-électronique des rayons X (XPS, *X-ray Photoelectron Spectroscopy*). Les résultats ont montré que les bio-huiles avaient toutes deux de bonnes propriétés de lubrification. La teneur en poids adaptée des bio-huiles dans l'huile moteur était de 10 %. Les propriétés de lubrification de la bio-huile (BO_{sup}) préparée dans de l'éthanol supercritique ont été légèrement meilleures que celles de la bio-huile (BO_{sub}) préparée dans de l'éthanol sous-critique. Les mécanismes de lubrification ont été attribués aux actions combinées de différents films de lubrification (y compris un graissage à film d'huile, et de films de dépôts) et de films de réaction chimique tribologiques. Les effets tribo-chimiques plus forts de l'huile BO_{sup} contenant des teneurs supérieures en composés contenant de l'azote ont contribué à rendre ses propriétés de lubrification supérieures à celles de l'huile BO_{sub}.

INTRODUCTION

The lubrication properties of automotive fuels are important for vehicles. Active sulfur in the fuels is the main antiwear component; however, recently, owing to the demands for environmental protection, the sulfur content of automotive fuels is restricted to 10 ppm, which leads to the malignant wear of some key engine parts including the spray nozzle, injection pump and fuel filter, etc., since these parts are mainly lubricated by the fuels [1]. Therefore, the lubricity of a novel low-sulfur fuel is worth studying.

Bio-oil has been considered as one of the most promising alternative fuels for traditional Diesel oil. However, there are some obvious disadvantages of the bio-oil, including low heating value, high oxygen content, high viscosity and high corrosive properties, which prevent the application of the bio-oil in automotive engines [2, 3]. Thus, many researchers have focused on upgrading the bio-oil [4-8]. Sub- and supercritical technology is proved an effective way to solve these problems. Actually, because the bio-oil has low sulfur content, the lubrication properties of the bio-oil before and after upgrading are worthy of attention in particular. We previously studied the lubricity of a blend of bio-oil from rice husk and Diesel oil [9, 10]. The results showed that the lubricity of the fuel blend was better than that of the traditional Diesel fuel. However, the antiwear properties of the fuel blend were inferior to those of conventional Diesel fuel. As known, the raw material and the preparation process have a significant influence on the properties of the bio-oil. Compared with other biomass, microalgae have a higher photosynthetic rate, faster growth rate and higher yield. Bio-oil from microalgae has become a hot topic in biomass energy [11-13]. Unfortunately, to the best of our knowledge, the lubrication properties of microalgal bio-oil have not been reported.

In view of the fact that there are some nitrogen elements in the microalgal bio-oil [14], the cost of removal of N-containing components is high when using the bio-oil as fuel. Moreover, the viscosity of the bio-oil is high and nitrogen is an environmentally friendly antiwear component [15]. Therefore, here we used the bio-oil as a renewable partial substitute for the conventional engine lubricant oil. Two kinds of novel microalgal bio-oils from co-liquefaction of *Chlorella* and *Spirulina* were prepared under sub- and supercritical ethanol conditions. The basic components and tribological performances of the bio-oils were characterized, and the lubrication mechanisms are discussed in order to provide a scientific basis for expanding the application of the microalgal bio-oil.

1 EXPERIMENTAL

1.1 Materials

Two kinds of microalgae, *Chlorella* and *Spirulina*, were purchased from *Wudi Lv Qi Bioengineering Co. Ltd*. Anhydrous ethanol was purchased from *Hefei Medicines Pharmaceutical Co*. The CD SAE 15W-40 Diesel engine oil was a product of *China Petrifaction the Great Wall Lubricating Oil Co. Ltd*. All other reagents were analytically pure.

1.2 Preparation of the Microalgal Bio-Oils

The preparation process was carried out in an autoclave and the details and similar experiments are described in our previous work [16]. A typical test is described as follows. The algal powders, 2.8 g *Chlorella* and 4.2 g *Spirulina*, were mixed with 70 mL anhydrous ethanol and then placed inside the reactor. The reaction system was sealed and the upper air was replaced with 2.0 MPa nitrogen. The reactor was heated to a set temperature (230°C or 250°C) at a rate of 10°C/min, keeping the reactor at the set temperature for 30 min. After that, the reactor was cooled to room temperature and the exhaust valve was opened to release the pressure of the autoclave. The liquid products were separated with filtration, and the solvent was removed by vacuum distillation at 68°C and 0.03 MPa. The condensed dark brown viscous liquid was then collected as bio-oil. One of the bio-oils (BO_{sub}) was produced under subcritical ethanol conditions at 230°C and ~5 MPa. The other bio-oil (BO_{sup}) was prepared under supercritical ethanol conditions at 250°C and ~9 MPa.

