



One-pot catalytic hydrocracking of diesel distillate and residual oil fractions obtained from bio-oil to gasoline-range hydrocarbon fuel



Xianwei Zheng, Jie Chang, Yan Fu *

The Key Lab of Enhanced Heat Transfer and Energy Conservation, Ministry of Education, School of Chemistry and Chemical Engineering, South China University of Technology, Wushan Road 381#, Guangzhou 510640, China

HIGHLIGHTS

- Bio-oil was converted into C₇–C₁₄ hydrocarbon fuels by one-pot hydrocracking.
- The high heating value of liquid products was 42.35 MJ/kg.
- The amount of coking was only 1.15 wt.% and the catalysts could be recycled.
- This technique provides an economically feasible route for the preparation of biofuels.

ARTICLE INFO

Article history:

Received 21 January 2015

Received in revised form 17 April 2015

Accepted 1 May 2015

Available online 9 May 2015

Keywords:

Bio-oil

One-pot

Hydrocracking

Gasoline-range fuels

ABSTRACT

Bio-oil can be fractionated into three parts according to their boiling point. Here we report that diesel distillate and residual oil fractions can be converted into high-quality fuels by catalytic hydrocracking with the combined CoMoS/Al₂O₃ and HZSM-5 catalysts. Under the conditions of 390 °C and 6 MPa H₂, a high yield (87.0 wt.%) of liquid products was obtained. The compositions were C₇–C₁₄ hydrocarbons, including 23.3% of saturated naphthene, 23.4% of saturated chain hydrocarbons, 30.5% of aromatic hydrocarbons, and 22.8% of polycyclic aromatic hydrocarbons with one of ring saturated. The high heating value of products was 42.35 MJ/kg. The amounts of coking was only 1.15 wt.%, and the combined catalysts were recycled three times without the obvious decline of activity. Moreover, the reaction process did not need any solvent, and the products were easily separated. Based on the material balance, the net hydrogen consumption for the hydrocracking process was 38 g of H₂/kg of bio-oil, and the energy efficiency could reach up to 84%. This approach provides a high-efficiency route for the preparation of high-quality hydrocarbon fuel from bio-oil.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The depletion of fossil fuels and the warming global climate have boosted research on alternatives for fossil derived liquid transportation fuels. Biomass is one of the most important renewable resources for the sustainable production of liquid biofuels and chemicals in the future [1]. Flash pyrolysis of biomass is considered to be a promising technology to convert solid biomass into liquid bio-oil. And the yield of bio-oil can reach up to 70 wt.% [2–4]. However, because of its high oxygen content, corrosion, high viscosity, and instability, bio-oil cannot be directly used as transportation fuels [5,6]. Thus, it is imperative to upgrade bio-oil to obtain high grade fuels that can be adapted to the conventional engines.

Currently the most effective techniques for bio-oil upgrading are hydrotreatment [7,8], hydrocracking and hydrodeoxygenation (HDO) [9–11]. Hydrocracking has been extensively researched in the past decades, and it was typically performed at a high temperature with zeolite catalysts [12]. HDO is considered to be one of the most promising methods for bio-oil upgrading, because the majority of catalysts and reactors are derived from hydrodesulfurization (HDS) of fossil feeds [13,14]. Bio-oil is typically upgraded via a one-stage or two-stage HDO process with CoMo/NiMo-based catalysts, or noble-metal catalysts (such as Pd, Pt, Ru and Rh) [15–18]. However, the low yields (10–40 wt.%) and poor quality of liquid products are obtained. Besides, the upgraded process produces a large number of coke and tar (10–30 wt.%), which can result in catalyst deactivation and reactor clogging. These previous studies mainly focused on upgrading all the components of bio-oil. The good quality of liquid fuels could not be obtained because of complicated compositions of bio-oil. Hence, classified separation of

* Corresponding author. Tel.: +86 20 87111640.

E-mail address: fuyan@scut.edu.cn (Y. Fu).

bio-oil prior to upgrading was proposed, which was good for the enrichment of compounds with similar properties [19,20]. In addition, the number range of carbon atom in each separated fraction of bio-oil can be similar to gasoline, diesel, and residual oil of petroleum. Then the upgraded bio-oil can be used either as a gasoline/diesel replacement or as a blending material with gasoline/diesel. Wang et al. [21,22] reported a high-efficiency molecular distillation separation of bio-oil, which also produced fractions for subsequent upgrading.

In this study, one-pot catalytic hydrocracking of diesel distillate and residual oil fractions (C_7 – C_{36}) separated from bio-oil to gasoline-range fuels was investigated. The combined catalysts CoMo-based and HZSM-5 were used. The active components of CoMo-based catalysts are usually available in the oxide form. The activity of oxides is relatively low, so a sulfurizing procedure must be conducted to convert into the active sulfides. The process of sulfidation is quite complicated [23,24]. So the sulfidation of CoMo-based catalyst was discussed in detail. The compositions of gas, liquid and solid phase after reaction and the properties of liquid products were determined. Moreover, the energy efficiency of the whole process was calculated to evaluate the economic feasibility.

