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RESEARCH

Mild hydrogenation of simulated bio-oil based on molecular distillation

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Abstract: A mild hydrogenation of simulated bio-oil was carried out in a fixed-bed reactor. Based on the experimental results, 300 ^{o}C/4 MPa was chosen as an optimum condition for the mild hydrogenation, the simulated bio-oil was nearly completely converted. Besides, the liquid product selectivity achieved 85.0% and its $(H/C)_{eff}$ was significantly promoted from 1.266 to 1.554. The liquid composition was greatly improved and a notable decrease of phenols and acids contents was observed. In this case, the product activity was significantly enhanced and then the subsequent catalytic cracking was favored.

Key words: bio-oil; model compounds; mild hydrogenation; effective hydrogen to carbon ratio

The bio-oil produced from biomass fast pyrolysis is generally considered to be a potential substitute of conventional transportation fuels. However, some inferior properties of crude bio-oil, such as high oxygen and water contents, strong corrosiveness and low heating value, severely limit its high-grade utilization[1,2]. Therefore, it is required to upgrade the crude bio-oil.

Various upgrading technologies, including catalytic cracking, catalytic hydrogenation, catalytic esterification, catalytic reforming and emulsification, etc., have been developed in recent decades[3–5]. Catalytic cracking is a promising upgrading technology, which can remove oxygen from bio-oil in the forms of CO, CO_2 and H_2O to produce liquid fuel rich in aromatic hydrocarbons[6]. However, the chemical composition of crude bio-oil is rather complicated, which consists of ketones, acids, aldehydes, phenols and sugars, etc., and different chemical families have different activities. A series of studies on catalytic cracking of bio-oil model compounds showed that, ketones and acids could be converted into hydrocarbons, but large-molecular-weight phenolic oligomers and sugars had a strong tendency to produce coke, responsible for rapid catalyst deactivation[7–9]. Consequently, the removal of phenolic oligomers and sugars is of great significance to improve the activity of bio-oil. Molecular distillation is an efficient separation technology, which can separate bio-oil into a distilled fraction with high activity and a residual fraction with low conversion capacity. The distilled fraction mainly enriches acids and ketones, whereas sugars and phenolic oligomers are reserved in the residual fraction[10,11]. Therefore, study on catalytic cracking of bio-oil distilled fraction is of great significance to proceed. And because of high oxygen content and unsaturated degree, the components in bio-oil distilled fraction, such as acids and ketones, still have propensity for coke formation. As a result, the concept of effective hydrogen to carbon ratio ($(H/C)_{eff}$) was introduced to evaluate the cracking activity of different oxygenated compounds[12]. As shown in Eq. (1), H, C and O each represent the mole percentages of hydrogen, carbon and oxygen in the corresponding compounds, respectively.

$$(H/C)_{eff} = \frac{(H-2O)}{C} \quad (1)$$

It was reported by Mentzel et al[12] that a high $(H/C)_{eff}$ had a positive effect on the catalyst stability in catalytic cracking of bio-oil model compounds. Considering the differences between bio-oil ($(H/C)_{eff}<1$) and targeted aromatic hydrocarbons ($1<(H/C)_{eff}<2$), it is required to increase the integral $(H/C)_{eff}$ to promote the activity and stability of cracking process. Wang et al[13–16] introduced ethanol as a co-reactant and carried out a series studies on catalytic cracking of bio-oil distilled fraction and model compounds, and high yield of oil products and inhibition of coke formation were observed.

Catalytic hydrogenation is another conventional technology for bio-oil upgrading. It can be classified into hydrodeoxygenation and mild hydrogenation. The former removes oxygen of bio-oil in the form of H_2O under high

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hydrogen pressures (10–20 MPa) to produce aliphatic hydrocarbons[17–19], which not only has strict requirements for equipment but also involves high consumption of hydrogen. The latter is used to saturate the unsaturated double bonds and thus improves the bio-oil stability[20–25]. Typical catalysts for hydrogenation include groups such as noble metals[20,22–24], Mo-based sulfides[26,27], metal phosphides[28] and other metal catalysts[21,25], among which Pd-based catalysts exhibit high activities for hydrogenation[20,23]. In view of the low $(H/C)_{eff}$ of bio-oil, mild hydrogenation can be applied prior to catalytic cracking to improve the conventional upgrading process. Vispute et al[29] performed catalytic hydrogenation of water-soluble bio-oil at 10 MPa in a fixed bed reactor, followed by catalytic cracking of condensation products in a fluidized bed reactor, in which the coke selectivity obviously decreased from 32.3% to 12.6%. To investigate the proper condition for hydrogenation and improve the integral upgrading technology, catalytic hydrogenation of simulated bio-oil under mild conditions (2–4 MPa, 200–300°C) was carried out in this work. Unsaturated double bonds in the reactants were saturated over 3%Pd/nano-SiO_2 catalysts. As a result, the integral $(H/C)_{eff}$ of bio-oil was improved remarkably, as well as the activity and stability of subsequent cracking process. Typical compounds in the bio-oil distilled fraction, including hydroxyacetone, cyclopentanone, acetic acid, guaiacol, phenol and furfural, were selected and dissolved in ethanol.