1.3 Characterization of the Bio-Oils

The basic elements C, H, S and N were analyzed by a EuroEA3000 model elemental analyzer (*Leeman Ltd*, USA). The contents of O were calculated by difference. The chemical structures and component analysis were performed using a Spectrum 100 model Fourier Transform InfraRed spectrometer (FTIR, *PerkinElmer*, USA) within the range of 4 000-450 cm^{-1}.

1.4 Tribological Tests

The friction and wear tests were performed on a MQ-800 model four-ball tribometer (*Jinan Testing Machine Manufacturing Co. Ltd*, China), referring to the ASTM D4172 standard conditions (speed: 1 450 rpm, load: 392 ± 4 N, testing time: 30 min, temperature: 25 ± 2°C). As reported in our previous work [17], the lubricant oils were the conventional Diesel engine oil SAE CD 15W-40 and a blend of bio-oil and 15W-40. The weight percent of bio-oil in the blend oils was 5%, 10% and 15%, respectively. Each oil sample and test condition was repeated three times to estimate the deviations. The testing balls with 12.7 mm diameter are made of GCr15 steel (AISI 52100) with a hardness of 60 ± 1 HRC and the roughness (*Ra*) is less than 0.020 μm. The friction force of the testing process was recorded in real time and automatically converted into the friction coefficient.

1.5 Analysis of Wear Surface

After wear tests, the steel balls were washed in acetone. The Wear Scar Diameters (WSD) of the lower balls and wear scar width of upper balls were measured by a TPF-1 model optical microscope (*Olympus Co*., Japan). The profiles and roughness of worn surfaces of upper balls were analyzed along the vertical direction of friction by a HT-SURF10000 model surface roughness measurement system (*Harbin Precision Co*., China). The magnified surface topographies of worn surfaces of upper balls were observed by a JSM-6490LV SEM (*JEOL*, Japan). The contents and chemical valences of the typical elements on the rubbed surfaces of upper balls were characterized by an ESCALAB 250 model XPS (*Thermo Scientific*, USA).

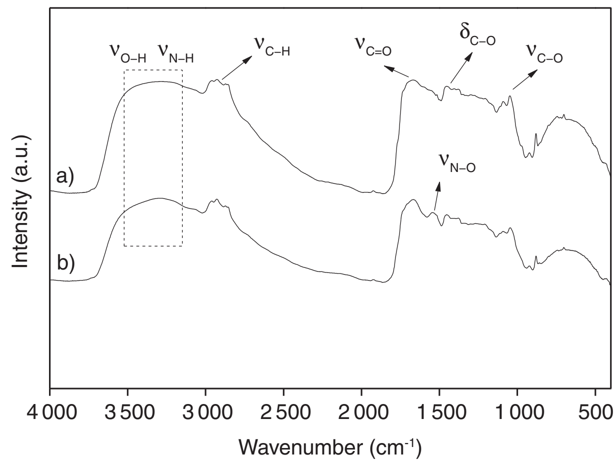

Figure 1

FTIR spectra of: a) BO_{sub}, b) BO_{sup}.

2 RESULTS AND DISCUSSION

2.1 Components of the Bio-Oils

The elemental contents of the bio-oils are shown in Table 1; it can be seen that the contents of S of the bio-oils were not detected because they were less than 0.01%. This result was consistent with a previous study [13] and proved their environmentally friendly properties. Besides C, H and O elements, there was 3.59% and 4.66% N in the two kinds of microalgal bio-oils, BO_{sub} and BO_{sup}, respectively, which came from the algal protein of the microalgae [13].

The detailed chemical structures and components were analyzed from the FTIR results (Fig. 1). As can be seen, the very similar figures show that the two kinds of bio-oils have very similar components. A wide peak at 3 200-3 600 cm^{-1} was ascribed to stretching vibration of O-H or N-H groups, which indicated the presence of alcohols, water or amide in the bio-oils. The absorption at 2 850-2 950 cm^{-1} was the stretching vibration of the C–H group of hydrocarbon [18]. The peaks at 1 650-1 800 cm^{-1} were the absorption of the C=O group of ketone, ester or acid. The peaks at about 1 100 cm^{-1} were the vibration of the C–O group of alcohol, ether or ester. The absorption at 1 400-1 480 cm^{-1} was ascribed to the formation vibration of the C–H group of hydrocarbon in BO_{sub}; however, the peak shift to the 1 500-1 550 cm^{-1} belonged to the stretching vibration of the N–O group in BO_{sup}. This indicated that there were more N-containing compounds in BO_{sup} than in BO_{sub}. This was also confirmed by elemental analysis (Tab. 1). From all the above analysis, it can be seen that the components of the microalgal bio-oil were similar to the results reported by other authors [12], who studied many complex compounds including alcohol, ether, ester, acid, ketone, hydrocarbon, N-containing chemicals, etc.

