TG–FTIR Study on the Pyrolysis Properties of Lignin from Different Kinds of Woody Biomass

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Abstract: Pyrolysis properties of lignin separated from four different kinds of wood (fir, larch, poplar, and eucalyptus) compared with commercial lignin were investigated using a thermogravimetric analyzer coupled to a Fourier-transform infrared spectrometer (TG-FTIR). Kinetic parameters of lignin thermal cracking reaction, such as activation energy and pre-exponential factor, were calculated using a three-dimensional diffusion model. The carbon residue rate and activation energy of softwood lignin were higher than those of hardwood lignin, showing that the decomposition of the former is relatively more difficult than that of the latter during pyrolysis. The distinct characteristic peaks of small-molecule gases and oxygenated chemicals such as ethers, phenols, acids, aldehydes, and alcohols were observed near the maximum weight loss rate by analyzing the 3D IR spectrum of the gas phase products. The formation routes of the main gaseous products were discussed, and the following order of releasing amounts was noted: CO₂>CH₄>H₂O>CO. It is believed that these results will provide valuable information for the thermochemical conversion process of lignin from the point of view of feedstock.

Keywords: woody biomass; lignin; pyrolysis; TG-FTIR; kinetics; gaseous product

1 Introduction

Biomass is the only renewable carbon resource that can be used to produce renewable chemicals, energy, and bio-materials[1-2]. The thermo-chemical conversion technology can effectively convert low-energy-density agricultural and forestry waste into high-energy-density fuels and chemical products. Among the thermo-chemical conversion technologies, fast pyrolysis of biomass with moderate temperatures and short
vapor residence time is one of the most promising technologies for converting biomass to valuable liquid fuels. The pyrolysis liquids known as bio-oils have been regarded as promising candidates to replace petroleum fuels for use in various thermal devices\[^3\].

Recently, several studies have shown that the type of biomass and chemical composition have significant impacts on the yield and quality of the pyrolysis bio-oil\[^4-5\]. The pyrolysis property of feedstock is an important factor to determine the energy consumption of the utilization process, product properties, and process control methods during the thermo-chemical processing of biomass. The components of biomass decompose into different chemical compounds. The chemical composition and thermal cracking behavior of spruce, willow, grass, and straw were studied by Butler et al\[^6\]. Yang et al\[^7\] studied and compared the pyrolysis characteristics of Sigma cellulose, alkaline lignin, and xylan. Lou et al\[^8\] investigated the thermal decomposition and composition characteristics of bamboo enzymatic hydrolysis lignin in nitrogen atmosphere. A pyrolysis–gas chromatography–mass spectrometry (Py-GC-MS) study showed that saccharides and ketones were the major compounds in the pyrolysis vapor obtained from microcrystalline cellulose and xylan, respectively, whereas the most abundant compounds in the pyrolysis vapor obtained from alkaline lignin were sulfur compounds and phenols\[^9\].

It is critical to understand the effect of chemical and physical variability of biomass feedstock on the pyrolysis processes. In previous studies\[^10-11\], the weight-loss characteristics and gas evolution rule of larch wood at different heating rates were investigated, and the results were compared with those of larch wood model-component mixture, cellulose, and holocellulose. It was concluded that the thermal conversion process of holocellulose was the result of interaction between cellulose and hemicellulose under the dominant role of cellulose.

However, lignin, as one of the three major components, often has significant variability in different tree species; its thermal decomposition characteristics are also important factors affecting the thermo-chemical processing of biomass raw materials. Therefore, it is meaningful to study the thermal decomposition characteristics of wood lignin separated from different tree species. In this study, four kinds of typical wood species were used as raw materials to comparatively study the pyrolysis degradation process and release rule of typical vapor gases.

2 Experimental

2.1 Materials

Two kinds of softwood (larch and fir) and two kinds of hardwood (poplar and eucalyptus) were used as the raw materials in this study. Larch and poplar are grown in the area of Heilongjiang province, China, whereas fir and eucalyptus are produced in Meizhou, Guangdong province, China. The wood was debarked, dried, and ground into powder of size 40–60 mesh. Lignin samples were separated from the four kinds of wood using the Klason method (benzene-alcohol extraction followed by ambient-temperature pre-hydrolysis with 72% sulfuric acid and high-temperature hydrolysis with 3% sulfuric acid). Commercial alkaline lignin (CAS: 9005-53-2) was purchased from Tokyo Kasei Kogyo Co., Ltd. (TCI).

