Fuel Processing Technology 146 (2016) 76–84

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Different reaction behaviours of the light and heavy components of bio-oil during the hydrotreatment in a continuous pack-bed reactor

Mortaza Gholizadeh [a], Richard Gunawan [a], Xun Hu [a], Md Mahmudul Hasan [a], Sascha Kersten [b], Roel Westerhof [a], Weerawut Chaitwat [a,1], Chun-Zhu Li [a,*]

[a] Fuels and Energy Technology Institute, Curtin University of Technology, GPO Box U1987, Perth, WA 6845, Australia
[b] Sustainable Process Technology Group, Faculty of Science and Technology, University of Twente, Postbus217, 7500AE, Enschede, The Netherlands

ARTICLE INFO

Article history:
Received 13 November 2015
Received in revised form 19 January 2016
Accepted 24 January 2016
Available online 22 February 2016

Keywords:
Hydrotreatment
Bio-oil
Light and heavy species
Biofuel
LHSV

ABSTRACT

This study aims to investigate the hydrotreatment of bio-oil in a continuous packed-bed reactor at around 375 °C and 70 bar. The bio-oil was produced from the grinding pyrolysis of mallee wood in a grinding pyrolysis pilot plant. Our results indicate that the lighter and heavier components in the same bio-oil could behave very differently. Their behaviour can be affected very significantly by the overall bio-oil liquid hourly space velocity. While the residence time of the light species that evaporate instantly could be very short, the residence time of heavy species passing through the catalyst bed in the form of liquid could be very long. When a commercial pre-sulphided $NiMo/Al_2O_3$ catalyst came into contact with the heavy bio-oil species, significant exothermic reactions would take place, which result in the deactivation of hyperactive sites in the catalyst. The $NiMo/Al_2O_3$ catalyst used was less active in hydrotreating the heavier bio-oil species than in hydrotreating the lighter bio-oil species. However, even at very low extents of hydrotreatment, the bio-oil structure and properties, e.g. coking propensity, could be drastically improved.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Increasing concerns about climate change and increasing demand for energy as a result of wide economic development, including that in rural and remote regions, have stimulated the development of various renewable energy technologies. Biomass holds a special position because biomass is the only carbon-containing renewable resource that can be used to produce liquid fuels to replace the petroleum-derived conventional ones. Pyrolysis of biomass would produce gases, biochar and bio-oil with their yields strongly depending on the feedstock and pyrolysis conditions [1–3]. Compared with the bulky biomass, bio-oil is a liquid that can be transported relatively easily and economically. This allows for the pyrolysis to be carried out in a modular and “distributed” mode, saving the costs to transport the wet bulky biomass over a long distance and greatly improving the economic competitiveness of biofuel production.

However, bio-oil is acidic and contains water and high molecular mass components [3–5]. Therefore, bio-oil cannot be used directly as a replacement of petrol and diesel. Bio-oil must be upgraded, e.g. via hydrotreatment [6–15]. During the hydrotreatment of bio-oil, a significant fraction of its oxygen will be removed in the forms of H_2O, CO and CO_2. The hydrotreatment could also result in decreases in molecular mass [13–14].

In order to improve the commercial feasibility of the hydrotreatment of bio-oil, the liquid hourly space velocity (LHSV) must be high enough so that the hydrotreatment reactor size can be reduced. The pressure of hydrogen should be as low as possible. LHSV, i.e. the rate at which bio-oil is fed into the hydrotreatment reactor, can significantly affect the formation of coke on the hydrotreatment catalyst, which would ultimately result in the deactivation of the catalyst. Unfortunately, little information is available in the literature about the effects of LHSV on the product quality and coke formation, lagging behind the requirement of technology development.

As a product from the random thermal breakdown of macromolecular networks and other species in biomass, bio-oil has an inherently complicated composition with abundant reactive functional groups. More importantly, the bio-oil components would have a very wide molecular mass distribution with light species such as formic acid and heavy species that are the products from the partial thermal breakdown of the polymeric structures in biomass. During hydrotreatment, the residence time for bio-oil species could vary over an extremely wide range [15]. While some heavy bio-oil species would exist in the liquid phase in the hydrotreatment reactor, some would become vapour on entering the reactor. The overall LHSV value does not describe in any way the true residence time of various species in the reactor. This situation is worsened when operation is carried out at low pressures that is preferred to reduce the costs of biofuel production.