TABLE 1
Elemental contents of the bio-oils

Oils	C/wt%	H/wt%	N/wt%	O^a/wt%
BO_{sub}	57.58	7.44	3.59	31.39
BO_{sup}	59.09	8.49	4.66	27.76

[a] by difference.

2.2 Antifriction Properties of the Bio-Oils

The effect of the content of the bio-oils on the average friction coefficient is shown in Figure 2. The error bars in this figure indicate the deviation of the average friction coefficient in the three duplicate tests. It can be seen that the average friction coefficient decreased significantly with the addition of the bio-oils, which shows the excellent antifriction properties of the bio-oils. However, the decrease rate of the antifriction declined with the increase in the content of the bio-oils. Additionally, the effect of antifriction of BO_{sup} was a little better than that of BO_{sub}. This is mainly caused by a higher content of the N-containing compounds in BO_{sup}, since they can form an adsorbed film on the steel rubbing surface [19]. The integrity and strength of the lubrication film improved with the increase in the bio-oils, and thus the average friction coefficient decreased sharply. This decrease became slight when the rubbing surface had a saturated adsorption of the bio-oils, since continual increase in bio-oil had little effect on the integrity and strength of the adsorbed film after saturated adsorption [20].

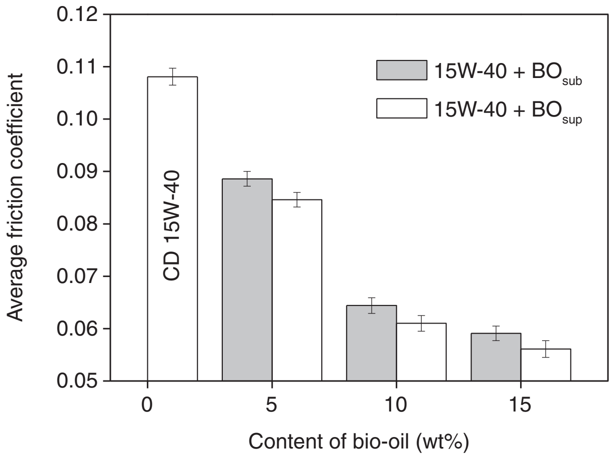

Figure 2

Effect of content of the bio-oils on the average friction coefficient.

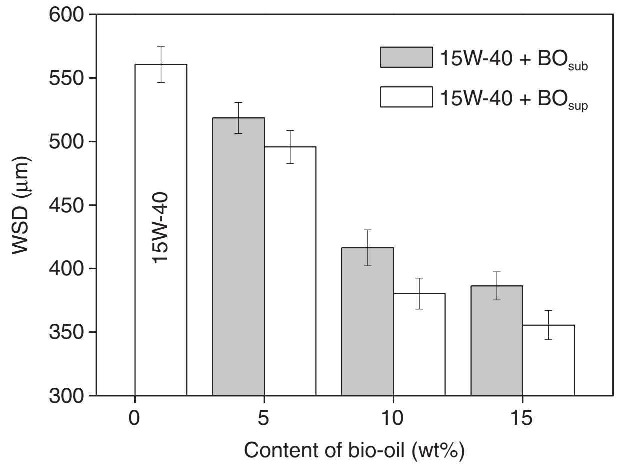

Figure 4

Effect of content of the bio-oils on the average WSD.

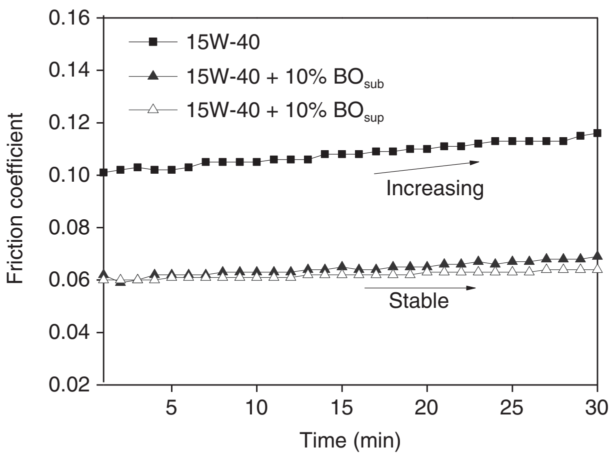

Figure 3

Variation of friction coefficient with time under different oils.

The variations of the real-time friction coefficient of Diesel engine oil and blend oils (with 10% bio-oil) with time are shown in Figure 3. It can be noted that with the increase in friction time, the friction coefficient of 15W-40 increased slightly. This phenomenon was also observed by Hu [21]. The friction coefficient decreased significantly after adding 10% bio-oil to the conventional engine oil, and the friction coefficient decreased by 40.4% and 42.7%, when using, respectively, 10% BO_{sub} and 10% BO_{sup} as additives in 15W-40. Moreover, compared with the pure 15W-40 without bio-oil, the friction coefficients of the blend oils are more stable. Therefore, the bio-oils can not only decrease the friction coefficient, but also contribute to maintaining the stability of lubrication.

