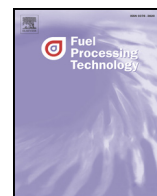




Contents lists available at ScienceDirect

Fuel Processing Technology

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

Coke formation during the hydrotreatment of bio-oil using NiMo and CoMo catalysts

Sri Kadarwati, Xun Hu, Richard Gunawan, Roel Westerhof, Mortaza Gholizadeh, M.D. Mahmudul Hasan, Chun-Zhu Li *

Fuels and Energy Technology Institute, Curtin University, GPO Box U1987, Perth, Western Australia 6845, Australia

ARTICLE INFO

Article history:

Received 8 March 2016

Received in revised form 17 August 2016

Accepted 17 August 2016

Available online xxx

Keywords:

Bio-oil

Hydrotreatment

Coke formation

Levoglucosan

ABSTRACT

This study aims to investigate the coke formation during the hydrotreatment of bio-oil at low temperature. The catalytic hydrotreatment of bio-oil produced from the pyrolysis of mallee wood was carried out using pre-sulphided NiMo and CoMo catalysts at a temperature range of 150–300 °C. Our results show that the catalysts play an important role in reducing the coke formation. The transformation of light products during the hydrotreatment was investigated. The role of levoglucosan in the coke formation was investigated by adding additional levoglucosan into the bio-oil prior to the hydrotreatment. In the presence of the catalyst, the hydrotreatment of bio-oil with the added levoglucosan did not yield more coke than that of original bio-oil under identical conditions. However, in the absence of the hydrotreating catalyst, coke formation was intensified. Our data indicate that levoglucosan could cross-link with other compounds in bio-oil in the absence of a hydrotreatment catalyst.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Pyrolysis of biomass is a promising method to produce bio-oil that is easier to store and transport than the bulky solid biomass. However, upgrading is required before the bio-oil can be used as a transportation fuel due to its adverse properties such as high acidity, high water content and high instability. Hydrotreatment has been shown to be a promising method to overcome these problems [1–3]. However, when bio-oil is heated up, many compounds become very reactive and tend to form coke [4–6]. This leads typically to reactor fouling and product deterioration. An additional stabilisation step has been suggested to suppress or prevent the coke formation by stabilising bio-oil [7,8]. In such approach, bio-oil is first stabilised by using a noble metal catalyst prior to full deoxygenation of the oil in a second stage with conventional commercial catalysts [8] such as sulphided NiMo/ γ -Al₂O₃ or CoMo/ γ -Al₂O₃ catalyst (referred hereafter as CoMo and NiMo catalysts). The use of noble catalysts would greatly increase the overall costs of biofuel production. Furthermore, coke formation is still a problem even when the noble catalysts are used to stabilise the bio-oil [9,10].

Coke formation is a complicated process. During the hydrotreatment, a break-down of the chemical bonds in the bio-oil is first required. The breakage of these chemical bonds would generate radicals. The radicals may further break down or be hydrogenated to form stable molecules, or re-combine to form larger molecules towards coke [11]. Herein, active hydrogen plays an essential role in suppressing coke formation [11,12].

The active hydrogen would react with and terminate those radicals. Otherwise, significant amounts of coke could form during the hydrotreatment at elevated temperature due to the lack active hydrogen supply, which cannot match the demand of the broken bonds [11–15].

Catalysts play an important role in providing adequate hydrogen supply in a catalytic reaction [9,11,12]. Although the commercial CoMo and NiMo catalysts are commonly used at high temperatures of typically >350 °C, they might still be sufficiently active in providing active hydrogen at lower temperatures. However, little information is currently available about the coke formation at low temperature using non-noble catalysts such as NiMo and CoMo catalysts. The knowledge about coke formation at low temperature during bio-oil heating up is essential. Therefore, this study aims to gain insights into the coke formation during the hydrotreatment of bio-oil at low temperature using NiMo and CoMo catalysts.

