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Effect of catalytic esterification on the friction and wear performance of bio-oil

Yufu Xu [a,*], Xiaojing Zheng [b], Xianguo Hu [a], Karl D. Dearn [c,**], Hongming Xu [a,c]

[a] Institute of Tribology, School of Mechanical and Automotive Engineering, Hefei University of Technology, Hefei 230009, China
[b] School of Arts and Media, Hefei Normal University, Hefei 230601, China
[c] School of Mechanical Engineering, University of Birmingham, Edgbaston, Birmingham B152TT, United Kingdom

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ABSTRACT

The tribological response of bio-oil derived from *Spirulina* algae has been assessed, according to the choice of catalyst during esterification. The bio-oil was upgraded over the selected catalysts of KF/HZSM-5 and KF/Al_2O_3 with ethanol. Physical and chemical properties were assessed throughout with the crystal structure of the catalysts was characterized by X-ray diffraction (XRD), chemical groups and components of the bio-oil by Fourier Transform infrared spectroscopy (FTIR) and Gas Chromatograph–Mass Spectroscopy (GC–MS). Tribological experiments were conducted using a bespoke piston ring-on-cylinder liner tribometer. Worn surfaces were observed by Scanning Electron Microscope (SEM), and the elemental contents and valences were tested by X-ray Energy Dispersive Spectroscopy (EDS) and X-ray Photoelectron Spectroscopy (XPS). It is shown that choice of catalyst used during the upgrading of the bio-oil has a significant effect on tribological performance. Catalytic esterification improved friction resistance and the anti-wear properties of the bio-oil. KF/Al_2O_3 was a better catalyst for doing this than KF/HZSM, a result of the ester and organic groups present in the KF/Al_2O_3 upgraded bio-oil. These groups acted to form a protective tribo-film between surfaces.

1. Introduction

Biomass is viable source of renewable energy that has the potential to meet the increasing demand for energy in the face of declining fossil fuels. Thermochemical conversion techniques such as fast pyrolysis or high pressure liquefaction mean that biomass can be conveniently converted in the more functional crude bio-oil. There are many forms for this, including bio-oils derived from algae. The algal species *Spirulina* is one of many species that has received an increased interest [1]. This includes integration of algal cultivation into municipal and agricultural effluents treatment from both a water resource and renewable energy perspective.

For the many benefits, there are conversely some problems with the use of bio-oil that need to be overcome. These include a general instability, a high water contain (~20 wt%) and a high acidity (pH 2–3) [2]. Combined these can, amongst other problems, lead to corrosion and hence can be difficult to use directly in internal combustion engines. Like diesel fuel, bio-oils need to be atomised before ignition which can lead to adsorption of the bio-oil on engine cylinder. This can lead to significant levels of corrosive wear [3]. Therefore, the tribological performance of bio-oil is underlined, as is the need to improve properties through upgrading.

Finding efficient methods of doing this, has been the subject of much research. Emulsification has been shown to be particularly effective for blending bio-oils with diesel fuels. However, as the emulsification process does not affect acidity levels in the crude bio-oil, blend ratios have been limited to 30% (by volume) [4]. Catalytic hydrogenation has been used to improve stability and heating value of the fuel by decreasing oxygen content and increasing hydrogen. However, the extreme conditions required to initiate hydrogenation lead to high productions costs and other obstacles to application [2,5]. Bio-oil can be converted to gasoline using a catalytic hydrocracking process. Generally mesoporous catalysts have been shown to be the most effective in terms of yield and properties of the upgraded oil, but the catalysts have proved to be costly due to the complex production processes [6,7].

Of all of the upgrading processes described above, it is only catalytic esterification that can convert acids to esters and reform the chemical components of a bio-oil [8]. The conditions required for esterification are also comparatively less severe. It is therefore a very useful method of upgrading bio-oil, providing that is, that the optimum catalyst pair is selected. Dang et al. [9] studied the effects of 5% Pt/SO_4^{2-}/ZrO_2/SBA-15 as a catalyst for the upgrade of bio-oil. Results showed that increasing the mass ratio of ethanol to

* Corresponding author. Tel.: +86 551 62901359.
** Corresponding author. Tel.: +44 121 4144190.
E-mail addresses: xuyufu@126.com (Y. Xu), k.d.dearn@bham.ac.uk (K.D. Dearn).

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Table 1
Main compounds (> 1%) of the GC–MS chromatogram areas from *Spirulina* crude bio-oil.

RT/min	Compound	Formula	Area /%
6.24	Picolinic acid N-oxide	$C_6H_5NO_3$	4.01
8.84	2-Cyclopenten-1-one,2-methyl-	C_6H_8O	3.88
8.92	Pyrazine, ethyl-	$C_6H_8N_2$	1.46
11.46	2-Cyclopenten-1-one,3,4-dimethyl-	$C_7H_{10}O$	1.5
11.61	Pyrazine,2-ethyl-5-methyl-	$C_7H_{10}N_2$	3.07
12.76	trans-1,4-Hexadiene	C_6H_{10}	1.46
15.07	Pyrazine, isopropenyl-	$C_7H_8N_2$	1.14
15.51	2-Cyclopenten-1-one,2,3,4-trimethyl-	$C_8H_{12}O$	1.26
16.28	N-(3-Methylbutyl)aceta mide	$C_7H_{15}NO$	1.38
17	Pyrrolidine, 1-acetyl-	$C_6H_{11}NO$	1.71
17.97	Cyclopropane,[(1-propenyloxy)methyl]-	$C_7H_{12}O$	1.21
18.07	2-Piperidinone	C_5H_9NO	1.33
22.95	3-Hydroxy-3-methylglu taric acid	$C_6H_{10}O_5$	1.38
26.33	Acetic acid,2-phenylethyl ester	$C_{10}H_{12}O_2$	1
33.35	Pyrrolidine,1-(1-oxo-11-methyloctadecyl)-	$C_{23}H4_5NO$	2.16
34.6	2,6-Diazaspiro(4,4)nonane-3,7-dione	$C_7H_{10}N_2O_2$	4.97

Table 2
Tribological testing conditions.