The main reason for this was that, compared with the hydrocarbon chains of traditional lubricating oil such as CD SAE 15W-40, the various polar groups of the bio-oils can form stronger secondary bonds including hydrogen bonds on the friction surfaces [22], which play an important boundary lubrication protection role.

2.3 Antiwear Properties of the Bio-Oils

The effect of the content of the bio-oils on the average WSD of the lower balls is presented in Figure 4. The error bars in this figure denote the deviation of WSD of the stationary balls in the three duplicate tests. As can be seen from this figure, the WSD decreased with the increase in the content of the bio-oils; however, just like the antifriction properties, the decrease rate of the wear declined with the increase in the content of the bio-oils. Thus, the suitable weight content of the bio-oils in the engine oil was 10%. Additionally, the antiwear effect of BO_{sup} was a little better than that of BO_{sub}. This can be explained by the fact that there are more N-containing compounds in the BO_{sup} than in the BO_{sub} (Tab. 1), since nitrogen is an excellent antiwear component [15, 23, 24]. The chemical activities of N in friction are discussed with the XPS results in the following section.

2.4 Lubrication Mechanisms of the Bio-Oils

The optical micrographs of the wear scars on the steel balls lubricated with different oils are given in Figure 5. As shown

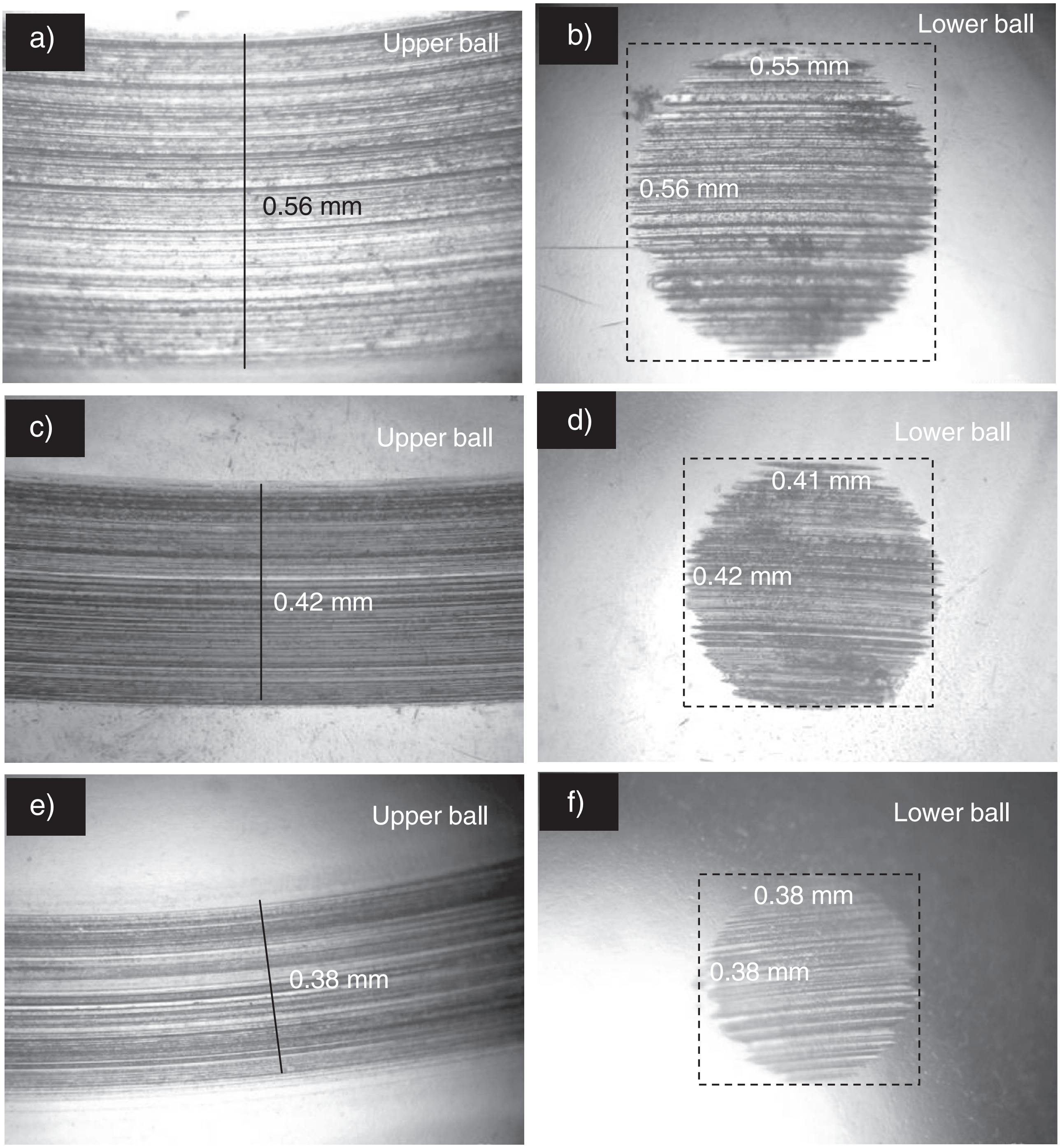

Figure 5

The optical micrographs of the wear scars on the steel balls lubricated with: a, b) 15W-40; c, d) 15W-40 + 10% BO_{sub}; e, f) 15W-40 + 10% BO_{sup}.

