



Catalytic fast co-pyrolysis of biomass and food waste to produce aromatics: Analytical Py–GC/MS study



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HIGHLIGHTS

- We promoted the production of aromatics by catalytic fast co-pyrolysis process.
- Co-pyrolysis temperature of 600 °C was optimal for the formation of aromatics.
- Content of aromatics increased with increasing hydrogen to carbon effective ratio.
- There was an apparent synergistic effect between biomass and food waste.

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ABSTRACT

In this study, catalytic fast co-pyrolysis (co-CFP) of corn stalk and food waste (FW) was carried out to produce aromatics using quantitative pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS), and ZSM-5 zeolite in the hydrogen form was employed as the catalyst. Co-CFP temperature and a parameter called hydrogen to carbon effective ratio (H/C_{eff} ratio) were examined for their effects on the relative content of aromatics. Experimental results showed that co-CFP temperature of 600 °C was optimal for the formation of aromatics and other organic pyrolysis products. Besides, H/C_{eff} ratio had an important influence on product distribution. The yield of total organic pyrolysis products and relative content of aromatics increased non-linearly with increasing H/C_{eff} ratio. There was an apparent synergistic effect between corn stalk and FW during co-CFP process, which promoted the production of aromatics significantly. Co-CFP of biomass and FW was an effective method to produce aromatics and other petrochemicals.

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1. Introduction

Currently a range of conversion routes has been researched to obtain high-quality liquid fuels (hereinafter “bio-oil”) from lignocellulosic biomass, and one of the most prevailing and promising methods is catalytic fast pyrolysis (CFP) technology (Wang et al., 2013; Du et al., 2013a; Lu et al., 2009), which employs fast pyrolysis and catalytic upgrading processes. When pyrolysis vapors pass through certain catalysts, it is expected that the produced bio-oil can be refined before condensation. Over the past years, dozens of microporous, mesoporous and macroporous catalysts have been well studied for biomass CFP process, such as ZSM-5, MCM-41, FCC, LOSA-1, SBA-15, CNT and their modified derivatives (Zhang et al., 2014a; Iliopoulou et al., 2007; Lee et al., 2014; Zhou et al., 2014). Among them, ZSM-5 zeolite has been proved to be one of the most

effective catalysts because it can accomplish the significant removal of oxygenated organic compounds and favor the production of aromatics (Du et al., 2013b; Xie et al., 2014; Dickerson and Soria, 2013). The 3-dimensional pore system of ZSM-5 zeolite contains 10-membered rings with Z-shaped channels of 0.51×0.55 nm and straight channels of 0.53×0.56 nm. When the primary pyrolysis vapors diffuse into the internal pores of ZSM-5 catalyst, they will be adsorbed on the acid sites and be converted into hydrocarbons through serious deoxygenation reactions. Besides, the ZSM-5 pore diameter is similar to the dynamics diameters of benzene, toluene and xylene, so ZSM-5 catalyst has a significant shape-selective effect on the production of aromatics.

The main challenge for biomass CFP conversion with zeolites is to promote the production of hydrocarbons. Chen et al. (1988) introduced a parameter called hydrogen to carbon effective ratio (H/C_{eff} ratio) to indicate the relative hydrogen content of different feedstocks. The H/C_{eff} ratio is defined on the assumption that all the heteroatoms are completely converted to H_2O , NH_3 and H_2S :

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$$H/C_{\text{eff}} = \frac{H-2O-3N-2S}{C} \quad (1)$$

The C, H, O, N and S in Eq. (1) are the mole number of carbon, hydrogen, oxygen, nitrogen and sulfur, respectively, in a molecular form. Solid biomass is hydrogen-deficient. The H/C_{eff} ratio of lignocellulosic biomass and its derivatives is only between 0 and 0.3 (Valle et al., 2014; Czernik and Bridgwater, 2004). According to previous literature (Chen et al., 1986), feedstocks with H/C_{eff} ratio <1.0 cannot be economically converted to premium petrochemicals over ZSM-5 zeolite. Zhang et al. (2011) carried out in-depth research to investigate the catalytic conversion of ten different biomass-derived feedstocks with different H/C_{eff} ratios in a fixed-bed reactor using ZSM-5 catalyst, and they stated that the yields of primary premium products, such as aromatics or olefins, could be increased by increasing the H/C_{eff} ratios in feed. A feasible way to improve the overall H/C_{eff} ratio of feedstocks is catalytic fast co-pyrolysis (co-CFP) of biomass with addition of another hydrogen-rich feedstock that has a high H/C_{eff} ratio, and it has been proved that some feedstocks with a high H/C_{eff} ratio can provide hydrogen for biomass conversion (Dorado et al., 2014).

