



# Catalytic transformation of lignin to aromatic hydrocarbons over solid-acid catalyst: Effect of lignin sources and catalyst species



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## ABSTRACT

Catalytic pyrolysis of two lignin samples extracted from Chinese fir and rice straw was investigated by Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), concerning the effect of reaction temperatures (550–900 °C) and catalyst species (HZSM-5 (25), HZSM-5 (50), HZSM-5 (210), H- $\beta$  and H-USY) on the production of specific aromatic hydrocarbons (such as benzene, toluene and xylene). The yield of specific aromatic hydrocarbons from catalytic pyrolysis of the two lignin samples with HZSM-5 (25) achieved the maximum value at 650 °C. Formation of p-xylene was remarkably promoted with the decreased Si/Al ratio of HZSM-5 over that of toluene. Production of o-xylene from two lignin samples under 650 °C was selectively enhanced by H-USY due to its compatible pore structure. HZSM-5 (25) with suitable distribution of acidic sites identified by NH<sub>3</sub>-TPD was estimated to be the potential commercial catalyst for production of toluene and p-xylene from catalytic pyrolysis of lignin. Yield of oligo-aromatic hydrocarbons (naphthalene and methylnaphthalene) from catalytic pyrolysis of Chinese fir lignin under 650 °C is remarkably higher than that from rice straw lignin possibly due to their different oxygen contents.

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## 1. Introduction

The huge consumption of fossil fuels and the alarming change of environmental surroundings gave rise to the essential attention on the utilization of renewable sources. Lignocellulosic biomass has been widely used as one of the substitutes for fossil fuel due to its outstanding characteristics as renewable, carbon-neutral, abundant and indigenous [1–3]. Lignin, as one of the three principal components in biomass, is a three dimensional amorphous polymer consisting of methoxylated phenylpropane structures [4]. Generally, lignin from woody biomass only contains guaiacyl and syringyl units in different proportions [5,6]. Lignin from hardwood contains guaiacyl and syringyl units while the lignin from softwood is mainly composed of guaiacyl unit. The lignin from straw (herbaceous biomass) is composed of p-hydroxyphenyl (up to 15% in rice straw), guaiacyl and syringyl units [7,8]. Lignin is considered to be a potential feedstock for the production of petroleum-based fuel and high-valued chemicals with regard to the huge annual amount, low-cost and abundant content of aromatic units [9,10].

Fast pyrolysis is one of the promising methods to convert biomass and its components to value-added chemicals [11–14]. Fast pyrolysis of biomass using magnetic solid base catalyst performed in Py-GC/MS could produce quantity of phenolic-rich bio-oil [14]. The thermo-chemical conversion of Alcell lignin and Asian lignin was investigated using Py-GC/MS at different temperatures, presenting that the production of phenolic compounds achieved the maximum yield at 600 °C for both lignins [11]. And the production of alkylphenol and polyhydroxybenzene at higher temperatures was increased due to the occurrence of demethylation, demethoxylation, decarboxylation, and alkylation.

Distribution of the products from fast pyrolysis of lignin can be substantially changed with the addition of zeolite catalyst. The structure and porosity of zeolite are important properties for the performance on the catalytic pyrolysis of lignin samples [15]. The fast pyrolysis of alkaline lignin with different zeolite catalysts confirmed that pore size and framework played an important role in catalytic process through the limitation of molecular diffusion [16], performing that the highest yield of liquid product (75 wt%) mostly consisted of aromatic hydrocarbons could be obtained through the catalytic pyrolysis of lignin by H-USY. Yu et al. [17] reported that among the four zeolite catalysts with different pore sizes, ZSM-5 was the optimal catalyst for the production of hydrocarbons from catalytic fast pyrolysis of softwood due to the

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facilitation of the molecular diffusion inside the pores. Compared to H-Mordenite, H-Y, H-Beta, H-Ferrierite and other types of commercial zeolite catalysts, HZSM-5 was estimated as the most effective catalyst for deoxygenation of the vapors from lignin fast pyrolysis [18–20]. Mullen and Boateng [21] carried out the catalytic pyrolysis of lignin from several sources with two heterogeneous catalysts, found that the production of aromatic hydrocarbons from lignin was obviously increased by the addition of HZSM-5 catalyst. The content of aromatic hydrocarbons from the bio-oil refined by HZSM-5 was increased with the decreased Si/Al ratio of the catalyst [22]. It can be concluded that zeolites are applicable and effective catalysts for promoting the conversion of biomass and its constituents to petroleum-based aromatic hydrocarbons. Nevertheless, catalytic mechanism of the catalyst on the production of aromatic hydrocarbons from lignin was not sufficiently studied in the literature.

In order to consolidate the understanding of catalytic pyrolysis of lignin by zeolite, lignin samples from different sources (Chinese fir and rice straw) isolated by Klason method were pyrolyzed using Py-GC/MS under different temperatures in absence and presence of five zeolite catalysts (HZSM-5 (210), HZSM-5 (50), HZSM-5 (25), H- $\beta$  (25) and H-USY (20)). The production of specific aromatic hydrocarbons (such as benzene, toluene, and xylene) would be intensively discussed with regard to the effect of lignin sources, reaction temperatures, catalyst species and Si/Al ratios. The relevant results can also give a conceptual guide for utilization of lignin to produce petroleum-based chemicals.

