



Full Length Article

Novel in situ tribo-catalysis for improved tribological properties of bio-oil model compound



Yubin Peng^a, Yufu Xu^{a,*}, Karl D. Dearn^b, Jian Geng^a, Xianguo Hu^a

^a Institute of Tribology, School of Mechanical Engineering, Hefei University of Technology, Hefei 230009, China

^b Mason Institute of Tribology, Mechanical Engineering, School of Engineering, University of Birmingham, Edgbaston, Birmingham B152TT, United Kingdom

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ABSTRACT

A novel in situ tribocatalytic esterification reaction has been developed driven by frictional processes, to alleviate the corrosion wear induced by the high content of organic acid in bio-oil. Solid superacid ($\text{SO}_4^{2-}/\gamma\text{-Al}_2\text{O}_3$) was formulated and prepared as the catalyst. Acetic acid was as the base for the bio-oil, and glycerol was used as a modifying agent. The tribological properties of the bio-oil with varying amounts of solid superacid were evaluated on a HDM-20 end-face tribometer. Scanning electron microscope and X-ray photoelectron spectroscopy were employed to measure the micro-morphologies and elemental contents on the worn surfaces after sliding. The effect of tribocatalysis on the composition of the bio-oil was analyzed by Fourier transform infrared spectrometer and Gas chromatography-Mass spectrometry. The results show that when lubricated by pure bio-oil the worn surfaces showed severe furrows and bulk exfoliation of the surface material. With the solid superacid added to the bio-oil, abrasive wear and material exfoliation were alleviated. The reason for the improved tribological properties is that the solid superacid not only could roll on the friction surface and act as lubricating particles, but also catalyzed esterification between acetic acid and glycerol, which simultaneously improved the tribological properties of bio-oil.

1. Introduction

Bio-oil is a promising alternative to fossil fuels processing a range of renewable and environmentally-friendly advantages [1]. Fast pyrolysis technology is a general way to produce bio-oil from biomass [2]. Although pyrolysis technology is a simple, convenient and very effective method, the chemical composition of bio-oil production from pyrolysis is very complicated. When produced, the bio-oil is mainly composed of organic acids, alcohols, phenols, alkanes, aldehydes and ketones [3,4]. In this form, crude bio-oil, cannot be directly deployed as a fuel for internal combustion engines (replacing for example diesel oil) because of its undesirable characteristics, such as high corrosion, high viscosity, and low heating value [5]. If it were to be used as a crude fuel the engine would likely suffer from, amongst other things, severe corrosive wear of the friction pairs in the engine such as the piston rings and cylinder liners, leading to a decrease in the service life of the engines [6]. Upgrading and enhancing the quality of crude bio-oil is a vital step towards a wider adoption of this promising biofuel [7].

Catalytic esterification has been shown to be an effective process for improving the properties of bio-oil, by converting organic acids into the corresponding esters [5,8]. Song et al. [9] used esterification to upgrade

bio-oil with a $\text{SO}_4^{2-}/\text{SiO}_2\text{-TiO}_2$ catalyst. In doing so the pH value of the subsequent bio-oil increased from 3.22 to 5.43, and demonstrated enhanced stability. Wang et al. [10] were able to decrease the acid numbers of upgraded bio-oil by 88.54% and 85.95% with 732 and NKC-9 type ion exchange resins, respectively. The choice of catalyst used in the esterification process can be vitally important. From a tribological perspective, Xu et al. [11] compared the tribological properties of crude and esterified bio-oil. Results showed that esterified bio-oil had better friction-reducing and anti-wear properties compared to the crude oil. The tribological improvement was as result of the decrease in acidic corrosion combined with the formation of a protective tribo-film that included ester and other organic groups. Bio-oil could therefore be used in IC engines with the correct upgrade using optimized catalytic esterification [12].

Tribocatalysis is an emerging aspect of tribochemistry, linking the properties of a catalyst to the effects of rubbing energy [13]. Onodera et al. [14] investigated the tribocatalytic activity of $\gamma\text{-Al}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ for the degradation of PTFE. It was found that $\gamma\text{-Al}_2\text{O}_3$ had a stronger catalytic activity at lower temperatures during friction. This resulted in a discontinuous transfer film and inferior tribological properties. Hiratsuka et al. [15] studied catalytic oxidation of ethylene,

* Corresponding author.

E-mail address: xuyufu@hfut.edu.cn (Y. Xu).

with palladium sliding against Al_2O_3 . The catalytic effect was strengthened, and the products of catalytic reaction were more completely oxidized as a result of rubbing. In essence, mechanical energy in the complicated friction system enhanced the activity of the catalyst.

These tribocatalytic principles could be applied to the esterification process to promote catalyst activity leading to improved tribological properties. However, to the best of our knowledge, few reports have described the tribocatalytic esterification of bio-oil for improved fuel design. In this paper, solid superacid ($\text{SO}_4^{2-}/\gamma\text{-Al}_2\text{O}_3$) was prepared as the catalyst and the effect of tribocatalytic esterification on bio-oil was studied during friction process. Optimum catalytic concentrations for tribological properties of bio-oil have also been studied.

