



Production of aromatic monomers from catalytic pyrolysis of black-liquor lignin



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ABSTRACT

Lignin, mostly existing in forms of solid residue from pulping process of biomass, has been intensively investigated as a potential feedstock for producing high-value chemicals. In this work, lignin precipitated from the acidified black liquor was pyrolyzed under different temperatures (550, 650, 800 and 900 °C) using the analytical pyrolysis technology coupled with GC/MS (Py-GC/MS). The experiments in absence and presence of five solid zeolite catalysts (HZSM-5(25), HZSM-5(50), HZSM-5(210), H-β and H-USY) were carried out, in order to identify the optimal reaction temperature and the best catalyst for producing aromatic monomers (such as guaiacol, phenol, benzene, toluene, etc) from lignin. HZSM-5(25) played an important role in promoting the yield of aromatic monomers from lignin under 650 °C, while H-USY enhanced the formation of aromatic hydrocarbons such as benzene, toluene and xylene.

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1. Introduction

Lignocellulosic biomass, as an abundant renewable resource on earth, is mainly composed of cellulose, hemicellulose and lignin [1,2]. Lignin is a complex and heterogeneous polymer with a three-dimensional (3-D) cross-linked structure through ether bonds or carbon-carbon linkages between the three phenyl propane monomers, i.e. guaiacyl (G), syringyl (S) and *p*-hydroxyphenyl (H) units [3–5]. Studies on thermochemical conversion of lignin to bio-fuels and high-value chemicals such as phenolic compounds and aromatic hydrocarbons have been carried out for recent decades [6–9]. The utilization of black-liquor lignin from the pulping process attracts particular attentions due to its huge amount annually and the low cost.

Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) is one of the analytical experiment methods to investigate the thermal conversion of lignin to variable valuable products [10–13]. The effect of temperature on the product distribution from the fast pyrolysis of Alcell lignin and Asian lignin was studied by Jiang et al., finding that the maximum yield of phenolic compounds was obtained at 600 °C for both lignins [14]. The production of alkylphenol and polyhydroxybenzene was promoted by the elevated temperature due to the enhancement of demethylation,

demethoxylation, decarboxylation and alkylation reactions. Shen et al. reported that the guaiacol- and syringol-type compounds were the predominant products during the primary pyrolysis process, and the formation of phenol-, cresol- and catechol-types derivatives was enhanced under higher temperatures due to the intensive cracking of methoxyl group on the aromatic rings [7].

Catalytic fast pyrolysis of lignin is a further method directed towards modifying the production of high-value chemicals. Compared to Al-MCM-41, solid phosphoric acid and Co/Mo/Al₂O₃ catalysts, HZSM-5 was the best catalyst for producing the deoxygenated liquid fraction from catalytic pyrolysis of lignin, mostly composed of simple aromatic hydrocarbons (46.7%) and naphthalenic ring compounds (46.2%) [15]. Fast pyrolysis of kraft lignin with HZSM-5, FCC and Olivine catalysts was carried out by Choi and Meier, finding that guaiacol-type compounds were decreased significantly in presence of HZSM-5 [9]. Concerning the pyrolysis of lignin with zeolite catalysts, HZSM-5 might be one of the most effective zeolite catalysts for promoting the yield of phenol alkoxy compounds, while H-USY played an important role in the production of aromatic hydrocarbons during the pyrolysis of lignin [16]. The inherent mechanism between catalytic pyrolysis product distribution of lignin and effective pore size of four type zeolites was investigated by Yu et al., proposing that the molecular structure of ZSM-5 can coordinate the deoxygenation and aromatization simultaneously [17]. Rezaei et al. presented that the number of acid sites present in a proper porous structure of zeolite catalysts together

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with their strength distribution can also influenced the yield of aromatics from lignin pyrolysis [18]. It needs to be noted that the pyrolytic performance of lignin are strongly related to the lignin properties, catalyst species and reaction temperatures. The distribution of specified aromatic monomers against catalyst species and temperature from catalytic pyrolysis was not sufficiently investigated in the literature, together with the inherent mechanism.

The production of aromatic monomers from catalytic pyrolysis of lignin would be systematically investigated in this work, involving the effect of reaction temperature and catalyst species. Lignin isolated and purified from black liquor was pyrolyzed using Py-GC/MS under different temperatures with and without catalysts, regarding the distribution of aromatic monomers and their formation mechanism.

2. Materials and methods

2.1. Materials

The black liquor was obtained from a pulping company in Hunan Province, China, where Chinese poplar and reed are used as the main feedstock. Lignin sample was precipitated from the acidified black liquor through the procedure described in the literature [13]. The yield of lignin obtained through this method accounted for 18.43 wt% of the black liquor. Five commercial zeolite catalysts would be used as follows: HZSM-5(25), HZSM-5(50), HZSM-5(210), H- β and H-USY from Catalyst Plant of Nankai University, China. Lignin and zeolites were grinded and sieved by 325 mesh to ensure the sample particle size less than 44 μm . And then all samples were dried for 20 h before the experiments.

2.2. Lignin characterization

According to the elemental analysis in a Vario MICRO analyzer, the content of C, H and N was measured and the O content was calculated by difference and the molecular formula can be determined from molar ratio of the element C, H and O. KBR disc containing 1% lignin sample was prepared and tested in the IR spectrometer (Bruker Vector 22). The scanning range of FTIR spectra recorded was from 4000 cm^{-1} to 400 cm^{-1} .

