Utilization of biodiesel soot particles as additives for improved aqueous lubrication

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Abstract. Biodiesel soot particles (BSPs) and first heat-treated and then acid-treated BSPs (T-BSPs) were employed as lubricant additives for GCr15 steel/316 austenitic stainless steel contacts in aqueous media. Their tribological performances and mechanisms were tested. The result shows that T-BSPs exhibited better lubricating performances than BSPs in aqueous media. Moreover, it is proved that both BSPs and T-BSPs could enter the friction surfaces and prevent the direct steel–steel contact. In addition, T-BSPs exhibited better dispersion in water, which aided uniform adsorption on the friction surfaces, resulting in better friction-reducing and antiwear performances.

1. Introduction
With rapid economic development and the gradual depletion of fossil fuels, research on renewable energy has received considerable attention. Biodiesel is a topic of great interest in this field. Animal and vegetable oils, which are abundant worldwide, are the source of biodiesel. These substances can be converted into liquid fuels by transesterification. Biodiesel is preferable over petroleum diesel as it is environmentally friendly, results in low pollution emissions, and exhibits good combustion performance and biodegradability [1]. Therefore, the conversion of animal and vegetable oils into biodiesel is considered to be one of the most promising approaches for energy conversion.

In general, incomplete combustion of any fuel in engines, including biodiesel, leads to the generation of soot [2]. The soot exhausted from engines not only pollutes the environment, but also adversely affects human health, so the problem of soot needs to be addressed. Meanwhile, carbon nanomaterials such as graphene, nanodiamonds, and carbon nanotubes are widely used as lubricant additives to improve the antiwear and friction-reducing properties of lubricants [3]. Soot too is a carbonaceous material. Low content of diesel soot could effectively improve the tribological behaviors of polyalphaolefin (PAO4) oil [4]. Therefore, soot has great potential for use as a lubricant additive to enhance the tribological properties of the lubricant. With the recent surge in research on biodiesel, biodiesel soot recycling and utilization demands attention. In this paper, we present the tribological performances of biodiesel soot particles (BSPs) and first heat-treated and then acid-treated BSPs (T-BSPs) additives in aqueous media. Furthermore, the tribological mechanism of BSPs and T-BSPs in water is proposed. This work aims to provide a reference for the reuse of biodiesel soot as a new lubricant additive.
2. Experiment

2.1. Materials
Ultrapure water was obtained using a UPT-11-10T water purification system (Sichuan Ulupure Super Pure Technology Co., Ltd.). Concentrated nitric acid (68%, Analytical reagent) was provided by Sinopharm Chemical Reagent Co., Ltd. The BSPs used in this work were collected using a self-made soot-capturing device \[5\]. The preparation process of T-BSPs is as follows: first, BSPs were treated under air flow (40 mL/min) at 500°C for 1 h. They were then treated with concentrated nitric acid at 80°C for 15 h. Finally, the mixture was washed with ultrapure water and dried at 120°C for 15 h.

2.2. Analytical methods
The tribo-tests were performed with a ball-on-disc reciprocating tribometer (CFT-I, Lanzhou Zhongke Kaihua Technology Development Co. Ltd.). The ball samples (GCr15 steel, hardness 760-840 HV) and disc samples (316 austenitic stainless steel, hardness 200 HV) were used as friction pairs. The morphologies of BSPs and T-BSPs were obtained using field-emission transmission electron microscopy (FETEM, JEM-2100F, JEOL). The chemical states of BSPs and T-BSPs were obtained via X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi Thermo). The optical images and profile curves of friction surfaces on the disks were obtained via three-dimensional laser scanning microscopy (VK-X100, Keyence). The Raman spectra of friction surfaces were obtained using a Raman spectroscopy (LabRAM HR Evolution, Horiba Jobin Yvon).

3. Results and discussion

3.1. Characterization of BSPs and T-BSPs
Figure 1a and 1b show that both BSPs and T-BSPs comprise of nearly spherical primary particles, and agglomerates of BSPs or T-BSPs have chain-like structures. The samples of 0.3 wt% BSPs and 0.3 wt% T-BSPs in water were ultrasonically treated for 1 h, and then digital images were immediately obtained. Figure 1c shows that most of BSPs dispersed in water and the remaining BSPs were attached to the tube walls. However, all T-BSPs were dispersed in the aqueous media. These images indicate that compared to BSPs, T-BSPs disperse better in water. The spectra of BSPs and T-BSPs (Figure 1d and 1f) have peaks at 284.8 eV and 286.9–287.0 eV, which are attributed to C–C and C–O, respectively. In addition, the spectra of T-BSPs has a peak at 288.6 eV, corresponding to C=O. This indicates that new oxygenated groups are formed on the surface of T-BSPs subsequent to the heat and acid treatment. For O1s of BSPs and T-BSPs (Figure 1e and 1g), the curves can be divided into two regions with peaks at 531.5–531.8 eV and 533.0–534.0 eV, which are indexed to (C–O–C, C=O) and C–OH, respectively. Additionally, for BSPs and T-BSPs, atom content of O(C–OH) was 5.62% and 16.11%, respectively, and that of O(C–O–C, C=O) was 2.50% and 9.74%, respectively. The results showed that the amount of (C–O–C, C=O) and C–OH in the T-BSPs is higher than in the BSPs. These results also imply that T-BSPs are more hydrophilic than BSPs. Therefore, as compared with BSPs, T-BSPs can be easily dispersed in aqueous media.
3.2. Tribological performances of BSPs and T-BSPs in aqueous media