Bio-oil has an exceedingly complex composition, having thousands of compounds. Various catalysts including NiMo, CoMo and noble metal catalysts have been used in the hydrotreatment of model compounds such as furfural and acetic acid [16], various phenolic compounds [17–19] including guaiacols [19,20], ketones and carboxylic compounds [17,19] and carbohydrate fraction [21] to understand their hydrotreatment behaviour. Special attention has been given to sugars and its model compounds [4,21]. These sugars have the tendency to react towards coke formation when heated [4,22]. Due to their high concentration in bio-oil, they are an important fraction determining the tendency of bio-oil towards coke formation. It is important to understand how the sugars in bio-oil contribute to the coke formation.

* Corresponding author.

E-mail address: chun-zhu.li@curtin.edu.au (C.-Z. Li).

This paper presents the effects of the NiMo and CoMo catalysts on the coke formation during the hydrotreatment of bio-oil under mild conditions (150–300 °C and ≤ 100 bar (gauge) hydrogen pressure). Since levoglucosan is always found in high concentrations in bio-oil, its role in the coke formation has been studied. Blank experiments were also performed in order to get the information on the catalyst activity and the importance of the non-catalytic thermal reactions.

2. Experimental

2.1. Materials

The bio-oil used as the feedstock in the hydrotreatment experiments was produced from the pyrolysis of mallee wood in a grinding pyrolyser operated at 450 °C [23]. The details of the pyrolysis procedures can be found elsewhere [23]. The commercial hydrotreating catalysts, pre-sulphided NiMo and CoMo (containing 3–4 wt.% of Ni or Co and 12–16 wt.% of Mo) were purchased from EureCat. They were ground to 250–600 μm before use. The chemicals used as standards in the GC–MS analyses were obtained from Sigma Aldrich. Hydrogen and nitrogen (high purity grade, 99.99%) were obtained from BOC.

2.2. Hydrotreatment

The catalytic hydrotreatment experiments were performed in a batch autoclave reactor system described in our previous work [9]. Briefly, in each experiment, 4.0 g of NiMo or CoMo catalyst, 1.5 g of zinc oxide (to prevent the corrosion of the batch reactor by H_2S gas formed from the pre-sulphided catalysts) and raw bio-oil (40.0 g) were introduced into the reactor. For comparison, blank experiments (feeding bio-oil and hydrogen but without a catalyst) were conducted. For some experiments, levoglucosan was added to the bio-oil so that the final concentration of levoglucosan in the bio-oil was 21.5 wt.% (called NiMo–LGA) or 31.6 wt.% (called NiMo–LGB). It was observed that this amount of levoglucosan is soluble in bio-oil. The reactor was flushed with N_2 prior to the experiment and was subsequently pressurised with H_2 (100 bar (gauge)) at room temperature to check for possible leakage. The reactor was then pressurised with hydrogen (50 bar (gauge)) at room temperature and heated to the desired reaction temperature (150–300 °C) under continuous agitation at a stirring rate of 400 rpm. After the system reached the desired temperature, the total pressure was kept constant at 100 bar (gauge) by feeding additional hydrogen when needed. An exception is the experiments at 300 °C in which the pressure was 120 bar (gauge).

After the pre-set reaction time (3 h), the reactor was rapidly cooled to room temperature by cooling water running through a coil in the reactor. The produced gases were quantified by a gas chromatograph (GC, Agilent 6890) equipped with a methaniser and a flame ionisation detector. The residual pressure was recorded from which, together with the gas composition, the gas yield and hydrogen consumption could be determined.