2.3. Characterization of catalysts

The morphological characteristics of the zeolite catalysts were observed by scanning electron microscopy (SEM) (FEI Inspect F50). The surface area and volume of pore were measured by means of low-temperature nitrogen adsorption (ASAP 2020 M). The surface area was calculated with the Brunauer–Emmett–Teller (BET) method based on adsorption data. All catalytic samples were dried at 350 $^{\circ}\text{C}$ for 8 h under the vacuum before the test. The pore volume was determined from the amount of the nitrogen adsorbed at $P/P_0 = 0.99$. X-ray diffraction (XRD) patterns were recorded using Smartlab XRD-3 with Cu K α radiation in order to confirm the crystal structure and phase of the zeolites. The scans were taken at a 3–55 $^{\circ} 2\theta$ range and the power used was 3 kW.

2.4. Fast pyrolysis of lignin by Py-GC/MS

Fast pyrolysis experiments were conducted using a Pyroprobe analytical pyrolyzer (CDS 5250) coupled with GC/MS (Agilent Technologies 7890A/5975C), in order to obtain the distribution of volatiles from lignin pyrolysis against temperatures. About 0.5 mg of lignin particles was loaded into a quartz pyrolysis tube, and the pyrolysis temperature was set to be 550, 650, 800 and 900 $^{\circ}\text{C}$ with the heating rate of 20,000 $^{\circ}\text{C}/\text{s}$. The residence time for the

reaction was 30 s to ensure that most of the solid sample was completely pyrolyzed. The evolved volatiles were identified by GC/MS with the conditions set to be as follows: the injector temperature was kept at 300 $^{\circ}\text{C}$, and the inject split ratio was 60:1, the GC/MS interface was kept as 280 $^{\circ}\text{C}$, the chromatographic separation was performed with a Agilent HP-5MS (30m \times 0.25mm \times 0.25 μm) capillary column, the oven temperature was programmed from 50 $^{\circ}\text{C}$ (2 min) to 290 $^{\circ}\text{C}$ (1 min) with a heating rate of 8 $^{\circ}\text{C}/\text{min}$, the mass spectra were operated in electron ionization (EI) mode at 70 eV and obtained from m/z 50 to 650. For catalytic pyrolysis, the catalysts and lignin were loaded into the quartz tube like “sandwich” style with the catalyst/lignin weight ratio of 2:1 (about 1 mg catalyst loaded). Most aromatic monomers can be identified by the GC/MS spectra, according to the database of NIST library and the previous published data [7,13,14,19,20], the yield of which was determined by the absolute peak area [5,21]. The detected aromatic monomers can be classified into five groups: aromatic hydrocarbons or non-phenolic aromatics (AH); guaiacol-type compounds (G), syringol-type compounds (S), phenol-type compounds (H) and catechol-type compounds (C). It needs to be noted that the first group of aromatic monomers has no oxygen-contained group, while all compounds in the other four groups are phenolic aromatics but different from the content of number of methoxyl group.

3. Results and discussion

3.1. Structural identification of lignin

The elemental composition of lignin was 67.98% C, 9.18% H, 0.22% N and 22.62% O, giving the molecular formula as $\text{C}_9\text{H}_{14.584}\text{O}_{2.246}$. Compared with formulas of maple lignin ($\text{C}_{4.64}\text{H}_{4.017}\text{O}_{2.482}$) and Chinese fir lignin ($\text{C}_{4.939}\text{H}_{5.255}\text{O}_{2.219}$) [22], formula of lignin precipitated from black liquor has higher hydrogen ratio and oxygen ratio. The FTIR spectra of lignin is shown in Fig. 1, the relevant peaks of which were identified according to the previously published works [23–26]. The absorbance peak at 3425 cm^{-1} (peak 1 in Fig. 1) is due to the O–H stretching vibration. The peak at 2920 cm^{-1} (peak 2 in Fig. 1) indicates the apparent C–H stretching vibration in methyl and methylene groups and C–H bending vibration in methyl and methylene groups can be found at 1457 cm^{-1} (peak 6 in Fig. 1). Signal at 1715–1705 cm^{-1} (peak 3 in Fig. 1) corresponds to the stretching vibration of C=O in unconjugated carbonyls. Peaks located at 1605–1595 cm^{-1} , 1510–1505 and 1430–1425 cm^{-1} (peaks 4, 5 and 7 in Fig. 1) are attributed to aromatic skeletal vibrations. The band around 1370–1365 cm^{-1} (peak 8 in Fig. 1) indicates the aliphatic C–H stretching vibration in CH_3 . The peaks at 1270 cm^{-1} and 1220 cm^{-1} (peaks 9 and 10 in Fig. 1) are characterized to be C–O stretching vibration in guaiacyl rings, while the C–O stretching vibration in syringyl rings designated to

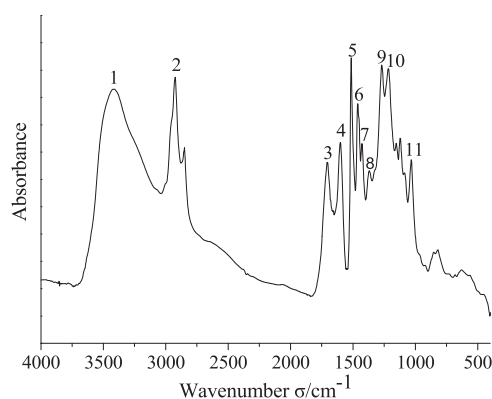


Fig. 1. FTIR spectra of black-liquor lignin.

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