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Upgraded bio-oil production via catalytic fast co-pyrolysis of waste cooking oil and tea residual

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ABSTRACT

Catalytic fast co-pyrolysis (co-CFP) offers a concise and effective process to achieve an upgraded bio-oil production. In this paper, co-CFP experiments of waste cooking oil (WCO) and tea residual (TR) with HZSM-5 zeolites were carried out. The influences of pyrolysis reaction temperature and H/C ratio on pyrolytic products distribution and selectivities of aromatics were performed. Furthermore, the prevailing synergetic effect of target products during co-CFP process was investigated. Experimental results indicated that H/C ratio played a pivotal role in carbon yields of aromatics and olefins, and with H/C ratio increasing, the synergetic coefficient tended to increase, thus led to a dramatic growth of aromatics and olefins yields. Besides, the pyrolysis temperature made a significant contribution to carbon yields, and the yields of aromatics and olefins increased at first and then decreased at the researched temperature region. Note that 600 °C was an optimum temperature as the maximum yields of aromatics and olefins could be achieved. Concerning the transportation fuel dependence and security on fossil fuels, co-CFP of WCO and TR provides a novel way to improve the quality and quantity of pyrolysis bio-oil, and thus contributes bioenergy accepted as a cost-competitive and promising alternative energy.

1. Introduction

The dependence on fossil energy and transportation fuel together with environmental impacts of greenhouse gas emissions associated with fossil fuels have become an issue of common concern. According to some literatures (Kuo and Wu, 2016; Zhao et al., 2015), the coal reserves will be unavailable at 2112, and it will be the only fossil energy after 2042. For this regard, renewable and alternative resources which dominate the advantages of sustainable application and energy saving have been investigated widely around the world (Abnisa and Wan Daud, 2014). Note that biomass energy has attracted more and more attention for the features of low price, renewability and high abundant in raw materials, which can relieve the dependence on fossil fuels and enhance the energy security (Hwang et al., 2014; Isaksson et al., 2014). Beside the influence of shortage of fossil fuels, environmental concerns also play a vital role in advancing the development of renewable energy (Houshfar et al., 2014; Turrado Fernández et al., 2015). In the past decades, the environmental issues have drawn public attentions in the world, especially in China, the environmental concerns have caused diverse baneful influences. Acid rain, ozone layer depletion, and global climate change are negative effects that have resulted from the widely consumption of fossil fuel (Abnisa et al., 2013, 2014; Abnisa and Wan Daud, 2014, 2015). In order to mitigate the contradiction between environment protection and economic development, it seems that some measures should be urgently made to control the primary pollutant emissions (Alper et al., 2014). Considering the prominent contributes to reducing the dependence on fossil fuels and decreasing the serious environmental effects, it should be noted that bioenergy is one of the most promising alternatives since it is the only renewable and non-polluting energy source that can be converted into several types of fuels, such as bio-fuel, char, and gas (Upham et al., 2011; Zhou et al., 2015).

Catalytic fast pyrolysis (CFP), which is known as an *in situ* upgrading process, has attracted more and more attention for the capacity of converting biomass energy into liquid products or high value-added chemicals (Ghorbel et al., 2015). Compared with hydrodeoxygenation (HDO) process, which needs complicated equipment and high reaction conditions, CFP is cost-competitive and more efficient (Abnisa and Wan Daud, 2014). However, the quality and quantity of liquid products obtained from CFP of

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biomass is so low that some efforts should be further made to achieve an upgraded bio-oil production. In this regard, catalytic fast co-pyrolysis (co-CFP) can be accepted as a prevalent alternative. Researches on co-CFP have found that the pronounced advantage of this novel pyrolysis process is to improve the grade of bio-oil concisely and effectively (Abnisa and Wan Daud, 2014; B. Zhang et al., 2015a). For example, co-CFP can be realized without any improvement of pyrolysis equipment and system process of CFP, thus leads to cost-competitive and energy conservation. A defined parameter called H/C molar ratio is a critical key during the co-CFP process (B. Zhang et al., 2015a), and the expression can be written as follows:

$$H/C = \frac{H - 2O - 3N - 2S}{C} \tag{1}$$

where H, O, N, S and C are the mole percentages of hydrogen, oxygen, nitrogen, sulfur, and carbon in samples, respectively. Note that the H/C ratio of biomass is only between 0and 0.3, which is hydrogen-deficient and limits the conversion of bioenergy into high-grade liquid products. B. Zhang et al. (2015b) carried out several co-CFP experiments with different H/C ratios, and their experimental results proved that a strong correlation (known as synergetic effect) existed between H/C ratio and the quality of bio-oil products. Brebu et al. (2010) co-pyrolyzed pine cone with synthetic polymers to analyze the influence of biomass and plastic on the production yields, and they indicated that higher quality of bio-oil could be achieved compared to the pyrolysis of biomass alone. Nevertheless, the effects of H/C ratio and pyrolysis reaction temperature on synergetic effect have not been studied thoroughly yet.