in this figure, there was a friction band on the upper balls and a round spot on the lower balls. The upper steel ball concerning 15W-40 presented the largest wear scar width, and both of the wear scars of upper balls and lower balls were decreased after adding the bio-oils to 15W-40. The widths of the wear scars of upper balls were consistent with those of the lower balls, and this figure also shows that plowing was the main pattern of wear [25, 26] on the steel balls.

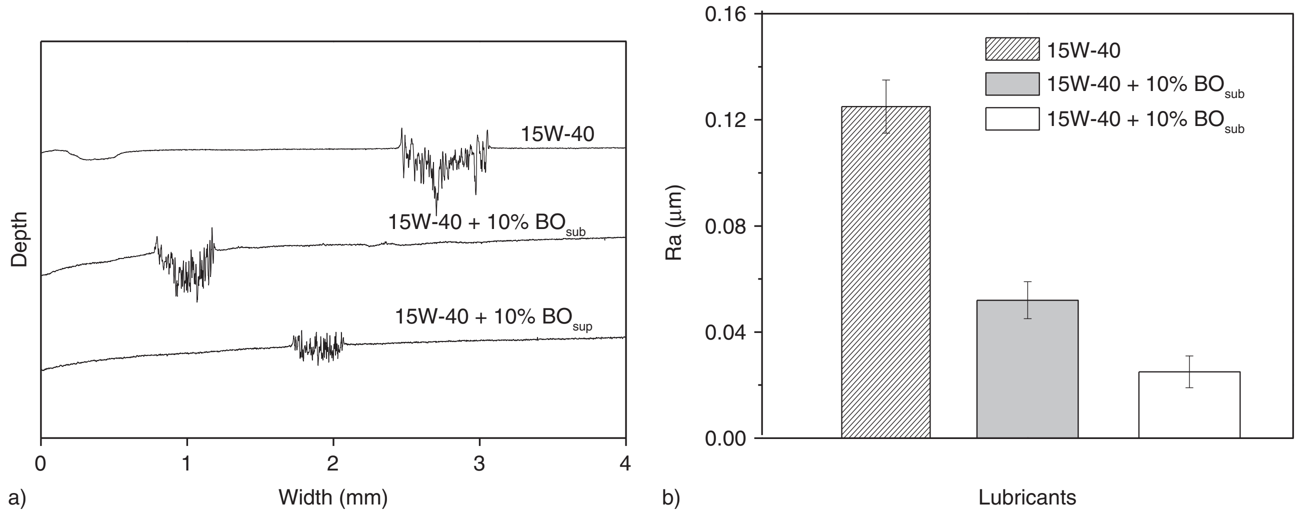

Figure 6

Worn surface profiles a) and surface roughness b) of the wear scars of upper balls lubricated with different oils.

Figure 6 provides the worn surface profiles (Fig. 6a) and surface roughness (Fig. 6b) of the wear scars of upper balls lubricated with different oils. The upper ball lubricated with 15W-40 with 10% BO_{sup} added presented the smallest wear scar width, depth and surface roughness (*Ra*). The wear scar widths, depths and surface roughness of the upper steel balls lubricated with blend oils (adding 10% BO_{sub} or BO_{sup}) were smaller than those lubricated with 15W-40. This figure also indicates that the bio-oils helped to protect the friction surface from severe wear. These results were consistent with the tribological behaviors of the lubricants.

In order to know the detailed wear information of the friction surfaces of the steel balls, the SEM images of the wear scars of upper balls lubricated with different oils are shown in Figure 7. The worn surface lubricated with 15W-40 had many obvious spalling pits, wide furrows and wear humps, and these were typical spalling wear on the contact area [25]. The spalling pits on the worn surface disappeared, and the furrows and humps became smaller when lubricated with 15W-40 with 10% BO_{sub} added, and furrow wear was the main manner of wear [27]. There were little light furrows and small humps on the worn surface lubricated with 15W-40 with 10% BO_{sup} added, which can be ascribed to the lubricating action of organic compounds in the bio-oils.

