



# Thermo-chemical conversion of lignin to aromatic compounds: Effect of lignin source and reaction temperature



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## ABSTRACT

The structural characteristics of three lignin samples (maple lignin, rice straw lignin and rice husk lignin) prepared by Klason method were examined by elemental analysis and FTIR. Rice husk lignin has the highest H/C ratio among the three lignins, presenting molecular formula as  $C_9H_{8.56}O_{9.60}$  against  $C_9H_{6.98}O_{8.21}$  for rice straw lignin and  $C_9H_{7.79}O_{4.81}$  for maple lignin. Maple lignin contained more methoxyl groups due to enrichment of guaiacyl and syringyl units, while rice straw lignin and rice husk lignin contained more *p*-hydroxyphenyl units. Thermal degradation of the three lignin samples was investigated by thermogravimetric-Fourier transform infrared spectrometry (TG-FTIR), exhibiting three mass loss stages: the evaporation of water, the intensive evolution of aromatic compounds and the sequent release of light gases. Maple lignin was estimated to be most thermally unstable among the three lignins due to the earliest evolution of phenolic compounds,  $CH_4$  and methanol. Distribution of the prominent products from pyrolysis of lignin was determined by Py-GC/MS, regarding the effect of lignin sources and reaction temperature ( $550\text{ }^\circ\text{C}\sim 900\text{ }^\circ\text{C}$ ). The cleavage of typical inter-unit linkages on lignin macromolecules under relatively low temperatures can produce the guaiacol-type and syringol-type compounds, whereas the cracking of methoxyl group and hydroxyl group might be promoted by the elevated temperature with regard to the notable increase of phenol-type compounds and aromatic hydrocarbons. The formation of aromatic hydrocarbons (such as benzene, toluene and xylene) from rice straw lignin and rice husk lignin at higher temperature was remarkably more than that from maple lignin, possibly ascribed to the vigorous dehydroxylation of the phenol-type compounds enhanced by inorganic impurities.

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## 1. Introduction

Lignin, one of the three major constituents in lignocellulosic biomass, consists of *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units polymerized by ether bonds or carbon-carbon linkages [1–3]. The content and chemical structure of lignin is substantially influenced by its origins and separation methods [4]. The difference in chemical structure for the lignin from different sources mainly regards the content of the *p*-coumaryl-, coniferyl-, and sinapyl-alcohols (C9 unit) [5,6]. The C9 unit of softwood lignin was estimated to be dominated by coniferyl-alcohol (more than 95%), while that of hardwood lignin was both coniferyl-alcohol and sinapyl-alcohol in a roughly equal proportion [7–9]. The chemical structure of straw (herbaceous biomass) lignin was determined to be different from that of woody lignin due to the extra content of H-type unit mainly in forms of hydroxycinnamic acid (up to 15% in rice

straw) [10,11]. Due to the abundant content of phenylpropanoid units and huge existence annually from pulping and bio-ethanol production industries, lignin has been considered as one of the potential feedstock for producing the petroleum-based chemicals (such as phenolic compounds and aromatic hydrocarbons) [12,13].

Pyrolysis is well-established as one of the promising technologies to convert lignin to aromatic compounds. Thus, a number of research works on the pyrolysis process of lignin and the product distribution were reported in the literature [14–17]. Thermogravimetric analysis coupled with Fourier transform infrared spectroscopy (TG-FTIR) has been widely adopted to investigate the thermal behavior of lignin regarding the mass loss stages and time/temperature-dependence evolution of volatiles. Pyrolysis of lignins precipitated from black liquor and extracted with two different solvents in TG-FTIR exhibited two main mass loss stages, and the evolution of  $CH_4$ , CO and phenols can be observed in the main mass loss stage for both two lignin samples by Hu et al. [18]. Methanol and phenols from pyrolysis of lignin (the residue from corncob acidic hydrolysis) in TG-FTIR were the dominant volatiles between  $150\text{ }^\circ\text{C}$  and  $420\text{ }^\circ\text{C}$ , while  $CO_2$ , CO and  $CH_4$  were intensively

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released after 400 °C [19]. The mass loss process of lignin along with the evolution of the volatiles was also examined in other published papers [20–22], regarding the variation of sample source and pyrolysis temperature.

During recent decades, Py-GC/MS was widely employed to examine the effect of reaction temperature and structural properties on the distribution of products from lignin fast pyrolysis. Jiang et al. [23] reported that the maximum yield of phenolic compounds was obtained at 600 °C for the fast pyrolysis of Alcell lignin and Asian lignin in Py-GC/MS, while the demethylation, demethoxylation, decarboxylation and alkylation reactions were mostly promoted under higher temperatures. In the pyrolysis of lignin from wheat straw enzymatic acidolysis (EMAL) at 500 °C by Py-GC/MS [24], the derivatives related to the three C9 units (guaiacyl, syringyl, and hydroxyphenyl units) of lignin were identified as the key marker compounds, which was dominated by the guaiacyl unit related compounds. The thermal degradation of four lignins in TG-MS/FTIR and Py-GC-MS was studied by Mihai et al. [25], finding that the Klason wheat straw lignin produced mainly catechols and phenols, and syringol was the dominant compound from hardwood lignins, while neither syringol nor its derivatives was found from pyrolysis of Lignoboost® softwood lignin.