It was worth noting that tea is a significant symbolize of traditional culture in China and is consumed all around the world. The International Tea Committee (ITC) reported that the global tea yield reached 406.7 million tons in 2011 (Kraujalyte et al., 2016; Sharpe et al., 2016). According to the statistical data of Euromonitor, Turkey, Ireland, and England occupied the top three consumption of tea (Sharpe et al., 2016). Note that tea residual (TR) is discarded arbitrarily in daily life, thus leads to a high pressure for waste management and environment protection. Therefore, a pronounced process to utilize TR is catalytic fast pyrolysis, which can convert it into liquid products. However, the very limited H/C ratio of TR restricts the achievement of high quality bio-oil products, it seems that co-pyrolysis TR with other hydrogen-rich feedstock samples can provide a promising management of tea residual.

Waste cooking oil (WCO), which is derived from cooking oil, such as sunflower, soybean, coconut and so forth, has already been a public concern in the world. Note that a prospective application approach is to utilize WCO as a raw material to generate bio-fuel, which makes significant contribution to addressing the environmental concerns and boosting the development of energy production. The conventional utilization of WCO lies in the biodiesel production through transesterification of triacylglycerides (Chen et al., 2014), which a pre-treatment step is necessary due to the complex constitutes of WCO (Karmee, 2016). Furthermore, a large amount of glycerol would be produced during the transesterification procedure (Li et al., 2016), which necessitates a corresponding costly extraction process for its recovery. However, compared with transesterification, catalytic cracking of WCO to produce bio-oil has been an attractive approach for waste management due to the low cost, relatively high conversion rates and both the energetic and chemical values (Lam et al., 2016). As WCO is a hydrogen-rich feedstock, co-CFP of it with TR will encourage the creation of innovative novel concepts in upgrading the quality and quantity of bio-oil, promoting the waste management, enhancing energy security, and solving environment concerns. It is important to point out that, to the best of our knowledge, researches on co-CFP of WCO with TR are limited. In this contribution, co-CFP of WCO and TR over HZSM-5 zeolites was conducted using Py-GC/MS. The influences of pyrolysis temperature and H/C ratio on carbon yields and selectivities of target products were investigated. Furthermore, a critical key laid with the synergistic effect between different feedstocks during the co-CFP process, and in our work, the corrections between synergistic effect and pyrolysis temperature and H/C ratio were analyzed.

2. Experimental

2.1. Materials

WCO was achieved from a canteen in Xuanwu District, Nanjing, Jiangsu province, China. The results of ultimate analysis of WCO were as follows: 75.61 wt.% carbon, 11.08 wt.% hydrogen, 11.63 wt.% oxygen, and 1.83 wt.% nitrogen, and the H/C molar ratio of WCO was 1.43. TR was obtained from a garbage in Nanjing, Jiangsu province, China. The TR specimens were dried and crushed, and then were sifted through a 40-mesh sieve before conducting the pyrolysis experiments. Simultaneously, the elemental analysis of dried TR was carried out and the results were as follows: 47.97 wt.% carbon, 37.75 wt.% oxygen, 6.48 wt.% hydrogen, and 3.56 wt.% nitrogen. The H/C molar ratio of TR was 0.024.

2.2. Experimental methods

During the co-CFP experiments of WCO and TR, a CDS Pyroprobe 5200 pyrolyzer was applied to conduct the pyrolysis process. Note that the probe is heated by platinum resistance and possesses an open ended quartz tube. Prior to the experiment, some packed quartz wool, 0.50 mg HZSM-5 zeolite and 0.50 mg feedstock specimens (WCO and TR) were put in the quartz in order (as shown in Fig. 1). Simultaneously, the heating rate was fixed at 20 °C/ms and the pyrolysis temperature was controlled for 20 s. A high purity helium (99.999%) was used as carrier gas with a stable flow of 1.0 mL/min, which was supplied by Nanjing Maikesi Nanfen Special Gas Co., Ltd.

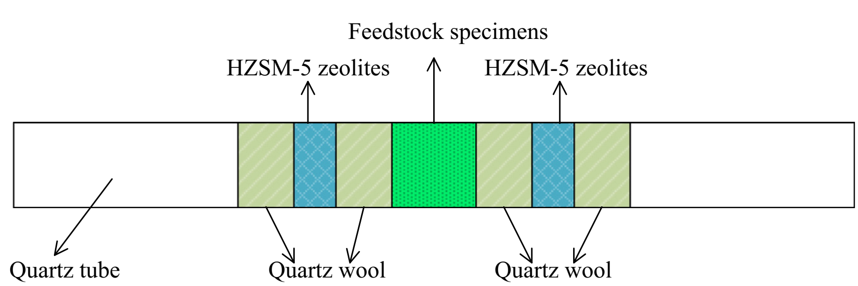

Fig. 1. Structure chart of the quartz tube.

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