Improving the hydrocarbon production via co-pyrolysis of bagasse with bio-plastic and dual-catalysts layout

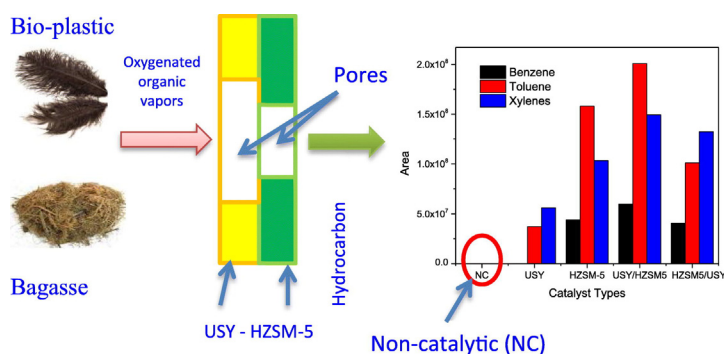Huiyan Zhang [a], Peter Keliona Wani Likun [a,b], Rui Xiao [a,*]

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HIGHLIGHTS

- Co-catalytic pyrolysis of bagasse and bio-plastic was conducted to produce aromatics.
- Dual-catalysts layout was designed to improve aromatic yield.
- Temperature and feed-to-catalyst ratio are crucial for aromatics production.
- The dual-catalysts layout of USY/HZSM-5 outperformed other designs.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Catalytic fast pyrolysis (CFP) of bagasse and bio-plastic (chicken feather keratin) and their mixtures were conducted to produce aromatic hydrocarbons over a HZSM-5, USY, and dual-catalysts layout. The effects of temperature, co-feeding ratios, feed-to-catalyst ratios and dual catalysts on hydrocarbon yields and selectivities were investigated. The results show a general improvement in the aromatic hydrocarbons yields in all cases compared to non-catalytic and pure biomass pyrolysis. The aromatic hydrocarbons increased by 10 fold with the increase of temperature from 400 °C to 700 °C. The aromatic yields increased 1.5 times at co-feeding, 2.0 greater at feed/HZSM-5 ratio of 1:6, 1.2 times at feed/USY ratio of 1:16, and 2.66 times at USY/HZSM-5 scenario. The selectivities towards benzene increased, at higher co-feeding ratios, while that of toluene shows an opposite trend. Xylenes selectivities were less sensitive to the changes of co-feeding ratios. In contrast, the USY catalyst only produced little amount of toluene and xylenes. The dual catalyst design (USY/HZSM-5) resulted in the highest aromatic yields, than other catalyst design scenarios. The pyrolysis temperature is a significant parameter for hydrocarbon production. Co-feeding bagasse and bio-plastic enhanced biomass conversion to aromatic compounds. For any type of zeolite catalyst, there was an optimum feed-to-catalyst ratio that generated maximum hydrocarbons. Dual catalyst layout shows a new opportunity for efficient conversion of biomass materials into hydrocarbons.

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1. Introduction

Petrochemicals derived from petroleum represent essential feedstocks for producing a variety of useful products such as plastics, synthetic fibers, solvents, and pharmaceuticals. The most important of

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these petrochemicals include aromatics (such as benzene, toluene and xylenes) and olefins (such as ethylene, propylene and butadiene) (Carlson et al., 2011; Das and Sarmah, 2015a, 2015b; Li et al., 2014b; Zhang et al., 2012). To decrease the current global rate of fossil fuels consumption, alternative sources of energy have to be identified and made usable. As a potential energy source, lignocellulosic biomass is renewable and abundant that can be converted into the petroleum-like products. A number of conversion routes are put forward to transform solid biomass into biofuels and other high valued products, and among them is the catalytic fast pyrolysis (CFP).

CFP is a promising method for converting lignocellulosic biomass to aromatics and olefins which are essential feedstocks for many factories and high-octane fuels (French and Czernik, 2010; Jackson et al., 2009; Mullen and Boateng, 2010). It involves rapid heating of biomass particles in an inert atmosphere and fast quenching of the pyrolysis vapors. Thus the intermediates species of volatiles (such as anhydrosugars alcohols and phenols) formed in the initial thermal decomposition of biomass are further catalytically transformed to hydrocarbon pools depending on the catalyst properties, via a series of reactions (such as cracking, deoxygenation, oligomerization, and aromatization) over zeolite catalysts (Carlson et al., 2008). Besides, CFP rejected the biomass inherent oxygen as CO, CO_2, and H_2O, which in turn increases the energy density of the final liquid products. The whole transformation process can be completed in a single reactor within short reaction times with satisfactory hydrocarbon yields from a variety of biomass feedstocks (Carlson et al., 2008; Chiang et al., 2014).

Although CFP of lignocellulosic can produce products analogous to petrochemicals, it also produces large quantities of solids residues, including biochar and coke (usually above 30% carbon) (French and Czernik, 2010; Li et al., 2014a). Bio-char herein refers to the primary solid product formed during non-catalytic pyrolysis of biomass materials (Mullen and Boateng, 2010), whereas coke is defined as the deposits on the catalyst surface and in pore channels via heterogeneous reactions of primary vapors (e.g. dehydration of biomass-derived oxygenates) at the catalyst sites of catalysts (Mullen and Boateng, 2010; Zhang et al., 2011). The coke usually blocks the catalyst pores reducing the catalyst performance. Because the coke deposits would lead to rapid deactivation, the subsequent conversion efficiency of pyrolysis vapors decreases significantly during CFP process (Jackson et al., 2009; Valle et al., 2012). Thus it represents a practical challenge to the development of CFP process which needs to be overcome.