Figure 2a and 2b shows that when BSPs and T-BSPs were used as additives in aqueous media, the friction coefficient and wear volumes decreased. Moreover, the friction coefficient and wear volumes of water containing BSPs were larger than those of water containing T-BSPs. This reveals that though both additives have lubricating effects, T-BSPs have better friction reducing-and antiwear performances in aqueous media. As shown in Figure 2c and 2d, the friction coefficient decreased with the increasing BSPs content up to 0.3% and it then increased. The wear volumes of water containing BSPs have similar tendencies. The friction coefficient of water with different BSPs contents as additive is lower than that of water itself. When BSP content is lower than 0.6%, the wear volumes of water with BSPs is lower than that of water alone. However, when the BSP content is 0.9%, the wear volumes of water with BSPs are higher than that of water alone. This implies that BSPs improve the friction reduction property and wear resistance of water. Moreover, under high content of BSPs, the aggregation of BSPs leads to an increase in the wears volumes [6]. In case of T-BSPs, the friction coefficient and wear volumes decreased with an increase in the T-BSP content from 0% to 0.3%, and then, they slightly increased when the content increased from 0.3% to 0.9%. For the same value of additive content, water with T-BSPs had a lower friction coefficient and wear volumes than water with BSPs. This is because T-BSPs dispersed better in water than in BSPs and therefore, they presented better tribological performances [7].
Figure 2. Tribological performances of different lubricant samples: (a) friction coefficient and (b) wear volumes of water, water containing BSPs and water containing T-BSPs (load: 5 N, speed: 50 mm/s, additive content: 0.3 wt%, testing time: 30 min), Variation in (c) friction coefficient and (d) wear volumes with increasing content of BSPs and T-BSPs in water (load: 5 N, speed: 50 mm/s, testing time: 30 min).

3.3. Tribological mechanism

As seen from Figure 3a, 3b, 3c, 3d, 3e, and 3f, the wear scar on the disk lubricated by water was severe, followed by that lubricated by water containing 0.3 wt% BSPs, the mildest wear scar was observed for water containing 0.3 wt% T-BSPs. This reveals that the wear of friction pair can be decreased to different degrees by adding two additives into water. In addition, T-BSPs enhanced the antwear property of water to a greater extent than BSPs.

Figure 3g, 3h, and 3i show two typical characteristic bands of 1346–1347 cm⁻¹ (D) and 1595–1599 cm⁻¹ (G) on friction surfaces lubricated with water containing 0.3 wt% BSPs and water containing 0.3 wt% T-BSPs. However, the D and G bands were negligible in the absence of additives. This indicates that the spherical BSPs and T-BSPs can enter the contact region of the ball and disk, avoiding the direct contact between the friction pairs [8]. In addition, both BSPs and T-BSPs can participate in the formation of lubricating films. However, as the hydrophilic property of BSPs is not as good as that of T-BSPs, BSPs easily form aggregates in aqueous media, which hampers the uniform adsorption of BSPs on the friction surfaces and the effective protection of sliding surfaces against the wear and friction [6]. Thus, the results of this study indicate that T-BSPs is more appropriate as a lubrication additive in aqueous media than BSPs.
4. Conclusions
Both BSPs and T-BSPs comprise of nearly spherical primary particles. Among them, T-BSPs have more oxygen-containing functional groups, which results in better dispersion of T-BSPs in aqueous media. The tribological performances of T-BSPs as lubricating additives are better than those of BSPs. In particular, when the T-BSP content was 0.3 wt%, the friction coefficient and wear volumes were dramatically less than those of water. The tribological mechanism indicated that both BSPs and T-BSPs can enter the friction surfaces and prevent the direct steel–steel contact. Moreover, T-BSPs get well dispersed in water and are uniformly adsorbed on the friction surfaces. However, BSPs exhibit poor dispersion in water, which limits the lubricating effects. Therefore, water containing T-BSPs showed better lubrication properties than water containing BSPs.

Acknowledgements
This work was supported by Anhui Province University Natural Science Research Project (KJ2019A0678), School-level Scientific Research Projects of Chaohu University (XLZ-201907), the Doctor Start-up Foundation of Chaohu University (KYQD-202001) and National College Students’ Innovation and Entrepreneurship Training Program of China (202010380012).

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