



In situ catalytic conversion of biomass fast pyrolysis vapors on HZSM-5[☆]

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ABSTRACT

In situ catalytic conversion of biomass fast pyrolysis vapors was carried out on HZSM-5 with varying Si/Al ratios (ranging from 20 to 300) at 450 °C. The effects of Si/Al ratios of HZSM-5 zeolites on the distribution of biomass fast pyrolysis products and carbon deposits on catalysts were investigated. It was quite remarkable that after in situ catalytic conversion the amount of light phenols and hydrocarbons increased significantly while that of heavy phenols decreased a lot. Besides, the yield of cyclopentenones with relatively low oxygen content generally increased. It also indicated that as the Si/Al ratios of HZSM-5 increased, the amount of hydrocarbons and light phenols was found to drop greatly. The amount of carbon deposits was found to be around 8.5% with the exception of HZSM-5 with the Si/Al ratio of 300, which is much lower. Moreover, the carbon deposits yield dropped gradually with increasing Si/Al ratios of HZSM-5. Calcination of spent catalysts at 600 °C helped to restore the catalytic activity to a large extent despite a relatively lower efficiency of deoxygenation. Results indicated that HZSM-5 with relatively high acidity displayed great catalytic performance.

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1. Introduction

Fast pyrolysis is considered as a promising alternative method to convert biomass into bio-oil. However, pyrolyzed bio-oil which is an extremely complex mixture of organic chemicals has its own drawbacks. It is notorious for exhibiting high viscosity, poor volatility, low heating value, high oxygen content, and high acidity. Besides, its thermal instability along with its tendency to age with time severely deteriorates its desirable properties as a fuel [1]. Therefore, it is necessary to upgrade the crude bio-oil before being used as vehicle fuel.

Various techniques to upgrade bio-oil, such as hydrotreatment [2–5], catalytic cracking [6], emulsification and solvent addition [7] have been investigated extensively. Among the above techniques, catalytic cracking is favored for its effectiveness and economical feasibility. Recently, in situ catalytic pyrolysis has attracted a lot of attention of large numbers of researchers. It directly converts biomass to pyrolysis oil while catalytically upgrading pyrolysis vapors in the same reactor. It is a quite simple solution to upgrade bio-oil by reducing the oxygen content during pyrolysis, which contributes to a lower cost during subsequent bio-oil im-

provement. A large number of researchers did a lot of research on the in situ catalytic conversion of biomass fast pyrolysis vapors [8–17]. Sources of biomass, operating temperatures, and catalysts are known to play a significant role in the composition of fast pyrolysis products. Therefore, quite a number of corresponding works have been done so far. The investigation of several different feedstock such as, wild reed [18], pinewood [19], mixture of palm oil biomass vapors with methanol [20], and duckweed and microalgae [21] employed during in situ catalytic pyrolysis has been reported in recent years. The chemical composition of bio-oil is undoubtedly influenced by the biomass, which mainly consists of three major chemical components: cellulose, hemicellulose, and lignin. The content of the three components differs in different biomass. However, it has been demonstrated that biomass influenced the properties of the bio-oil to a much lesser extent than catalysts did. Since catalysts play a dominant role in upgrading pyrolysis oil by enhancing its desirable characteristics as a fuel, many researchers focus their attention on how catalysts affect the pyrolysis products and screening the most efficient catalysts [19,21–23]. Fortunately, they have made a lot of progress, but that's far from enough. A lot of problems remain unresolved, and more detailed work needs to be done.

It has been demonstrated that zeolites, especially HZSM-5 zeolites, are efficient in lowering oxygen content, displaying a great capability of deoxygenation due to their strong acidity, which is characterized by Si/Al ratios. In fact, acid sites play a dominant role

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Table 1. Elemental analysis of teak wood chips.

C (%)	H (%)	O (%)	N (%)
47.63	5.5	46.73	0.13

in upgrading pyrolysis oil. It is of extreme significance to figure out how acidity influences the pyrolysis products. To our knowledge, although quite a few studies have been reported for in situ catalytic conversion of biomass fast pyrolysis vapors, few researchers have investigated effects of Si/Al ratios of HZSM-5 on the pyrolysis products during in situ catalytic conversion of biomass fast pyrolysis vapors.

In this work, in situ catalytic conversion of biomass fast pyrolysis vapors was carried out over HZSM-5 with varying Si/Al ratios. Regeneration of spent catalysts was also investigated. Results were analyzed and compared to clearly show the impact of zeolites acidity on the chemical composition of the bio-oil.

2. Experimental

2.1. Materials

2.1.1. Biomass

The biomass employed here in the experiments was teak wood chips. The sawdust was grounded and sieved to a particle size of about 0.1 mm. The sample to be used was dried at 130 °C for 240 min in order to eliminate water in the biomass, thus preventing water from entering the reactor and ending up in the bio-oil.

