

Research article

Production of aromatic hydrocarbons by hydrogenation-coccracking of bio-oil and methanol



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ABSTRACT

The hydrogen-lacking characteristic of bio-oil leads to a low yield of desired product and easy coke formation during its cracking for aromatic hydrocarbon generation. Therefore, an improved hydrogenation-coccracking process which could supply hydrogen in two stages to enhance aromatic hydrocarbon production was developed in this study. Furfural was chosen as the model compound of bio-oil to be coprocessed with methanol, and hydrogen supply behavior was regulated by varying hydrogenation temperature and methanol coprocessing ratio in the feedstock. The results showed that raising hydrogenation temperature in the range of 150–250 °C increased the hydrogenation degree and thus facilitated aromatic hydrocarbon production in the cracking stage. However, a further increase of temperature to 300 °C caused low-reactivity saturated gaseous hydrocarbon production, which decreased the ultimate oil phase yield. The increase of methanol coprocessing ratio in feedstock strengthened the hydrogen supply in the cracking stage, which could promote the deoxygenation of furanic ring and consequently increased aromatic hydrocarbon yield and reduced coke formation. By coprocessing 25% furfural and 75% methanol with a hydrogenation temperature of 250 °C, the oil phase yield reached 26.4% with an aromatic hydrocarbon content of 94.4%. Finally, the hydrogenation-coccracking mechanism was proposed according to the experimental results.

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1. Introduction

Due to the increasing demands for energy and the unsustainability of conventional fossil resources, the utilization of renewable resources is of great significance. Biomass, which is environmental friendly, holds an important position among the renewable energy all over the world. The bio-oil obtained from biomass fast pyrolysis has the advantages of high energy density and convenience for transportation. However, its application is limited due to its high oxygen content and poor stability and thus further refining is necessary. Catalytic cracking over zeolite catalysts is an important bio-oil upgrading technology. It can remove the oxygen in bio-oil in the forms of CO₂, CO and H₂O, and aromatic hydrocarbons in the gasoline distillation range can be obtained [1]. Therefore, it is a promising way to utilize bio-oil instead of fossil fuels to produce aromatic hydrocarbons. However, the problems of low aromatic hydrocarbon yield and serious catalyst deactivation by coke formation exist in the bio-oil direct cracking process. Zhang et al. [2] studied the direct cracking of bio-oil over HZSM-5 catalyst, and the results showed that the carbon selectivity of coke was up to 49.5%. Thus, the improvement of cracking process is necessary to increase the conversion efficiency of bio-oil. In view of the extremely complicated

composition of bio-oil, model compounds were often studied first when conducting cracking process improvement [3].

Furfural is a typical component in bio-oil, and the furanic ring and the aldehyde functional group in it are representative. It was reported that the content of furanic ring in the bio-oil volatile was about 24.3% [4]. In the study of furan cracking over ZSM-5 catalyst by Cheng et al. [5], the conversion of furan was only 48% and a high coke yield of 33.8% was obtained. Meanwhile, for the cracking of aldehyde compounds [6], it was also found that the conversion efficiency to hydrocarbons was low and the catalyst was easily coked and deactivated. Therefore, choosing furfural as a model compound of bio-oil to study the improvement of cracking process has a great referential significance for solving the coking problem during bio-oil cracking.

Researches have mentioned [7,8] that the coking problem in bio-oil cracking was attributed to the high oxygen content and high degree of unsaturation. When dehydration reaction happens to remove oxygen, some hydrogen is taken away, and combining with the low hydrogen content in the feedstock, the formation of cracking products with low H/C ratios is favored [8]. Therefore, if enough hydrogen can be provided for cracking, the coke formation can be suppressed and more liquid aromatic hydrocarbons can be produced. Now there are two ways to supply hydrogen for the cracking process: one is hydrogenation pretreatment of feedstock before cracking [9,10] and the other is coprocessing some hydrogen-rich compounds during cracking [11].

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Hydrogenation pretreatment is usually conducted under mild conditions. It aims at saturating some unsaturated compounds in bio-oil, such as compounds with carbon-carbon double bond and aldehydes. As a result, the coking problem in cracking due to the hydrogen-lacking property of feedstock was relieved. The research of bio-oil hydrogenation-cracking carried out by Vispute et al. [9] showed that, some unsaturated compounds like aldehydes and ketones were turned into the corresponding alcohols through mild hydrogenation, and because of the increase of hydrogen content in feedstock, the coke yield was reduced in the cracking stage. For the two-stage hydrogenation-cracking process, the hydrogenation degree of bio-oil components in the hydrogenation stage, which corresponds to the amount of hydrogen supplied, may affect the subsequent cracking process. In the studies of hydrotreatment of typical bio-oil components by Shin et al. [12] and Gutierrez et al. [13], it was found that the double bonds were saturated by hydrogenation at a low temperature first and then hydrodeoxygenation took place as the increase of hydrogenation temperature. Therefore, it is important to regulate the hydrogen supply by selecting the suitable hydrogenation temperature so as to improve the overall efficiency of the hydrogenation-cracking process. In addition, coprocessing hydrogen-rich materials like methanol can also supply hydrogen and thus promote the transformation of bio-oil. In the study of cocracking of bio-oil model compounds and methanol, Mentzel et al. [8] pointed out that the existence of methanol could suppress coke formation and extend the lifetime of catalyst. For the cocracking process, the coprocessing ratio will determine the amount of hydrogen that can be supplied. The results of cocracking of hydroxyacetone and ethanol obtained by Wang et al. [14] showed that, a too low coprocessing ratio of ethanol would lead to the low selectivity and quality of the generated oil phase. Meanwhile, taking the economy into consideration, it is necessary to find a suitable coprocessing ratio for cocracking.