2. Experimental

2.1. Materials

The $\gamma\text{-Al}_2\text{O}_3$ powders with an average particle size of 10 nm, used for the catalysts were supplied by Shanghai Macklin Biochemical Co., Ltd. The chemical agents including sulphuric acid, acetic acid and glycerol were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were analytical grade.

For the tribological testing, the lower samples were machined 36 mm diameter, 3 mm thick discs made using QT600 nodular cast iron. The upper specimens were ASTM 1045 medium carbon steel, which was quenched to give a hardness of 47–53HRC, machined to the geometry shown in Fig. 1.

2.2. Catalyst preparation

The solid superacid $\text{SO}_4^{2-}/\gamma\text{-Al}_2\text{O}_3$ was prepared using the impregnation method defined fully in [16]. $\gamma\text{-Al}_2\text{O}_3$ powders (1 g) were dispersed in a diluted H_2SO_4 solution (20 mL, 3 mol/L). The mixture was further stirred for 3 h to ensure full contact between the particles and acid solution. After aging overnight, the treated powders were centrifuged out, and then dried at 110 °C for 12 h and was then ground in an agate grinding bowl. The solid superacid was finally synthesized after calcination at 500 °C for 5 h.

2.3. Tribological tests

To simplify the formulation of and the interpretation of the performance of the tribocatalytic esterification of bio-oil (comprising of many kinds of organic components), acetic acid was selected as a model bio-oil [10,17], and glycerol was used as a modifying agent. The

Table 1
Tribological testing conditions.

Testing conditions	Values
Normal load/N	600
Contact pressure/MPa	12.5
Rotational speed/rpm	441
Rotating diameter/mm	26
Temperature/°C	25 ± 2
Duration/min	60

lubricating medium during the frictional tests was configured by with mass ratio of 1:1 acetic acid and glycerol. Hence forth, in this paper this formulation will be referred to as bio-oil for convenience. The solid superacid catalyst was ultrasonically dispersed in the bio-oil for 10 min with different mass fractions (0, 0.5, 1, 1.5, 2 wt%) at room temperature. The friction and wear properties were tested on a HDM-20 end tribometer. Fig. 1 shows the schematic diagram of the tribometer and the friction pairs. The lower specimen was fixed in the oil box. Three small bosses (4 × 4 mm) protruding from the upper specimen slid against the lower specimen with a rotational speed of 441 rpm during the frictional process. Further details of the test conditions are listed in Table 1.

Before the friction tests, the upper specimen prepared by mounting it first on the tribometer and then running the three raised bosses against 500 grit metallographic sandpaper. Doing so ensured a true plane between the frictional surfaces and a consistent surface roughness. After this and before testing, the upper and lower specimens were cleaned with acetone. During the experiments, the friction coefficient was measured in real-time. The wear loss was calculated by measuring the change in weight of the lower specimens before and after the tribotests. Each test was repeated three times to obtain a standard deviation. After the experiments, the lower specimens were ultrasonically cleaned with acetone for 30 min enable further characterization and analysis. Finally, the bio-oil was collected and then centrifuged at 8000 rpm for 30 min to remove remaining solid superacid and wear debris.

2.4. Characterization of materials and frictional surfaces

The size distribution of the solid superacid was measured using a Zeta potentiometer (Nano-ZS90). The Fourier Transform Infrared Spectrometer (FTIR, Nicolet 67) was used to characterize the functional groups of the solid superacid. To evaluate catalytic activity, an esterification experiment of bio-oil with 2 wt% solid superacid was carried out in a stirred glass reactor for 5 h at 120 °C. The conversion rate of

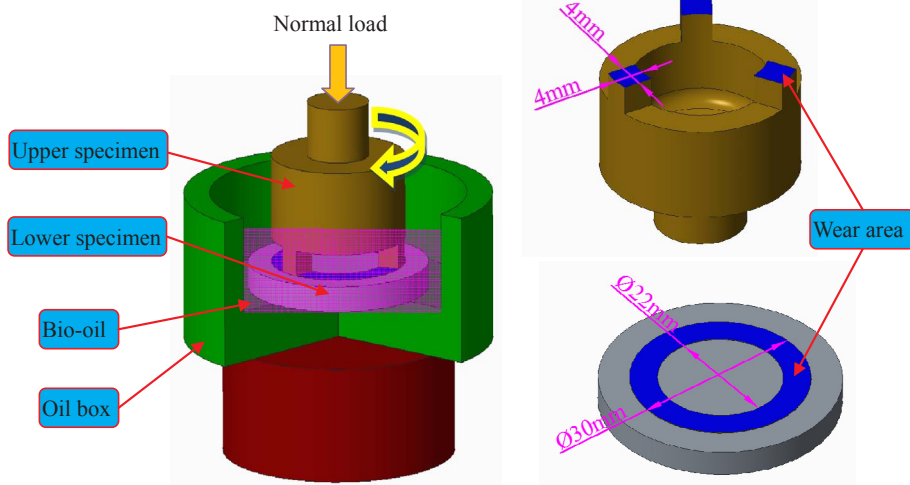


Fig. 1. Schematic diagram of the friction pairs and the tribometer.

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