The pyrolytic performance of lignin involving mass loss history, apparent kinetics and distribution of prominent compounds is highly related to its chemical structure depending on the origins and isolation methods. Understanding the relationship between pyrolytic performance of lignin and its chemical structure is demanding the investigation of lignin from different sources and isolation methods. Klason method would be employed for extracting lignin from maple (woody biomass), rice straw (herbaceous biomass) and rice husk (herbaceous biomass) in this study. The structural characteristics of lignin samples were identified by elemental analysis and FTIR spectroscopy. The thermal decomposition of lignin was examined by TG-FTIR and Py-GC/MS regarding the mass loss history along with the evolution of typical volatiles, distribution of the outstanding products and its association with the chemical structure of lignin.

## 2. Materials and methods

### 2.1. Materials

The three biomass materials (maple wood, rice straw and rice husk) were all obtained from a manufacturer in southern Anhui Province, China. Lignin samples were prepared by using Klason method described in published work [26,27]. All the extraction experiments were repeated three times and the yields of lignin were obtained as the average value of the result from three repeated tests. It accounted for 24.37 wt% of maple, 15.25 wt% of rice straw and 29.85 wt% of rice husk, respectively. All three lignin samples were grinded and sieved by 325 mesh to ensure the sample particle size less than 44 μm.

### 2.2. Methods

#### 2.2.1. Elemental analysis

Elemental analysis for the three lignin samples was performed on a Vario Micro analyzer. The contents of C, H and N were measured directly and the O content was calculated by the difference. Then the molecular formula can be determined from molar ratio of the element C, H and O.

#### 2.2.2. FTIR spectroscopy

The chemical information regarding the distribution of typical functional groups was recorded by FTIR spectrophotometer (Bruker

Vector 22). KBr disc containing 1% lignin samples was prepared and tested with the scanning range from 4000 to 400 cm<sup>-1</sup>.

#### 2.2.3. TG-FTIR

Thermogravimetric analyzer (Setsys-1750, Setaram) coupled to an FTIR spectrophotometer (Bruker Vector 22) was employed to investigate the mass loss history of lignin sample along with the evolution of typical volatiles. About 20 mg lignin sample was loaded and placed into the furnace and heated at a heating rate of 20 °C/min from 30 °C 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 through the pipe and the flow cell, which were preheated to 180 °C to prevent condensation of the evolved volatiles. The spectra for the evolved volatiles during lignin pyrolysis can be recorded by means of the FTIR real-time tracking mode with the scanning range from 4000 to 400 cm<sup>-1</sup>.

#### 2.2.4. Py-GC/MS

Fast pyrolysis experiments were conducted by using a Pyroprobe analytical pyrolyzer (CDS 5250) coupled with GC/MS (Agilent Technologies 7890 A/5975C), in order to obtain the distribution of products from lignin pyrolysis. About 0.5 mg of lignin sample was loaded into a quartz tube and placed into the pyroprobe. The pyrolysis temperature was set to be 550, 650, 800 and 900 °C with the heating rate of 20,000 °C/s. The residence time for the reaction was 20 s to ensure that most of the solid sample was completely pyrolyzed. The evolved volatiles were identified by GC/MS with the conditions set as follows: the injector temperature was kept at 300 °C, and the inject split ratio was 60:1; the GC/MS interface was kept as 280 °C; the chromatographic separation was performed with a Agilent HP-5MS (30m × 0.25mm × 0.25 μm) capillary column; the oven temperature was programmed from 50 °C (2 min) to 290 °C (1 min) with a heating rate of 8 °C/min; the mass spectra were operated in electron ionization (EI) mode at 70 eV and obtained from *m/z* 50 to 650. Most aromatic compounds can be identified by the GC/MS spectra, according to the database of NIST library and the previous published data [28–31], the distribution of which was determined by the absolute peak area [32,33].

## 3. Results and discussion

### 3.1. Structural identification of lignin

#### 3.1.1. Elemental analysis

The elemental composition of the lignin samples is shown in Table 1. It can be found that the content of carbon and hydrogen of maple lignin, accounting for 55.68% and 4.017%, respectively, are the highest among the three lignins, while the oxygen content of that is the lowest one. For the herbaceous-type lignin, the content of oxygen (52.429% for rice straw lignin and 56.158% for rice husk lignin) was predominant over the other two main elements, carbon and hydrogen. According to the molar ratio of the element C, H and O, the molecular formula of the three types of lignin was given as follows: C<sub>9</sub>H<sub>7.79</sub>O<sub>4.81</sub> for maple lignin, C<sub>9</sub>H<sub>6.98</sub>O<sub>8.21</sub> for rice straw lignin and C<sub>9</sub>H<sub>8.56</sub>O<sub>9.60</sub> for rice husk lignin. The highest H/C ratio of rice husk lignin indicates that the chemical structure of lignin is highly dependent on the sources, probably leading to the distinct pyrolytic behavior of the samples.

**Table 1**  
The elemental composition of three lignin samples.

Sample	C (%)	H (%)	N (%)	O (%)
Maple lignin	55.68	4.017	0.597	39.706
Rice straw lignin	43.12	2.787	1.664	52.429
Rice husk lignin	39.49	3.131	1.221	56.158

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