As another potential hydrogen supplier, food waste (FW) was introduced to be co-fed with biomass to promote the production of hydrocarbons in this paper. In China, FW currently accounts for the largest fraction (>40 wt.%) in municipal solid waste generated by households (Zhao et al., 2010; Luo et al., 2010), and it has caused serious adverse effects on human health and environment. In 2010, the total amount of FW reached nearly 90 million tons in China (Zhang et al., 2014b). Appropriate treatment and disposal of this large amount of FW is a challenging task and has caused increasing concern. Nowadays, the main methods for handling FW mainly include landfill, incineration and anaerobic digestion. However, they all can cause secondary environmental pollution and have become less acceptable (Ahmed and Gupta, 2010; Caton et al., 2010). As FW contains much energy, an effective technique is catalytic pyrolysis which could achieve significant solid waste reduction in volume and convert no-value FW into fuels (Liu et al., 2014). FW is mainly composed of uneaten food and food manufacturing leftovers (Hu et al., 2014). Compared to biomass, FW contains more hydrogen and its H/C_{eff} ratio is much higher because of its high content of carbohydrates and lipids (Sun et al., 2014). Therefore, co-CFP of biomass with FW offers the opportunity to increase the overall H/C_{eff} ratio of feedstocks, and we hypothesize that their co-CFP conversion may potentially promote the production of hydrocarbons.

To the best of our knowledge, co-CFP of biomass with FW over ZSM-5 catalyst has been seldomly studied. The purpose of our work was to investigate this coprocessing technique using analytical pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS) to identify if a higher yield of petrochemicals can be obtained, and corn stalk was used as the biomass feedstock. As vital precursors of various industrial products, aromatics were selected as the target products. In this paper, relative contents of aromatics were evaluated and the optimal conditions were determined. This study is obviously beneficial for the practical application of pyrolysis technology.

2. Methods

2.1. Materials

Corn stalk was collected from a farm field in the city of Yangcheng in Jiangsu Province, China. Prior to experiment, corn stalk was pulverized mechanically and sifted through a 40-mesh sieve. The proximate analysis of the air-dried corn stalk was 7.27 wt.% moisture, 82.37 wt.% volatile, 4.06 wt.% ash, and

6.30 wt.% fixed carbon. The elemental composition of the dried corn stalk was 41.77 wt.% carbon, 5.46 wt.% hydrogen, 42.34 wt.% oxygen, and 0.45 wt.% nitrogen. The H/C_{eff} ratio of corn stalk was 0.02. The component analysis of the dried corn stalk was 36.89 wt.% cellulose, 29.33 wt.% hemi-cellulose, and 13.93 wt.% lignin. During the pyrolysis of corn stalk, thermal decomposition of cellulose and hemi-cellulose will lead to the generation of anhydrosugars. Then the anhydrosugars will undergo rearrangement or dehydration reactions to form oxygenates. Meanwhile, thermal decomposition of lignin will lead to the generation of phenols. When these oxygenates pass through the ZSM-5 catalyst layer, some of them will be converted into hydrocarbons (especially aromatics).

FW was obtained from a residential quarter in Xuanwu District, Nanjing, Jiangsu Province, China. The original FW was pretreated to remove plastic and shells. The remaining was consisted of three components (wet basis): white/brown rice (25.08 wt.%), fruits/vegetables (36.18 wt.%), and meat/bones/waste oil (38.74 wt.%), respectively. The FW samples were dried at 105 °C for 24 h in a drying oven, and then also smashed and sieved through a 40-mesh sieve. The proximate analysis of FW samples (on dry basis) was 79.68 wt.% volatile, 10.02 wt.% ash, and 10.30 wt.% fixed carbon. The elemental composition of FW samples (on dry basis) was 43.26 wt.% carbon, 8.59 wt.% hydrogen, 30.25 wt.% oxygen, and 5.12 wt.% nitrogen. The H/C_{eff} ratio of FW was 1.03.

2.2. Catalyst

ZSM-5 zeolite (Si/Al ratio = 50, surface area = 308 m²/g, particle diameter = 2–5 μm) in the hydrogen form purchased from the Catalyst Plant of Nankai University (China), was used as the catalyst in this study.

2.3. Py–GC/MS

Co-pyrolysis experiments were carried out in an analytical CDS Pyroprobe 5200 pyrolyzer (CDS Analytical Inc.). The probe is a resistively heated element and holds an open ended quartz tube. Prior to the experiments, the quartz tube was successively filled with some packed quartz wool, 0.50 mg ZSM-5 catalyst, some packed quartz wool, 0.50 mg corn stalk and FW mixtures in the center, some packed quartz wool, 0.50 mg ZSM-5 catalyst and some packed quartz wool. The schematic cross-section of the quartz tube was shown in Fig. 1. The ZSM-5 catalyst was placed at both sides of the feedstock and acted as fixed beds. Thus, the non-catalytic fast pyrolysis took place first and then the primary

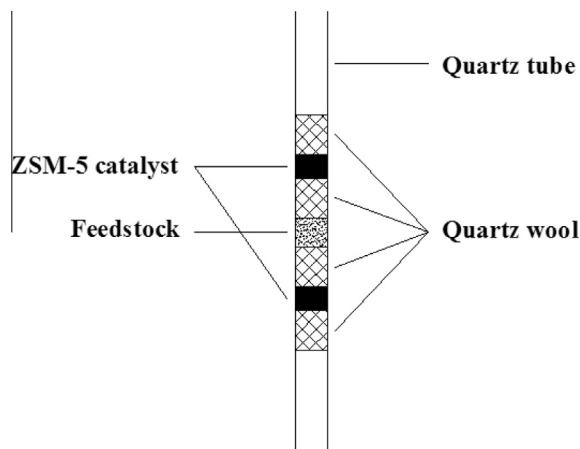


Fig. 1. Schematic cross-section of the quartz tube.

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