Generally, researchers found that coke yield depends on effective hydrogen index (also called hydrogen to carbon effective ratio, H/C_{eff}) of the biomass feedstocks (French and Czernik, 2010; Zhang et al., 2011), which reflects the relative abundance of hydrogen in a feedstock and calculated according to Eq. (1) (Chen et al., 1986). Biomass and its derivatives, on the other hand, has H/C_{eff} ratio only between 0 and 0.3 (Czernik and Bridgwater, 2004; Valle et al., 2014). According to Chen et al. (1986), feedstocks with the H/C_{eff} ratio < 1.0 cannot be economically converted to premium petrochemicals over ZSM-5 zeolite.

$$\frac{H}{C_{eff}} = \frac{H-2(O)}{C} \tag{1}$$

where, H, O, and C are the number of moles of hydrogen, oxygen, and carbon in the biomass, respectively.

A viable way to improve the overall H/C_{eff} ratios in hydrogen-deficient reactants such as biomass is to co-pyrolyze it with another hydrogen-rich reactant that has higher H/C_{eff} ratio. To minimize coke formation and improve hydrocarbons production from CFP of biomass, researchers have tried co-feeding of biomass (pine wood) with alcohols (such as methanol and butanol, and plastics) such as polyethylene and polypropylene which have high H/C_{eff} ratio (Jakab et al., 2000; Zhang et al., 2012).

Although several researchers have studied co-pyrolysis of biomass and plastics, none of them have considered utilization of bio-plastics

which is one of the hydrogen-rich biomass with H/C_{eff} ratio more than unity. Keratinous bio-plastic including horns, hooves, and feather, estimated to be 5,000,000 tones/year remain as a waste by-product of various industries that could lead environmental pollution, among which poultry feather is the most abundant keratinous waste material (Brebu and Spiridon, 2011). It is, therefore, still unknown how these two feedstocks would interact with each other and with single and dual catalyst layout during the co-CFP process.

The main objective of this study was to investigate co-pyrolysis of sugarcane bagasse with bio-plastic (chicken feathers waste) and their mixtures using pyroprobe coupled with Agilent gas chromatogram-mass spectrometer (Py-GC/MS) with a single (USY and HZSM-5) and dual (USY/HZSM-5 and HZSM-5/USY) catalyst layout. The product distributions were analyzed to evaluate the interactions between sugarcane bagasse and bio-plastic when co-pyrolyzed under single and dual zeolite catalyst layout.

2. Materials and methods

2.1. Materials

Sugarcane bagasse and bio-plastic (herein referred to chicken feather) were collected from the local market in Nanjing city, Jiangsu province, China. The bagasse was first dried at 105 °C in the oven overnight, then ground and sieved to 150 μm. The bio-plastic, on the other hand, was tight into a bundle and then brushed on an abrasive surface, resulting in fine powder, and then sieved to 150 μm particle size. Bagasse-to-bio-plastic mixtures were prepared at the ratios of 1:1, 1:2, 1:3, and 1:4. Two zeolite catalysts used were USY and HZSM-5. Both catalysts were heated at 105 °C for about 2 h to liberate water prior to the tests. The Si/Al ratio for HZSM-5 and USY was 30.

2.2. Experimental

Co-pyrolysis experiments were conducted in an analytical CDS pyroprobe 5200 pyrolyzer (CDS Analytical Inc.). The pyroprobe is a resistively heated platinum filament which holds an open-end quartz tube set to furnace and interface temperatures of 600 °C and 300 °C, respectively. The dimensions of the quartz tube were 25 mm long and 2 mm (i.d). The schematic of catalysts and biomass layout for all cases were shown in Fig. 1. Prior to each experiment, the sample and the catalyst were prepared in the following manner. A wool was inserted into the quartz tube, 0.5 mg of a catalyst was put carefully after the wool, second wool was placed, 0.5 mg of sample was put, then wool, catalyst and finally wool. In the case of dual catalyst layout, the two catalysts were first positioned on the both side in the similar method with the reactant in the middle. The filled quartz tube was then loaded into pyroprobe via a holder. The platinum filament was kept at 600 °C for the 20 s and the
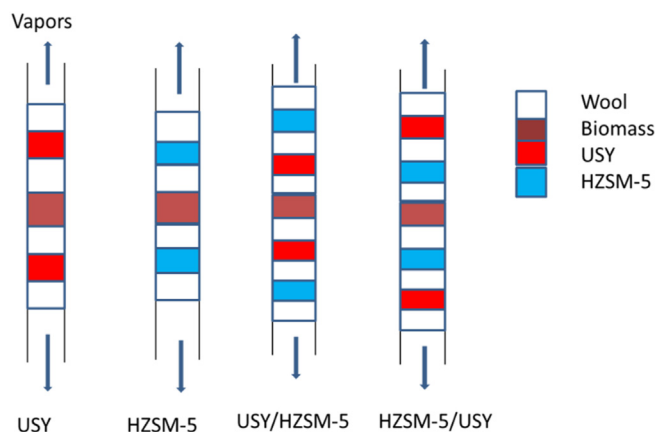

Fig. 1. Single and dual catalysts layout in the quartz tube.