Taking the inferior cracking characteristics of furfural into consideration, hydrogenation pretreatment and methanol-coprocessing were combined in this work to supply hydrogen for the conversion of furfural to aromatic hydrocarbons. The regulation of hydrogen supply was conducted by varying the hydrogenation temperature and the methanol coprocessing ratio.

2. Experimental

Furfural (FF) was purchased from Shanghai Lingfeng chemical co., LTD, and methanol (MeOH) was purchased from Sinopharm chemical reagent co., LTD. The hydrogenation catalyst Ni-Cu/SiO₂ was prepared by incipient impregnation method, and the loading amounts of Ni and Cu were both 5 wt.%. Before the hydrogenation experiment, the catalyst was reduced at 500 °C for 2 h with a H₂ flow rate of 50 mL/min. HZSM-5 (Si/Al = 25) zeolite was used as the cracking catalyst.

The experimental system is shown in Fig. 1. For the single-stage hydrogenation experiment, only one reactor was used, while two reactors were connected for two-stage hydrogenation-cocracking process. 2 g of Ni-Cu/SiO₂ and HZSM-5 catalysts were supported on quartz wool and packed in the hydrogenation and cracking reactors, respectively. The mixed reactants were pumped by a HPLC pump. H₂ was used to maintain the reaction pressure, and its flow rate was 50 mL/min. The weight hourly space velocity (WHSV) of the reactants was kept at 2 h⁻¹. Liquid product and non-condensable gas were separated and obtained after the condensation of outlet gas from the reactor. Each operation ran for 5 h. The cracking temperature and system pressure were set at 400 °C and 4 MPa, respectively. The effects of different hydrogenation temperatures (150 °C, 200 °C, 250 °C and 300 °C) and different methanol coprocessing ratios in the feedstock (0%, 25%, 50%, 75% and 100%) on hydrogenation-cocracking were studied. Here, the coprocessing ratio was defined as the mass percentage of a specific compound in the feedstock.

The obtained products included gaseous product, liquid product and coke. The gaseous products were analyzed quantitatively by a gas

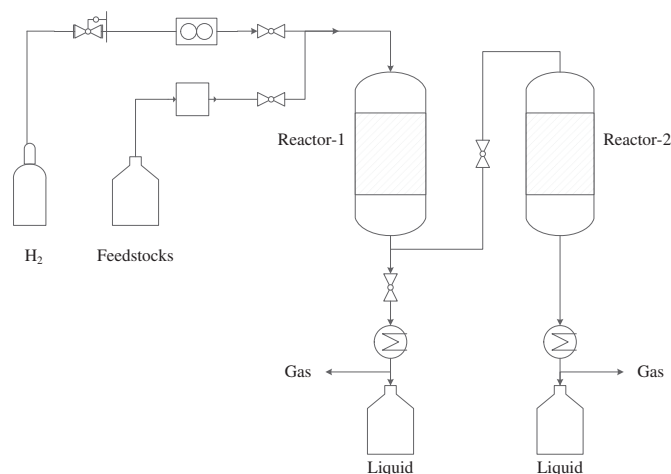


Fig. 1. Apparatus flowchart of hydrogenation-cocracking reaction.

chromatograph (Agilent 6820). The liquid product obtained from one-stage hydrogenation was homogeneous, while the liquid product after cracking contained separable oil phase and aqueous phase. The homogeneous liquid product from hydrogenation and oil phase product from cracking were analyzed qualitatively by a gas chromatography-mass spectrometry system (GC-MS), and then analyzed quantitatively through the area normalization method. The residual reactants in the liquid products were quantified by a gas chromatography. The mass of the coke on the surface of catalyst was measured by thermogravimetry analysis. The calculation formulas of reactant conversion and product yield are shown as follows, in which the symbol “m” represents the mass of the corresponding substances and the subscripts “in” and “out” represent inlet and outlet of the reaction system.

$$\text{Conversion} = \frac{(m_i)_{\text{in}} - (m_i)_{\text{out}}}{(m_i)_{\text{in}}} \times 100\% \quad (i = \text{FF}, \text{MeOH}) \quad (1)$$

$$\text{Yield} = \frac{m_i}{(m_{\text{Liquid Reactants}})_{\text{in}}} \times 100\% \quad (i = \text{Liquid}, \text{Gas}, \text{Coke}) \quad (2)$$

3. Results and discussion

3.1. Hydrogen supply regulation by varying hydrogenation temperature

3.1.1. Hydroprocessing behavior

Considering that the hydrogenation temperature may affect the hydrogenation degree of furfural which corresponds to the amount of hydrogen supplied in the hydrogenation stage and thus result in different cracking performances, the hydrogenation behaviors of furfural and methanol at different reaction temperatures were studied first. A mixture of 25% furfural and 75% methanol was used as the feedstock.

The conversions of the reactants in hydroprocessing at different temperatures are shown in Fig. 2(a). Furfural was almost completely converted at all hydrogenation temperatures, while the conversion of methanol remained at a low level in the range of 150–250 °C and a little increase at 300 °C was observed. The yields of products in hydroprocessing at different temperatures are shown in Fig. 2(b). The liquid product yield was above 95% between 150 °C and 250 °C, and it decreased to 85.2% at 300 °C. The yields of CO_x and gaseous hydrocarbons were low in the temperature range of 150–250 °C, while higher yields of CO_x and gaseous hydrocarbons were observed at 300 °C. In particular, the gaseous hydrocarbon yield (mainly saturated hydrocarbons) reached to 7.3% at 300 °C. This illustrated that decomposition and hydrodeoxygenation reactions were enhanced at high temperature, which generate more gaseous hydrocarbons. In the study of

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