After an experiment, the products (oil and aqueous phase) and the solids (catalyst, zinc oxide and coke) were separated and collected. The aqueous phase was on the top, while the oil phase was in the middle, and the solids were at the bottom of the reactor. Firstly, the aqueous phase and the oil phase were taken out. The reactor was then rinsed thoroughly using tetrahydrofuran (THF). The THF mixture of solids and remaining oil was then filtered and weighed. Knowing the weight of the filtrate and the concentration of THF (determined using GC–MS), extra oil yield could be added to the already collected oil phase. The amount of solids (filter residue) subtracted by the total weight of the catalyst and ZnO loaded into the reactor was defined as the amount of coke (solids) formed during hydrotreatment. The water content of the oil and aqueous phase was determined using GC–MS. The total water produced was determined by the difference between the water in the hydrotreated products (oil and aqueous phase) and that in bio-

oil. The mass balance was then expressed on a moisture free basis (per gram of bio-oil).

2.3. Analyses

The GC–MS analyses of the liquid products were performed using an Agilent 5973 MSD attached to an Agilent 6890 GC, equipped with a 30 m \times 0.25 mm \times 0.25 μm HP-Innowax (cross-linked polyethylene glycol) column. The parameters were similar to those specified in our previous work [24–26]. Briefly, 1 μL of acetone solutions containing 5–10 wt.% of sample was injected into the injection port set at 250 °C with a split ratio of 50:1. The oven temperature was kept at 40 °C for 3 min, heated up to 260 °C at a rate of 10 °C/min and then held at 260 °C for 5 min. Identification of compounds was based on the NIST library as well as the injection of standard solutions. For quantifying the compounds in bio-oil and hydrotreatment products, standard solutions (including water standards) were analysed to obtain reproducible response factors.

In this study, the synchronous UV-fluorescence spectra of hydrotreated oil and the bio-oil feedstock were recorded using a Perkin-Elmer LS50B spectrometer [9,27]. The solution of oil phase was diluted with methanol (Uvasol for spectroscopy; purity $\geq 99.9\%$) to 4 ppm. The synchronous spectra were recorded with a constant energy difference of -2800 cm^{-1} . The slit widths were 2.5 nm and the scan speed was 200 nm min^{-1} . At the same concentration, the fluorescence intensity was multiplied by the yield of organics in oil on a moisture free basis to express the fluorescence intensity on the basis of per gram of organics in bio-oil.

Thermogravimetric analysis (TGA) of bio-oil and hydrotreated oils was performed by using a SDT Q600 instrument over the temperature range of 25–500 °C at a heating rate of 10 °C/min in nitrogen (flow rate of 50 mL/min). In each run, 5–10 mg of sample was loaded into a crucible in the TGA instrument. The residue left behind after the experiment was referred as the “potential coke” following our previous work [9]. Elemental composition of C, H, and N was measured by using a Flash 2000 Interscience elemental analyser and oxygen content was calculated by difference. The elemental composition presented in this paper was expressed on a moisture free basis by excluding the water concentration in the hydrotreatment products [28].

2.4. Calculation of the yield

The yield of coke, organics in oil and aqueous phase, water and gaseous product was calculated as follows.

$$\text{Yield}_i(\text{wt.}\%) = \frac{\text{Weight of } i}{\text{Weight of BO} \times (1 - \text{water content})} \times 100$$

In case of the hydrotreatment of bio-oil with added levoglucosan, the calculation of the yield followed the equation below.

$$\text{Yield}_i(\text{wt.}\%) = \frac{\text{Weight of } i}{\text{Weight of LG} + (\text{Weight of BO} \times (1 - \text{water content}))} \times 100$$

The i symbol represents the coke, organics in oil or aqueous phase, water produced or gaseous product after each hydrotreatment experiment.

3. Results and discussion

3.1. The activity of pre-sulphided NiMo and CoMo catalysts

3.1.1. Yields of the oil and aqueous phases, gas and coke

The activity of pre-sulphided NiMo and CoMo catalysts was examined in the hydrotreatment of bio-oil under the mild conditions

Download English Version:

<https://daneshyari.com/en/article/4907160>

Download Persian Version:

<https://daneshyari.com/article/4907160>

[Daneshyari.com](https://daneshyari.com)