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Synthesis and tribological studies of nanoparticle additives for pyrolysis bio-oil formulated as a diesel fuel

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ABSTRACT

The tribological behaviour of pyrolysis bio-oil with a synthesized nano-Lanthanum oxide (La_2O_3) additive was evaluated using a point contact four ball tribometer under different frictional conditions. Results were compared against a micro (μ)-La_2O_3 additive and an un-additised bio-oil as a control. The results show that nano-La_2O_3 impregnated bio-oil had better tribological properties than the control groups. Under the operating loads, the optimum nanoparticle concentration within the bio-oil was investigated. At these levels, the combined action of adsorbed bio-oil films on the worn surfaces and the bearing effects of the nano-La_2O_3 minimized friction and wear. The tribo-mechanisms were ascribed to adhesive wear as a result of lubrication starvation under high loads, and abrasive wear at high rotational speeds as a result of combined deformation and aggregation of the nano-La_2O_3 particles.

1. Introduction

Since the energy crisis in 1970s, many countries have focused efforts on the development of alternative sources of energies. In recent decades, bio-oil derived from biomass has been shown as one of the most promising alternatives to the traditional fossil fuels [1–3]. The reasons for this are numerous but include the general availability of the raw materials for the bio-oil that can be derived from waste, and depending on how this is processed there is a potential for the process to be can be carbon neutral. The main components of such bio-oils are oxygen-containing organics including carboxylic acids, alcohols, aldehydes, ketones, phenols etc. Generally, such fuels are prepared though a fast pyrolysis process with the rapid thermal decomposition of biomass in the absence of oxygen at a moderate temperature of ~500 °C at an extremely high heating rate about 400–500 °C/s. As an alternative fuel in internal combustion engines, bio-oil has been shown to enhance combustion characteristics [4]. Bio-oils have also been shown to possess very good lubricating properties. The lubricity of diesel fuels is very important since it has a direct effect on the durability of the fuel injection equipment [5]. Tribologically, some bio-oils have been shown to possess better antifriction properties than those of the conventional fossil fuel. For others however, the wear properties can be much worse, as a result of corrosion and surface degradation. These effects can lead to severe damage of engine components to the extent that the application of bio-oils has been restricted [6–8]. This forms the motivation for seeking methods to upgrade the tribological performance of the bio-oil by inhibiting these negative properties.

Nano-materials exhibit great potential for improving tribological performance and as such they have been widely studied as lubrication additives. Lanthanum oxide is a functional rare earth material and as such, it has found many uses including as a catalyst, and hydrogen storage material [9,10] it also has potential as a tribological additive. For all these applications, the surface shape, particle size, and the dispersed state are of importance. As an example, Xue et al. [11] reported the sliding wear behaviours of nickel composite coatings containing micro- and nano-La_2O_3 particles. They found that the nano-La_2O_3 composite coatings exhibited excellent wear resistance. Nano-La_2O_3 may therefore improve the tribological properties of bio-oil and negate the potential wear limitations outlined above. Furthermore, the use of energetic

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nanoparticles such as La_2O_3, due to small particle size and the relatively low concentration levels, affords a promising method of altering the reactivity of liquid fuels for enhanced combustion stability, resulting in a reduction in ignition delay of some fuels [12].

In this paper, ball-like nano-La_2O_3 was synthesized and dispersed in a pyrolysis bio-oil to form a Bio-Oil/La_2O_3 (BO/La_2O_3) suspension via ultrasonic technology. The effect of La_2O_3 particle size, percentage concentration, friction load and rotational speed on tribological properties were evaluated using a four ball point contact tribometer and the corresponding tribological mechanisms are discussed.

2. Experimental

2.1. Materials

All of the chemicals used in the present work, such as the lanthanum carbonate ($La_2(CO_3)_3$), nitric acid (HNO_3), citric acid monohydrate ($C_6H_8O_7$ H_2O), acetone and the lanthanum oxide (micro-La_2O_3), were analytical grade reagents.

The BO used was from rice husk via fast pyrolysis technology and was provided by Anhui Province Key Laboratory of Biomass Clean Energy, University of Science and Technology of China. The components of bio-oil were as follows: carboxylic acids 32.72%; alcohols 8.14%; aldehydes 23.49%; ketone 7.09%; phenols 13.98%, and others 14.58%. The main physicochemical properties are as follows: The flash point is 68 °C; high heating value is 16.5 MJ/kg; kinematic viscosity is 13.2 $mm^2\ s^{-1}$ at 40 °C. It should be noted that although the low heating value and high viscosity of the bio-oil in its present form make it unsuitable for use a fuel, upgrading via emulsification would rectify this. More details of the pyrolysis process, chemical composition and physicochemical properties can be found elsewhere [13].