* Corresponding author.
E-mail address: chun-zhu.li@curtin.edu.au (C.-Z. Li).
[1] Present address: Environmental Engineering and Disaster Management Program, Mahidol University, Kanchanaburi Campus, Saiyok, Kanchanaburi, Thailand.

http://dx.doi.org/10.1016/j.fuproc.2016.01.026
0378-3820/© 2016 Elsevier B.V. All rights reserved.

This study aims to investigate the behaviour of bio-oil during the hydrotreatment in a continuous reactor using a commercial pre-sulphided $NiMo/Al_2O_3$ catalyst at a moderate temperature (375 °C) and a relatively low hydrogen pressure (70 bar). The study is focused on the effects of the overall LHSV on the hydrotreatment behaviour of lighter and heavier species in bio-oil. The hydrotreated products (termed as biofuel) were characterised with a wide range of analytical techniques in order to gain insights into the important processes taking place during hydrotreatment.

2. Experimental

2.1. Bio-oil sample

Bio-oil was produced in a grinding pyrolysis pilot plant [16,17] from the pyrolysis of mallee wood (*Eucalyptus loxophleba*, ssplissophloia) grown in the wheat belt of Western Australia [18,19]. Briefly, a mixture of wood chips having a wide range of particle sizes from microns to centimetres was continuously fed into a rotating reactor at 450 °C in which the pyrolysis and particle size reduction took place simultaneously. After the separation of biochar particles in two cyclones, bio-oil vapour was condensed to give the liquid bio-oil sample used in this study. The bio-oil sample was stored in a freezer (−18 °C) until use. The bio-oil was filtered (20–25 μm) before the hydrotreatment experiments.

2.2. Hydrotreatment

The hydrotreatment of bio-oil was carried out in a U-shape continuous pack-bed reactor, as is shown in Fig. 1. The reactor was made of stainless steel 316 and had a diameter of 3/4 in. with a total reactor length of 40 cm. The reactor was partly (about half, see "the sand bath level" shown in Fig. 1) immersed in a hot fluidised sand bath that was heated to 375 °C. The U-shaped reactor design made it easier to heat up the reactor in a sand bath. The packed-bed reactor contains two zones of catalysts. In the first zone (10 cm), 5% palladium supported on activated carbon (Pd/C, Bioscientific) catalyst was used. It was outside the sand bath. This section would have undergone a temperature transition ranging from room temperature to <250 °C, aiming to stabilise the incoming bio-oil based on the finding in the literature [20]. However, as will be demonstrated later in this paper, the use of Pd/C catalyst was marginally, if any, successful in avoiding coke formation. In the second zone, a commercial pre-sulphided $NiMo/Al_2O_3$ catalyst (from Eurecat, hereafter referred as "NiMo catalyst") was used. This section of the catalyst was immersed in the hot fluidised sand bath. The steady-state temperature at the border of the Pd/C and NiMo catalyst beds was between 235 and 270 °C under current experimental conditions.

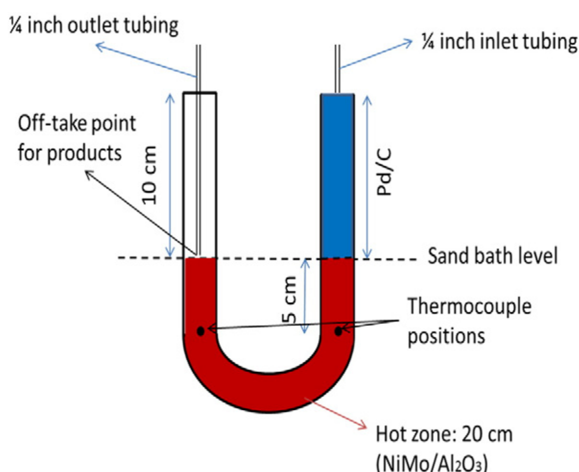

Fig. 1. A schematic diagram showing the reactor configuration.