Figure 8 shows the XPS spectra of typical elements on the friction surfaces of the three upper balls lubricated with 15W-40, 15W-40 with 10% BO_{sub}, and 15W-40 with 10% BO_{sup}, respectively, at 1 450 rpm under 392 ± 4 N for 30 min. The peaks at ~724.6 eV and ~710.9 eV (Fig. 8a) were ascribed to the Fe2p1/2 and Fe2p3/2 of –Fe(III)–O–, respectively, the tribological oxidation production of steel [28]. This was also confirmed by the O1s peak at ~529.7 eV (Fig. 8b), which was caused by the O1s of Fe_2O_3 and produced by the tribological oxidation of Fe. There were also two peaks at ~719.9 eV and ~707 eV (Fig. 8a) at the surface lubricated with 15W-40, which belonged to the Fe2p1/2 and Fe2p3/2 of Fe(0) simpler substances and they might be detected from the spalling pits. This was consistent with the SEM analysis (Fig. 7a). However, these two peaks disappeared at the surface lubricated with 15W-40 with added bio-oils. This indicated that the oxidation films on the surface lubricated with 15W-40 were not complete, and they were improved by adding bio-oils to 15W-40. Moreover, both of the surfaces lubricated with 15W-40 with 10% BO_{sub} added and that lubricated with 15W-40 with 10% BO_{sup} added had a small peak at ~709.4 eV, which was attributed to the Fe2p of FeN [29]. This was also confirmed by the N1s peak at ~397.3 eV (Fig. 8c), which was caused by N1s of FeN because of the tribological chemical reaction of N-containing compounds in the bio-oils with the Fe of the steel balls. The peak at ~404.9 eV (Fig. 8c) was attributed to the nitrites in 15W-40, and it was covered by FeN after adding the bio-oils. Both Figures 8a and 8c show that the relative peak areas of FeN on the surface lubricated with 15W-40 with 10% BO_{sup} added were larger than that with 10% BO_{sub} lubricant. This suggested the chemical reaction film of the surface lubricated with 15W-40 with 10% BO_{sup} added was thicker than that of the surface lubricated with 15W-40 with 10% BO_{sub} added, which might be the main reason for the better lubricity of BO_{sup}.

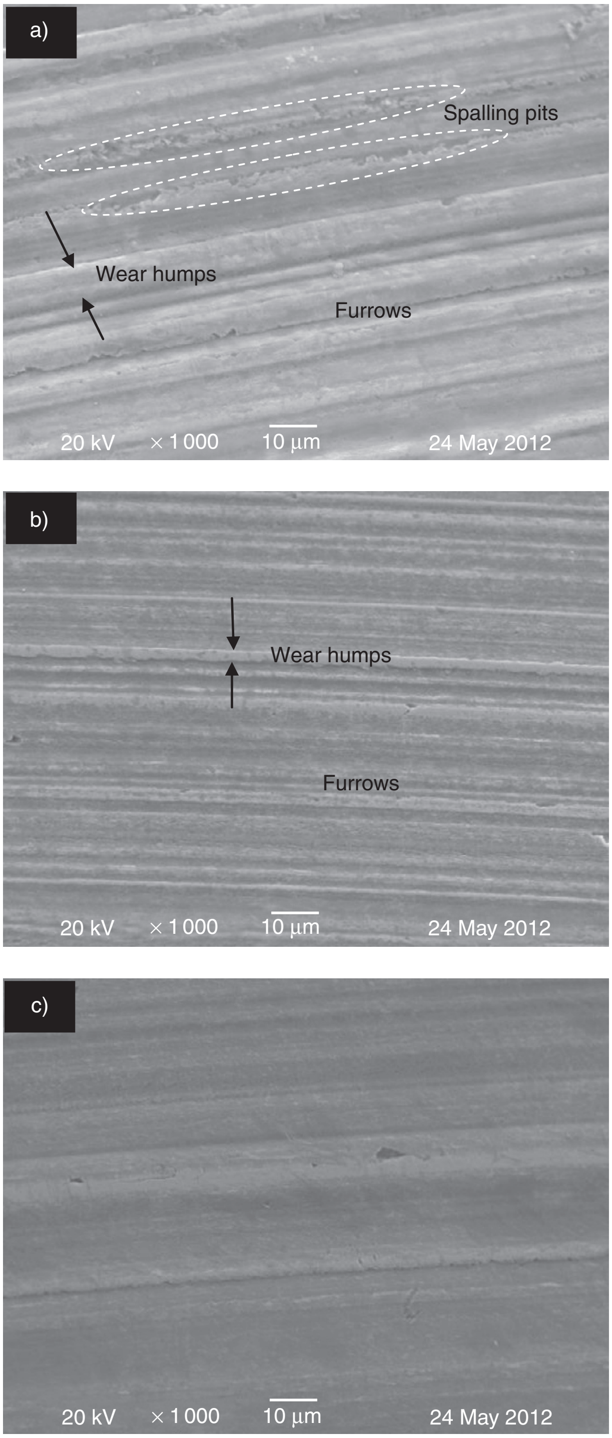

Figure 7

SEM images of the wear scars of upper balls lubricated with: a) 15W-40, b) 15W-40 + 10% BO_{sub}, c) 15W-40 + 10% BO_{sup}.