2. Materials and methods

2.1. Bio-oil fraction

The original bio-oil was provided by Toroyal Group (Shandong, China) and was produced from the straws. The flash pyrolysis reactor was circulating fluidized bed. The annual bio-oil yield was 200,000 tons. The bio-oil was fractionated into three parts according to the boiling point during pyrolysis. These fractions were gasoline distillates (C_5 – C_{10}), diesel distillates and residual oil (C_7 – C_{36}). The gasoline distillate fraction was hydrogenated to oxygenated liquid fuels which could be blended with gasoline directly. The oil used in this study was the diesel distillate and residual oil fractions. The integrated processing technology of bio-oil is illustrated in Fig. 1. Table 1 presents the properties of the feedstock in this research. The content of oxygen in bio-oil was much less than that reported in previous study. There were two reasons for this phenomenon. Firstly, the bio-oil was classified separation, and the gasoline distillate fraction contained a large number of oxygenated compounds. So the content of oxygen in diesel distillate and residual oil fractions was reduced. Secondly, the technology of biomass pyrolysis was quite different from the traditional pyrolysis process

Table 1

The properties of the feedstock and upgraded oil.

Property	Feedstock	Upgraded oil
Elemental content (wt.%)		
C	86.4	89.33
H	8.05	10.67
O	4.03	0
N	0.36	0
S	1.16	0
High heating value (MJ/kg)	38.25	42.35
Water content (wt.%)	<1.0	0
Density (g/cm ³)	1.09	0.81
Viscosity (mm ² /s, 40 °C)	27.12	7.81
Acid value (mgNaOH/g)	1.14	0
Carbon balance (%)	–	92.2

[25,26]. Biomass was first dealt with slow deoxidization process at the low temperature (<350 °C), and then performed by fast pyrolysis at the medium temperature (400–600 °C) [27,28]. This pyrolysis technology of the biomass has been industrial in China.

2.2. Catalysts

The catalyst of $MoO_3/CoO-Al_2O_3$ was sulfided in a batch reactor, and the sulfidizing reagent was CS_2 . The procedure included the low-temperature (230–260 °C) and high-temperature (310–370 °C) sulfidizing stages [29,30]. The catalyst of HZSM-5 was calcined at 450 °C for 2 h before use, and it was used to crack bio-oil forming small molecules [31]. These catalysts were all screened with 100 meshes of sieve.

2.3. Upgrading process

The bio-oil was upgraded in a 100 mL batch autoclave setup. The maximum pressure and temperature of the reactor were 200 bar and 400 °C, respectively. The temperature and pressure in the reactor vessel were digitally displayed.

The reactor was filled with bio-oil (30 g) and catalyst (1.5 g $CoMoS/Al_2O_3$, 1.5 g HZSM-5). The reactor was purged with H_2 five times and pressurized with 6 MPa of H_2 at room temperature. In a typical run, the reaction was produced at the conditions of 390 °C, 180 min, and 800 rpm. After the reaction was stopped, the reactor was cooled to room temperature. The pressure was recorded for mass balance calculation, and the gas phase was sampled using a gas bag. The liquid phase was removed from the reactor, and the

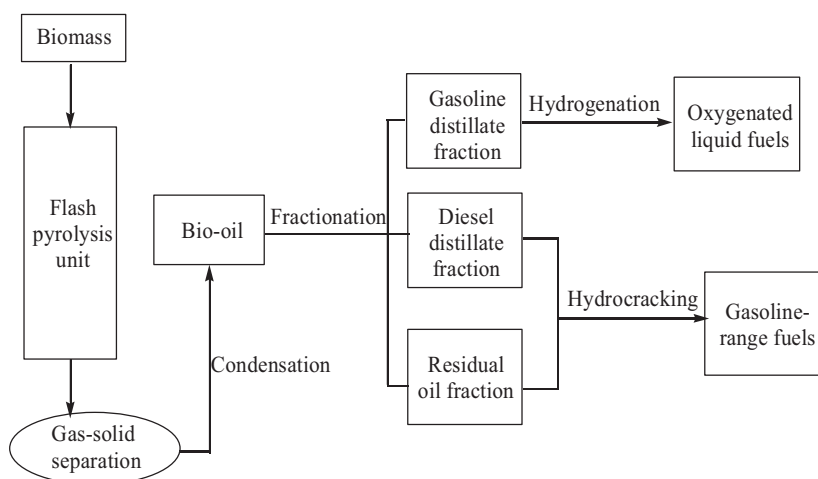


Fig. 1. The chart of the integrated processing technology of bio-oil.

Download English Version:

<https://daneshyari.com/en/article/6635269>

Download Persian Version:

<https://daneshyari.com/article/6635269>

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