Testing conditions	Value
Reciprocating frequency	5 Hz
Stroke	80 mm
Oil feed rate	25 ml h^{-1}
Sliding velocity	0.8 m s^{-1}
Normal load	350 N
Duration	60 min

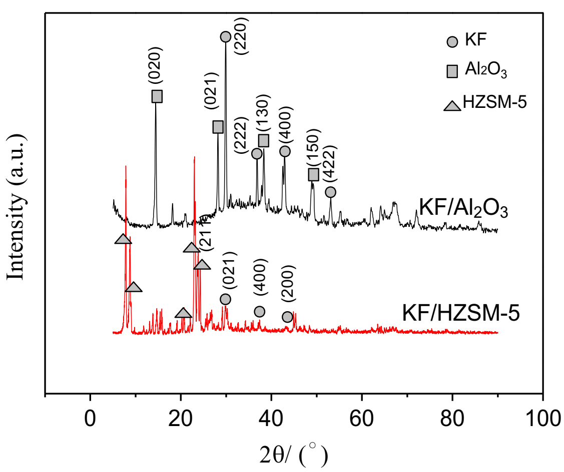

Fig. 1. XRD patterns of the KF/Al_2O_3 and KF/HZSM-5 catalysts.

bio-oil was helpful for producing the desired chemical products as well as physical properties such as increased heating value and lower coke yield. However, Hu et al. [10] found that some oligomers and organics of bio-oil may have a high affinity to the catalyst, serving to occupy the active sites and leading to catalyst deactivation. Potassium fluoride on alumina (KF/Al_2O_3) has been shown to be a novel and versatile catalyst during Michael addition, Wittig and Coupling reactions [11] because of its high activity, stability, availability and preferential experimental conditions required to induce reactions. Potassium fluoride on HZSM-5 zeolite (KF/HZSM-5) has also been widely used as a catalyst for upgrading bio-oil. Twaiq et al. [12] used a composite of micro porous HZSM-5 coated with a layer of a siliceous mesoporous crystalline material MCM-41 to convert palm oil to gasoline. Peng

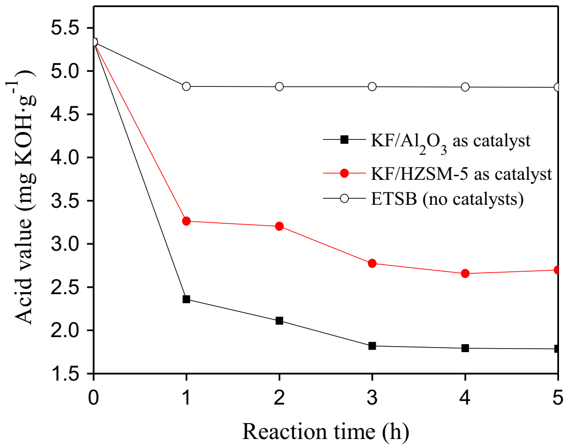

Fig. 2. Variation of the acid values of bio-oils with reaction time.

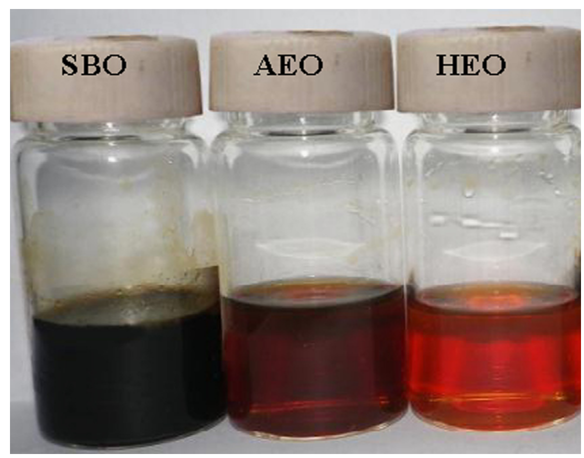

Fig. 3. A comparison of the crude bio-oil (SBO), the upgraded KF/Al_2O_3 oil (AEO) and the upgraded KF/HZSM-5 oil (HEO).

et al. [13] showed that bio-oil can be upgraded in a super-critical ethanol process with the aid of HZSM-5 as an acidic catalyst since that HZSM-5 promoted esterification between ethanol and acidic components in crude bio-oil.

In the light of the research conducted on effective processes for upgrading fuels, very few studies have been conducted on the effect that catalyst choice at the upgrade stage, has on the tribological properties of the processed bio-oils. This paper reports the effects that the chemical and physical properties of upgraded bio-oils have on tribological properties, when KF/Al_2O_3 and KF/HZSM-5 are used to drive the esterification reaction. These are contrasted against ethanol/bio-oil blends and well as discussed in the context of tribological mechanisms.

2. Experimental

2.1. Feedstock source and characterization

The crude bio-oil was derived from *Spirulina* algae (in dry powder form) and was prepared via hydrothermal liquefaction [14]. The Main compounds (i.e. those greater than 1%) of the GC–MS chromatogram areas from the crude *Spirulina* bio-oil are given in Table 1. The crude bio-oil was then upgraded via catalytic esterification, using two solid bases, potassium fluoride on alumina (KF/Al_2O_3) and potassium fluoride on HZSM-5 zeolite (KF/HZSM-5), with ethanol. Both the