Additionally, the peaks at ~531.4 eV (Fig. 8b) were ascribed to the O1s of hydroxides and oxygen-containing compounds [30], which may come from the adsorption and tribological deposition of the chemicals in the lubricant oils. This is also proved by the peaks at ~285.3 eV and ~284.9 eV (Fig. 8d), which belonged to the C1s of C—O—C, (or C—O—H) and C—C (or C—H), respectively. From the relative peak area of O1s (Fig. 8b), it was found that the peaks at ~529.7 eV were enhanced significantly after adding the bio-oils to 15W-40, which indicated that the friction oxidation film improved after substituting 10% of the conventional engine oil with bio-oils. However, the effect of BO_{sub} was more obvious than that of BO_{sup}, because the friction oxidation film could prevent the surface from further severe wear. It seemed that this result conflicted with the lubricity of the two bio-oils. This might be interpreted by the fact that the strength and integrity of the chemical reaction film of FeN were better than that of Fe_2O_3 [31], and the protection role of FeN was the main lubrication mechanism of the BO_{sup}, whereas the protection role of the tribo-oxide film Fe_2O_3 was the main lubrication mechanism of the BO_{sub}.

The relative atomic contents of typical elements on worn surfaces lubricated with different oils are shown in Table 2. As can be noted, the surface lubricated with 15W-40 had the highest content of O, the second highest content of C and the lowest content of N. This showed that the lubricating action of 15W-40 was mainly attributed to the adsorption and tribological deposition of the carbonaceous compounds in the lubricant oils. The finite strength of the deposition film caused acute spalling wear of the surface lubricated with 15W-40. The surface lubricated with 15W-40 with 10% BO_{sub} added had the highest content of Fe and the second highest content of O, which came from the thickest friction oxidation film. This indicated that the friction oxidation film played an important lubricant role and prevented the surface from further severe wear after adding 10% BO_{sub} to 15W-40. The content of Fe on the surface lubricated with 15W-40 was higher than that on the surface lubricated with 15W-40 with 10% BO_{sup} added, and one reason might be that iron came from both of the Fe_2O_3 and Fe(0) simpler substances in the spalling pits. The surface lubricated with 15W-40 with 10% BO_{sup} added had the highest content of N, which came from the tribological reaction production of FeN. The excellent integrity and strength of the FeN film helped to maintain the good lubricating role of 15W-40 with 10% BO_{sup} added.

According to the above analysis, the lubrication mechanisms of the microalgal bio-oils were ascribed to the combined actions of multiple protective films. On one hand, the adsorption and deposited films composed of carbonaceous compounds (alcohol, ether, ester, acid, ketone, hydrocarbon, etc.) and O-containing polar groups in the bio-oils formed boundary lubrication [32]. On the other hand, the tribo-oxide film composed of Fe_2O_3 and frictional chemical reaction film containing FeN enhanced the integrity and strength of the lubrication films on the friction surface.