The process flow diagram of this hydrotreatment set up has been shown elsewhere [15]. The bio-oil and hydrogen was pre-mixed before being fed into the reactor. The bio-oil was pumped, at a pre-set constant flow rate, into the reactor using a syringe pump (Teledyne Isco, 500D). The LHSV was defined as the ratio between the bio-oil feeding rate and the volume of the catalyst bed (i.e. the volume of the reactor occupied by the catalyst). The LHSV was increased by increasing the bio-oil feeding rate. The LHSV for the NiMo catalyst was varied between 1 and 3 h^{-1} in separate experiments. The LHSV for the Pd/C catalyst would be twice that for the NiMo catalyst for the same experiment. Hydrogen was supplied in large excesses via a mass flow controller at a constant flow rate of 4 L/min (measured under ambient conditions) for all experiments.

Two thermocouples were inserted into the catalyst bed to measure the catalyst temperature during the experiments. The tip of the first one was placed 5 cm at the inlet side below the surface level of the fluidised sand bath. The tip of the second thermocouple was also 5 cm, but at the outlet side, below the surface level of the fluidised sand bath. The distance between the tips of the two thermocouples in the flow direction was 10 cm.

The pressure at the outlet of the reactor was maintained at 70 bar by using a back pressure regulator (EquilibarEB1HP2) installed after the condenser system of two parallel traps. The temperature of the condenser system at its outlet was maintained below 10 °C by cooling the traps with ice water. The hydrotreated liquid products were collected into fractions every 45 min ($LHSV_{NiMo} = 2$), 60 min (LHSV = 3) or 90 min (LHSV = 1). The samples were then stored at −18 °C and were de-frozen prior to analysis.

The hydrotreated product was normally separated into two phases. The total water production is calculated as the sum of water in the aqueous and oil phases minus the water in the feed bio-oil. The yield of each product was expressed as the mass of product (e.g. the whole biofuel product or certain fraction) divided by the mass of bio-oil fed into the reactor over the same time interval. The product yields are always expressed on the basis of moisture-free (mf) bio-oil feedstock.

2.3. Product characterisation

2.3.1. UV-fluorescence spectroscopy

UV-fluorescence spectroscopy was used to understand the transformation of aromatic structures during hydrotreatment. A Perkin-Elmer LS50B spectrometer was used to measure the UV-fluorescence spectra of bio-oil and its hydrotreated products. Samples were diluted with UV grade methanol (purity ≥99.9%) to 4 ppm (wet basis). The energy difference for recording synchronous fluorescence spectra was $-2800\ cm^{-1}$ with slit widths of 2.5 nm (excitation and emission) and a scanning speed 200 nm/min. The fluorescence intensity was multiplied by the product oil yield to express the fluorescence intensity on the basis of bio-oil (moisture-free) to allow for comparison [21].

2.3.2. GC–MS

The raw bio-oil and the product oil phase were analysed with Agilent GC–MS (a 6890 series gas chromatograph with a 5973 mass spectrometric detector) equipped with a capillary column (HP-INNOWax) (length, 30 m; internal diameter, 0.25 mm; film thickness, 0.25 μm of crosslinked polyethylene glycol) [4,5,22]. The samples were diluted with acetone prior to analysis [10,15]. The following compounds were quantified: acetic acid, phenol, 2-ethyl-phenol, 2,4,6-trimethyl-phenol, 2,4-dimethyl-phenol, 4-(1-methylpropyl)-phenol and 3,4,5-trimethyl-phenol. The phenolic type of compounds are summed together and hereafter referred to as phenolics. Another group of compounds quantified included ethylbenzene, 1,3-dimethyl-benzene, 1,2-dimethyl-benzene, 1,4-dimethyl-benzene, propyl-benzene, 1-ethyl-2-methyl-benzene, 1,2,3-trimethyl-benzene and (1-methylpropyl)-benzene,

Download English Version:

https://daneshyari.com/en/article/209228

Download Persian Version:

https://daneshyari.com/article/209228

Daneshyari.com