1 Experimental

1.1 Chemicals

Nano-SiO_2 and $PdCl_2$ were purchased from Aladdin Industrial Corporation. Pd/nano-SiO_2 catalysts used for hydrogenation were prepared by incipient wetness impregnation and loading amount of Pd was 3% (weight percentage). A certain amount of $PdCl_2$ was dissolved in the deionized water at ambient temperature and the pH value was adjusted to 3 by adding hydrochloric acid. The calcined nano-SiO_2 was then added into the $PdCl_2$ solution. After stabilization for 12 h, the mixture was dried in an oven at 110°C overnight. Finally, the sample was calcined at 550°C for 6 h and sieved to 40–60 mesh before the experiment.

The selected model compounds were hydroxyacetone and guaiacol (Alfa Aesar), cyclopentanone (Aladdin), acetic acid, phenol and furfural (Sinopharm Chemical Reagent Corporation). The weight ratio was set based on the distribution of different chemical families in the bio-oil distilled fraction[13]. The weight ratio of simulated bio-oil and ethanol (Sinopharm Chemical Reagent Corporation) was 1:1. Consequently, the final composition of the feedstock was 20% hydroxypropanone, 5% cyclopentanone, 15% acetic acid, 5% guaiacol, 2.5% phenol, 2.5% furfural and 50% ethanol (weight percentage).

1.2 Catalytic run

Catalytic experiments were carried out in a fixed bed reaction system, as shown in Figure 1. The reactor was a stainless steel tube with an inner diameter of 8 mm. The catalysts (3 g) were placed in the reactor and supported by quartz wool. Pd/nano-SiO_2 was reduced at 350°C for 2 h in 30 mL/min H_2 prior to the experiment. The reactants were introduced by a high-performance liquid chromatograph (HPLC) pump and then entered into the reactor after nebulization with H_2. The reaction pressures were maintained by 30 mL/min H_2. The weight hourly space velocity (WHSV) of the reactants was set to be 1 h^{-1}. The outlet gas was cooled by a condenser and separated into liquid products and non-condensable gaseous products. The reaction temperatures and pressures ranged from 200 to 300°C and from 2 to 4 MPa, respectively.

The gaseous products were quantified online by a gas chromatograph (GC; Huaai GC 9560). The oven temperature remained at 50°C for 3 min and increased to 120°C at 5°C/min, then kept for 13 min. The homogeneous-phase liquid products were obtained in the mild hydrogenation process. The chemical structure of compounds was determined by gas chromatograph-mass spectrometer (GC-MS; TraceDSQII) system and the relative contents were calculated through the area normalization method. A DB-WAX polar column (Agilent Technologies) was used for GC-MS. The oven temperature was maintained at 40°C for 1 min and elevated to 240°C at 8°C/min, then held for 10 min. A gas chromatograph (Agilent 7890A) was used to quantify the liquid products by external standard method to calculate the reactant conversion. The INNOWAX capillary column was used and temperature programming was the same as GC-MS. The $(H/C)_{eff}$ of liquid products was determined by ultimate analysis (Vario Micro Element Analyzer). The conversion of each reactant (X_i), overall conversion of simulated bio-oil (X) and product selectivity (S_j) were defined by Eq. (2)–(4). When calculating the liquid product selectivity, the unconverted reactants were excluded. The symbol "m" in the equation is denoted as the mass of corresponding substances.

$$x_i = \frac{(m_i)_{in} - (m_i)_{out}}{(m_i)_{in}} \times 100\% \quad (2)$$

$$x = \sum x_i m_i \times 100\% \quad (3)$$

$$s_j = \frac{m_j}{(m_{reactants})_{in} - (m_{reactants})_{out}} \times 100\% \quad (4)$$

The distribution and Pd particle size were detected by high-resolution transmission electron microscopy (TEM,