## 2. Materials and methods

### 2.1. Materials

The Chinese fir and rice straw were both obtained from a manufacturer in southern Anhui Province, China. Lignin samples were extracted from the Chinese fir and rice straw through Klason method described in published works [23,24]. HZSM-5 with different Si/Al ratios of 210, 50 and 25, H- $\beta$  and H-USY zeolite catalysts were purchased from Catalyst Plant of Nankai University, China. Before the catalytic experiments, lignin and zeolite samples were all grinded and sieved to 200–300 mesh (48–75  $\mu\text{m}$ ). All lignin samples and catalyst particles were dried at 100  $^{\circ}\text{C}$  overnight to remove absorbed water.

### 2.2. Characterization of lignin samples

The elemental composition of lignin samples was analyzed in a Vario MICRO analyzer, the content of C, H and N was measured directly and the O content was calculated by difference. The FTIR spectra of two lignins were recorded by FTIR spectrophotometer (Bruker Vector 22) using a KBr disc containing 1% samples. The scan was taken in the range investigate from 4000 to 400  $\text{cm}^{-1}$ .

### 2.3. Characterization of catalysts

#### 2.3.1. XRD analysis

The crystal structure and phase of the zeolites confirmed by X-ray diffraction (XRD), which was carried out in Smartlab XRD-3 with Cu K $\alpha$  radiation. The scans were conducted in the range of  $2\theta$  from  $3^{\circ}$  to  $55^{\circ}$  and the power used was 3 kW.

#### 2.3.2. BET analysis

The physisorption experiments for characterizing the porosity of catalytic samples (such as the surface area and the pore volume) were performed by means of low-temperature nitrogen adsorption (ASAP 2020M).

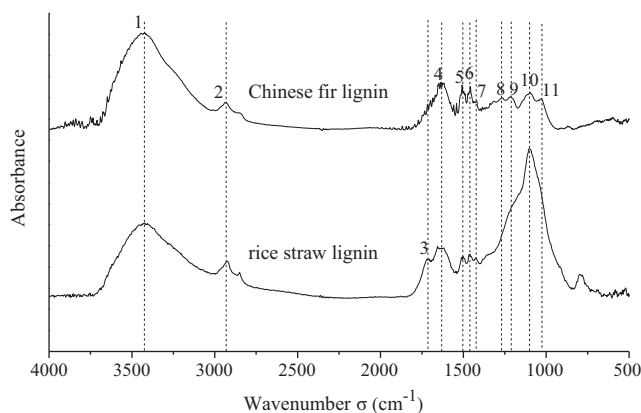


Fig. 1. FTIR spectra of lignin extracted from Chinese fir and rice straw.

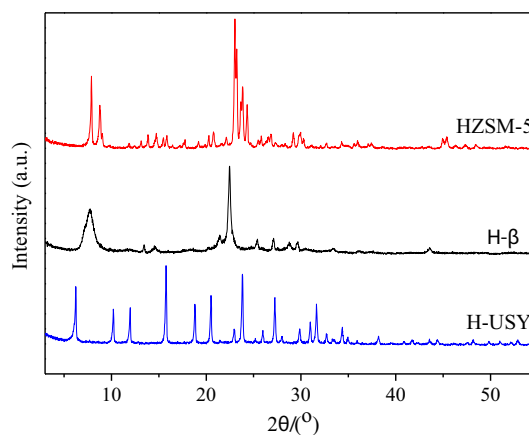


Fig. 2. XRD patterns of the zeolite catalysts.

Table 1  
BET characteristics of the catalysts.

Catalyst	Si/Al ratio	BET surface area ( $\text{m}^2/\text{g}$ )	Total pore volume ( $\text{m}^3/\text{g}$ )
HZSM-5 (210)	210	349.35	0.23
HZSM-5 (50)	50	231.88	0.12
HZSM-5 (25)	25	383.96	0.21
H- $\beta$	25	500.89	0.30
H-USY	20	668.45	0.36

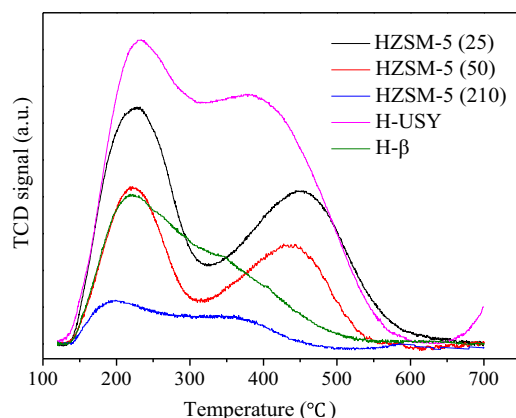


Fig. 3.  $\text{NH}_3$ -TPD analysis of the zeolite catalysts.

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