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Thermal degradation of softwood lignin and hardwood lignin by TG-FTIR and Py-GC/MS

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ABSTRACT

The structural characteristics of softwood (Chinese fir) lignin and hardwood (Maple) lignin prepared by Klason method were identified by elemental analysis and Fourier transform infrared (FTIR) spectrometry, and the pyrolytic behaviors of lignin were examined by means of thermogravimetric-Fourier transform infrared spectrometry (TG-FTIR) and Pyrolylisis-gas chromatography/mass spectrometry (Py-GC/MS). It was found that maple (hardwood) lignin contained more methoxyl groups than Chinese fir (softwood) lignin due to the enrichment of syringol units, presenting the chemical formula as $C_{4.64}H_{4.017}O_{2.482}$ against $C_{4.939}H_{5.255}O_{2.219}$ for Chinese fir lignin. The amounts of phenolics, methanol and CH_4 evolved from pyrolysis of maple lignin were all remarkably larger than that of Chinese fir lignin through TG-FTIR analysis. For both two lignins, aromatic compounds (such as benzene, toluene and xylene) were predominantly released between 650 °C and 800 °C, due to the intensive cleavage of aryl-O-R linkages and dehydroxylation reaction on benzene-ring. The distribution of produced volatiles during lignin fast pyrolysis against furnace temperature was intensively discussed, finding that the cleavage of typical inter-unit linkages under relatively low temperature produced the guaiacol-type and syringol-type compounds, whereas the elevated temperature facilitated the cracking of methoxyl group, giving rise to the notable increase of phenol-type, catechol-type compounds and aromatic hydrocarbons.

1. Introduction

Lignin, one of the three main components in woody biomass (18–40 wt.%) [1], is a natural polymer with a complex three-dimensional (3D) structure through ether bonds or carbon–carbon linkages in the three phenyl propane monomers, i.e. guaiacol (G), syringol (S) and p-hydroxylphenyl (P) units [2–4]. Lignin has notable distinctions in the chemical structure owing to the diverse origins and different extraction methods, leading to some significantly differences in the kinetics and product distribution of the pyrolysis process [5–8]. The Kraft lignin has the prominent content of free phenolic groups and of C–C linkages due to occurrence of hydrolysis reactions during the pulping process, while the chemical structure of Klason lignin was rearranged by the condensation reactions [9,10]. The monomer of hardwood lignin is composed of both guaiacol and syringol units, while that of softwood lignin is mainly guaiacol unit [11]. From the point of chemical structure view, lignin is estimated to be the potential feedstock to produce the biofuels and high-value chemicals such as phenolic compounds and aromatic hydrocarbons through thermal conversions [12–14]. A number of attempts both analytical experiments and theoretical estimation were carried out for understanding the inherent pyrolytic mechanism of lignin and achieving the highly value-added conversion technology [15–18].

Thermogravimetric analyzer coupled with analytical instruments (such as FTIR and MS) has been widely adopted to investigate the thermal behavior of lignin regarding the mass loss, evolution of volatiles and kinetic analysis. Liu et al. investigated birch and fir lignin by using TG-FTIR, proposing that phenols were some of the main volatiles released between 150 °C and 287 °C, while when temperature increased CO_2 and CH_4 were prominently released between 327 °C and 427 °C [11]. But the pyrolysis process of lignin derived from corncob acid hydrolysis residue only had one sharp mass loss stage between 260 °C and 420 °C and phenols and methanol as the prominent volatiles were observed [19]. Hu et al. studied the lignins isolated from black liquor and extracted with two different solvents, presenting there were two mass loss stages and CH_4, CO and phenols were the prominent evolution during the

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main mass loss stage for both lignins [17]. Similar results were also observed in other papers [10,20–22], concerning the mass loss and the evolution of the volatiles against the origin and pyrolysis temperature. This would give great contribution for understanding the degradation mechanism of lignin together with the product distribution during the process.

Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) is an analytic fast pyrolysis method, owning distinctive advantages over other analytical methods due to the high operating stability and repeatability. R. Fahmi et al. examined the fast pyrolysis of 15 Lolium and Festuca grasses by Py–GC/MS, finding that the derivatives of the three major lignin subunits (G, H, and S) exhibited a linear relationship with the lignin content [23]. As an accepted tool to study the fast pyrolysis of lignin, Py-GC/MS has been widely applied to examine the effect of the temperature and the structural characteristics on the pyrolysis behavior of lignin [16,18,20,24]: the guaiacol-type and syringol-type compounds were the main primary products of lignin pyrolysis in bio-oil and the production decreased when the temperature went up, while the amount of the derivatives such as the phenol-, cresol- and catechol-types increased with the temperature. Rodrigues and Meier reported that the syringol and guaiacol monomer ratios can be determined by Py–GC/MS and Rio et al. presented the lignin/carbohydrate and syringol/guaiacol ratios by testing the residue lignin from eucalyptus kraft pulps and milled wood lignin (MWL) in Py–GC/MS [25–27]. It can be found that the composition of pyrolysis oil is strongly related to the structure of lignin. Therefore, it needs to be noted that the correlation study between pyrolytic performance and its chemical structure is insufficient, resulting in the limitations in understanding the formation of typical aromatic compounds and designing the high value-added conversion process.