2.1.2. HZSM-5 zeolites

The acidic zeolite catalysts used in the experiments were HZSM-5-22, HZSM-5-30, HZSM-5-70, HZSM-5-100, HZSM-5-300, numbers after HZSM-5 corresponding to Si/Al ratios of the zeolites. The catalysts were purchased from the catalyst company of FuXu (Shanghai, China). The zeolite powder was first pressed into pellets, which were then crushed and sieved to get the ideal particle size. The particle size of HZSM-5 zeolites used here in the experiments was 20–40 mesh. The HZSM-5 zeolites were pretreated at 500 °C for 240 min. The calcinated zeolites were then stored in a dryer for later use.

2.2. Characterization

2.2.1. Elemental analysis

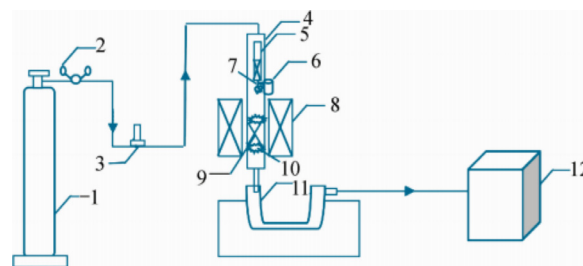
Carbon, hydrogen, nitrogen and oxygen contents of teak wood chips were analyzed with an elemental analyzer (vario micro, Germany). The results are listed in Table 1.

2.2.2. X-ray diffraction (XRD)

X-ray powder diffraction (XRD) was carried out to verify the crystallinity of the catalysts before and after regeneration. The diffraction patterns were recorded with a PAN analytical diffractometer using Cu K α radiation to generate diffraction patterns from powder crystalline samples at room temperature. The samples were scanned for angles between 5° and 50° with a resolution of 0.02°.

2.2.3. Thermogravimetric (TG) analysis of spent catalysts

About 21 mg of spent HZSM-5 zeolites was placed in an alumina pan in a thermogravimetric analyzer (TGA, SDT-Q600, America). The samples were then dried at 180 °C for about 30 min to a constant weight in the atmosphere of N₂. Finally, the temperature was raised from 100 °C to 800 °C at a heating rate of 10 °C/min with the air flow of 120 mL/min.



Scheme 1. Reaction system: 1—Steel cylinder of compressed nitrogen, 2—release valve, 3—mass flow controller, 4—quartz reactor, 5—biomass, 6—magnet, 7—spring coil, 8—heating equipment, 9—catalyst bed, 10—quartz wool, 11—cooler, 12—GC.

2.3. Bio-oil analysis

Liquid bio-oil was analyzed with GC–MS (Agilent 6890/5973). The GC separation was carried out with a HP-5 MS column (30 m × 0.25 mm × 0.25 μm film thickness, Agilent) with helium carrier gas flow of 1 mL/min. The GC inlet was at 290 °C, and a split ratio of 20:1 was employed. The temperature started at 50 °C and was held at 50 °C for 2 min. It was then raised to a temperature of 200 °C with a ramp of 10 °C/min and kept for 2 min, followed by a gradient of 20 °C/min up to a final temperature of 290 °C that was held constant for 10 min. The ionization mode on the MS was electron impact at 70 eV with the *m/z* range at 50–550 au. Peak identification was carried out by comparing all mass spectra to the National Institute of Standards and Technology (NIST) mass spectrum library.

2.4. Fast pyrolysis of biomass

Catalyst to sawdust (0.6 g) ratio was 1:2. At the beginning of the experiment, the pyrolysis tube was successively filled with quartz wool, catalysts and a layer of quartz wool again. It was then placed into the oven. Another smaller quartz tube filled with biomass and a layer of quartz wool was then put inside the pyrolysis tube with a coil spring which was gripped by a magnet supporting it. Nitrogen was fed through the top of the reactor and the gas flow was controlled by a mass flow controller. The cooler was cooled with a mixture of water and ice. The reactor set-up for the experiments was illustrated in Scheme 1. The pyrolysis tube was then heated from room temperature to a final temperature of 450 °C. The temperature was held at 450 °C for about 20 min to stabilize the catalysts. Then the fast pyrolysis experiment started by removing the magnet. Fast pyrolysis vapors of biomass were carried by high-purity nitrogen and passed through the catalysts. As comparison, biomass was also pyrolyzed in the absence of HZSM-5 zeolites.

Non-condensable gases were carried by high-purity nitrogen to a gas chromatograph (SP-6800A) equipped with a TCD detector and a column of Porapark Q (2 M). Liquid bio-oil was analyzed with GC–MS.

2.5. Catalysts regeneration

The partially deactivated catalysts (HZSM-5-22, HZSM-5-75, HZSM-5-300) were regenerated in a muffle furnace at 600 °C with a heating rate of 2 °C/min for 3 h in the presence of air. Most of the deposited coke was removed from the zeolite surface during the regeneration. Subsequent in situ catalytic conversion of biomass was carried out, employing regenerated catalysts.

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