2.2. Preparation of nano-La_2O_3

The preparation of the *nano-La_2O_3* comprised the following steps. 25 mmol of $La_2(CO_3)_3$ (~11.4 g) and 150 mmol of HNO_3 (~9.4 ml) were dissolved into 100 ml of distilled water to form a clear reaction solution. This was then heated at 60 °C for 5 min after which 8.3 mmol of $C_6H_8O_7\cdot H_2O$ (~1.74 g) was added to it, and magnetically stirred to form a uniform dispersion. This was then heated in a muffle furnace to remove excess water, allowing a gel to form. The precursor was then dried and the nano-La_2O_3 (nano lanthanum oxide) was produced via calcination at 850 °C for 6 h [14]. Finally the La_2O_3 was added to bio-oil at concentration levels of 0.2, 0.6, 1.0, 1.4 and 1.8% (all the % in this paper means wt.%). Each BO/La_2O_3 suspension was stable for at least 7 days after being ultrasonically dispersed for 10 min before each test.

2.3. Tribological tests

The tribological tests were carried out on a Jinan MQ-800 four-ball tribometer. The schematic of the tribological tests is shown in Fig. 1. Referring to ASTM D4172 (Standard Test Method for Wear Preventive Characteristics of Lubricating Fluid), the experimental conditions selected were nominally a load of 100 N with a rotational speed of 1250 rpm at 25 ± 2 °C for 30 min. ASTM E52100 bearing steel test samples were used with a diameter of 12.7 mm, a surface roughness (Ra) of 0.032 μm and a hardness of 61–63 HRC. Experiments were compared against a control sample comprising the bio-oil without additives. These experimental conditions ensured that all of the tribological tests were performed under the boundary lubrication.

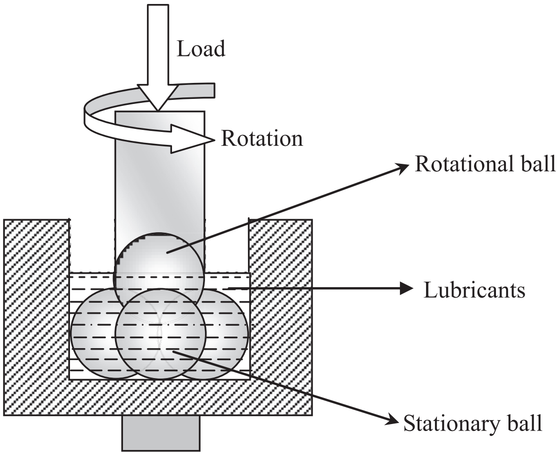

Fig. 1. Schematic of the tribological tests.

After each test, the steel balls were washed using acetone. Wear rates were was evaluated from the average WSD (wear scar diameter) of the three lower specimens. After an initial test programme, the effects of load and speed for the bio-oil with nano-La_2O_3 were also evaluated, at 150 N and 200 N and 1450 and 1650 rpm, respectively. Test conditions were repeated three times and the friction coefficient was collected in real-time during each experiment.

2.4. Characterization

The particle size distribution of the La_2O_3 powder was measured using a Bettersize BT-9300H laser particle size analyser. The crystal structure of the precipitate was analysed with a Rigaku D/Max-cB powder XRD (X-ray diffractometer) with Cu Kα radiation ($\gamma = 0.541$ nm) under 40 kV, 100 mA and a scanning speed of 5° min^{-1}. The topography of the particles and elemental composition of the worn surfaces was observed using a FEI Sirion 200 SEM (scanning electron microscope) with EDS (energy dispersive spectroscopy). The morphologies and chemical valences of elements on the worn surfaces were analysed using an Olympus TPF-1 optical microscope and a Thermo Scientific ESCALAB 250 XPS (X-ray photoelectron spectroscope), respectively. The WSD of the lower specimens was measured with an accuracy of 0.01 mm. In order to analyse the tribological mechanisms, the thickness of lubricating oil film was calculated with the following formula [15]:

$$\frac{h_{mean}}{R} = 2.69\left(\frac{U\eta_0}{ER}\right)^{0.67}(\alpha E)^{0.53}\left(\frac{W}{ER^2}\right)^{-0.067}\left(1-0.61e^{-0.73k}\right)$$

where h_{mean} is the mean oil film thickness; η_0 is the viscosity of the lubricant; R is the radius of curvature; U is the entraining surface velocity; E is Young's modulus ($E = 210$ GPa); α is the Pressure-viscosity coefficient, ($\alpha = 0.44 \times 10^{-8}$ $m^2/N\ pa^{-1}$); W is the contact load and k is the ellipticity parameter, $k = 1.03$.

3. Results and discussion

3.1. Characterization of the La_2O_3

Fig. 2 shows the variation in the surface morphologies of micro (μ) and nano-La_2O_3 particles. The μ-La_2O_3 is generally rod-like with particle diameters of between approximately 1.0–4.0 μm with a median diameter (D50) of 2.6 μm. However, the nano-La_2O_3 is quite different, displaying ball-like particles, with diameters of