In order to gain better understanding of association of volatile evolution and chemical structure of lignin, two types of lignin were prepared from softwood and hardwood through Klason method. The chemical structure of lignin sample was characterized by means of elemental analysis and FTIR spectroscopy. The thermal performance of lignin was examined by TG-FTIR and Py–GC/MS, concerning the distribution of prominent compounds and their variation against lignin species and reaction temperatures.

2. Materials and methods

2.1. Materials

Lignin sample was prepared from maple and Chinese fir wood by using Klason method [28,29]. Taking the ash content into account (around 3%), the experiment of removing ash was launched in order to limit the influence of ash on thermal degradation of Klason lignin. The lignin sample was grinded particles and sieved with the diameter less than 50 um. All sample particles were dried for 20 h before the experiments.

2.2. Methods

2.2.1. Elemental analysis

Elemental analysis of the maple lignin and Chinese fir lignin was performed on a Vario Micro analyzer. C, H and N contents were measured and the O content was calculated by difference. The molecular formula can be determined from the amount ratio of the main elements C, H and O.

2.2.2. FTIR spectroscopy

The chemical information regarding the distribution of monomeric units and typical functional groups was characterized by FTIR spectrophotometer (Bruker Vector 22). KBr disc containing 1% samples was prepared and tested with the scanning range from 4000 to 400 cm^{-1}.

2.2.3. TG-FTIR

A thermogravimetric analyzer (Setsys-1750, Setaram) coupled to an FTIR spectrophotometer (Bruker Vector 22) was employed to investigate the mass loss of lignins and the formation of typical volatiles. About 20 mg lignin sample was placed into the furnace and heated at a heating rate of 20 °C/min within the temperature range from the ambient temperature to 900 °C under a nitrogen flow of 20 mL/min to maintain an inert atmosphere. The FTIR instrument was connected to the thermogravimetric analyzer by a pipe and a flow cell, which were preheated to 180 °C to prevent condensation of the evolved gases. By means of the FTIR real-time tracking on the pyrolysis gases, the spectra for volatile evolution during lignin pyrolysis can be recorded by means of the FTIR real-time tracking mode with the scanning range from 4000 to 400 cm^{-1}.

2.2.4. Py-GC/MS

The fast pyrolysis analyzer (CDS 5250) was coupled with GC/MS (Agilent Technologies 7890A/5975C) to investigate the distribution of volatiles from lignin fast pyrolysis against reaction temperature. About 0.5 mg of lignin sample was loaded in the pyrolysis tube, and the pyrolysis temperature of furnace was set to be 550, 650 and 800 °C with the flash heating rate of 20,000 °C/s. The residence time for the sample was 30 s, to ensure that most of the solid sample was pyrolyzed. The evolved volatiles were identified by GC/MS, with the conditions given as : the injector temperature was kept at 300 °C; the chromatographic separation was performed with a TR-35MS capillary column; the oven temperature was programmed from 40 °C (3 min) to 200 °C (1 min) with a 4 °C/min heating rate and then to 280 °C (1 min) with a 20 °C/min heating rate; the mass spectra were operated in electron ionization (EI) mode at 70 eV. The mass spectra were obtained from m/z 50 to 650. The yield of the compounds can be determined by the characterized GC/MS spectrums, according to the database of NIST library and other previous reports [20,25–27].

3. Results and discussion

3.1. Structure identification

For both maple lignin and Chinese fir lignin, the content of carbon (55.68% and 59.27%, respectively) was predominant over the other two main elements, oxygen and hydrogen. The molecular formula of the two lignins could be determined from the (C, H and O) elemental analysis, giving: $C_{4.64}H_{4.017}O_{2.482}$ for maple lignin and $C_{4.939}H_{5.255}O_{2.219}$ for Chinese fir lignin.

The FTIR spectra of maple lignin and Chinese fir lignin was shown in Fig. 1 and the bands were assigned according to the previously published works [3,11,17,21,30,31]. The absorbance peak at 3425 cm^{-1} is due to the O–H stretching vibration. The peak at 2920 cm^{-1} indicates the notable C–H stretching vibration in methyl, methylene and methyne groups and C–H bending vibration in methyl groups can be assigned to the band of 1470–1460 cm^{-1}. Stretching signal at 1615–1600 cm^{-1} corresponds to the existence of C=O conjugated to the aromatic ring. Bands located at 1510–1505 cm^{-1} are attributed to aromatic skeletal vibrations. The peak at 1270 cm^{-1} is characterized to be C–O stretching vibration in guaiacol rings, while the C–O stretching vibration in syringol rings is designated to the peak at 1220 cm^{-1}. The absorbance peaks at 1085 cm^{-1} and 1030 cm^{-1} can be ascribed to the C–O deformation in secondary and primary alcohols or aliphatic ethers.