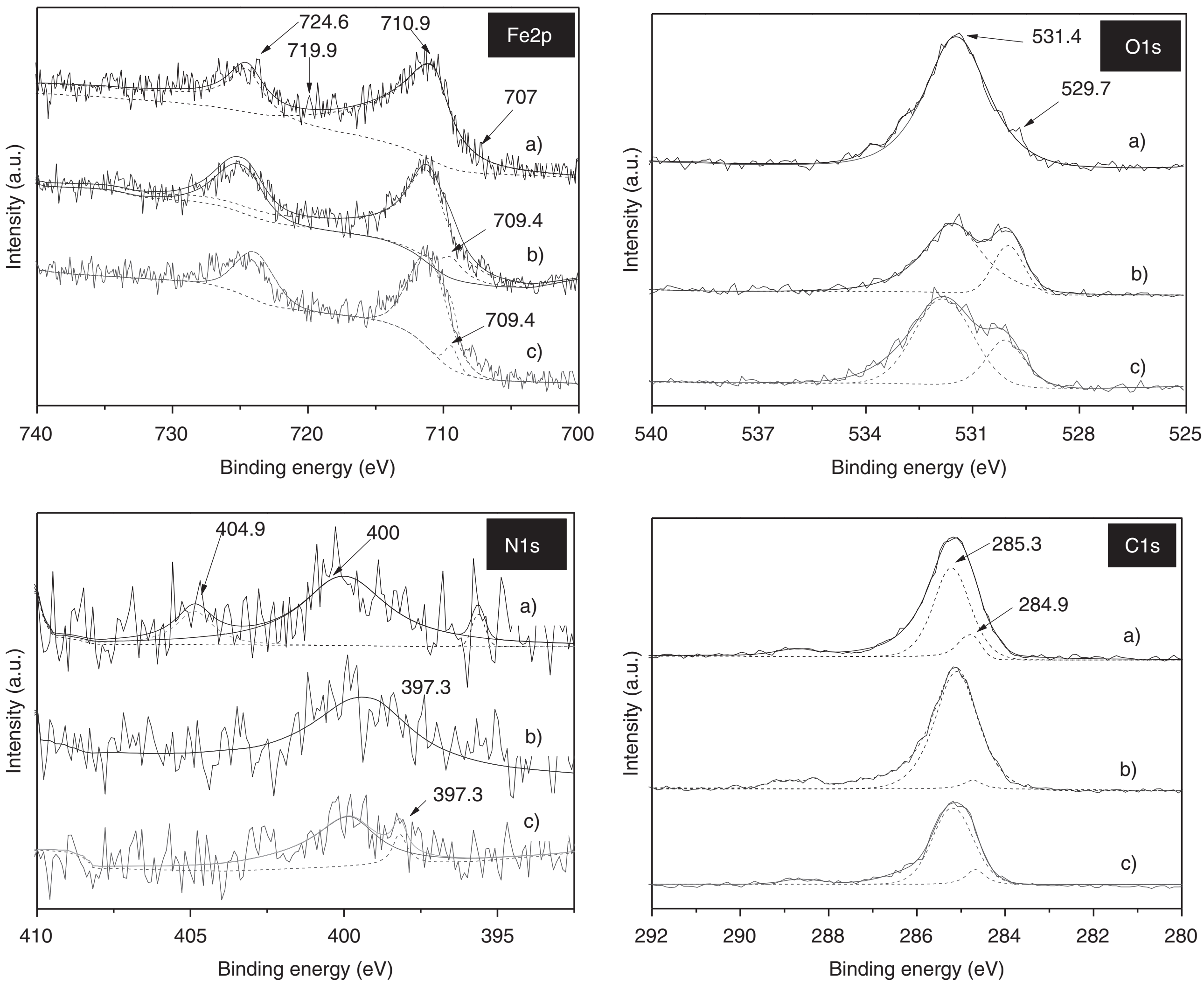

Figure 8

XPS spectra of typical elements on the friction surfaces lubricated with: a) 15W-40, b) 15W-40 + 10% BO_{sub}, c) 15W-40 + 10% BO_{sup}.

TABLE 2

Relative atomic content of typical elements on worn surfaces lubricated with different oils

Worn surfaces	Atom content (at.%)			
	Fe	O	C	N
Lubricated with 15W-40	6.6	31.5	59.9	2
Lubricated with 15W-40 + 10% BO_{sub}	12.2	31.3	53.3	3.2
Lubricated with 15W-40 + 10% BO_{sup}	4.8	29.4	62.1	3.7

BO_{sub} contributed to the integrity of the tribo-oxide film, while BO_{sup} helped to form a frictional chemical reaction film composed of FeN. The joint actions of these lubrication films resulted in the excellent antifriction and antiwear behaviors of the bio-oils.

CONCLUSIONS

The lubrication properties of the bio-oils (prepared *via* co-liquefaction of *Chlorella* and *Spirulina* under sub- and supercritical ethanol conditions) as a partial substitute for conventional engine oil SAE CD 15W-40 were studied using a four-ball tribometer. The influence of the contents of the bio-oils and their tribological behaviors were studied. The tribological mechanisms were discussed based on the comprehensive analysis of the worn surfaces. The following conclusions can be drawn from this study:

- both of the two kinds of microalgal bio-oils, BO_{sub} and BO_{sup}, had good lubrication properties. The average friction coefficient and wear loss of the steel balls decreased with the increase in the percent of the bio-oils in the engine oil. The frictional stability was enhanced by the introduction of bio-oils;
- the decrease rate of the antifriction and antiwear declined with the increase in the content of the bio-oils, and the optimized weight content of the bio-oils in 15W-40 was 10%. The lubrication properties of BO_{sup} were better than those of BO_{sub};
- the lubrication mechanisms were ascribed to the combined actions of multiple lubrication films including boundary lubrication, and deposited films and tribological chemical reaction films from 15W-40 as the base oil and the bio-oils as additives. The stronger tribological chemical effects of BO_{sup} came from its higher contents of N-containing compounds, in accordance with its better lubrication properties.

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