2.2 Instruments

The thermogravimetry–Fourier transform infrared spectroscopy (TG-FTIR) instrument used in this study is composed of a simultaneous thermogravimetric analyzer (NETZSCH STA449F3) coupled to a Fourier-transform infrared spectrometer (Bruker TENSOR 27). The samples were heated in a thermogravimetric analyzer. Subsequently, thermal cracking reaction occurred, and the pyrolysis products were moved into the infrared spectrometer in order to measure the composition of pyrolysis vapors with time. Approximately 5 mg of the sample was used in each test. The pyrolysis experiment was carried out at a linear heating rate of 20°C/min within the temperature range from ambient temperature to 850°C. Nitrogen was used as the carrier gas at a flow rate of 50 mL/min.
to provide an inert atmosphere. The spectrum scope of FTIR was in the range 500–4000 cm\(^{-1}\) and the resolution factor was selected to be 1 cm\(^{-1}\).

2.3 Kinetic calculation method

Data from TG and derivative TG (DTG) curves of the pyrolysis of lignin were used to determine the kinetic parameters. According to Coats et al integral dynamics method\(^{12}\) and 3D diffusion model\(^{13}\), a kinetic equation was obtained as follows:

\[
\ln\left[\frac{1-(1-\alpha)^{1/3}T^2}{T^2}\right] = \ln\left[\frac{AR}{\beta E} \left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT}
\]

\(\alpha\) — thermal decomposition conversion rate, \(\%\);

\(\beta\) — heating rate, \(\beta = dT/dt\);

\(A\) — frequency factor, \(min^{-1}\);

\(E\) — reaction activation energy, \(kJ/mol\);

\(R\) — gas constant, 8.314 J/(K \cdot mol);

\(T\) — reaction temperature, K.

By plotting and fitting the mass loss data from the TG curves, the kinetic parameters can be obtained according to the slope and intercept of the fitted curve. Generally, a straight regression line with a slope of \(E/R\) can be obtained by plotting \(\ln\left[\frac{1-(1-\alpha)^{1/3}T^2}{T^2}\right]\) versus \(1/T\). After deriving the value of \(E\), the arithmetic mean value of \(\left(1-\frac{2RT}{E}\right)\) can be calculated using the initial and final reaction temperatures. Finally, the frequency factor \((A)\) can be obtained from the intercept of the line.

3 Results and discussion

3.1 Pyrolysis process and kinetics analysis

Fig.1 shows the thermal weight loss curves of commercial lignin and lignin separated from the four kinds of wood. Lignin, an aromatic polymer compound, is formed by bonding of phenyl-propane structure unit with an ether bond or carbon-carbon bond. Klason lignin is obtained by hydrolyzing polysaccharides into simple sugars and dissolving them into water and being removed at last. Lignin is composed of aromatic rings with various branches. The thermal activity of the chemical bonds in lignin spans an extremely wide range, which leads to a wider temperature range of degradation of lignin compared with that of cellulose and hemicellulose\(^7\).

During the pyrolysis process of lignin, a weight loss peak is observed around 100°C, which is due to the presence of degraded monomers of lignin and small molecules (water, etc). The maximum weight loss temperature is in the range of 330–430°C in general, but the maximum weight loss temperature of Klason lignin is slightly higher than that of commercial alkaline lignin, probably because the polymerization degree of the former is larger than that of the latter. After 700°C, the thermal weight loss curve tends to be stable. The lignin separated from different tree species shows similar thermal behavior.

![Fig.1 TG and DTG curves of lignin pyrolysis process](image)

Table 1 lists the kinetic parameters of pyrolysis of lignin separated from different tree species. The content and structure of lignin in different biomass feedstocks are different. In general, the content of lignin in softwood is higher than that in hardwood; further, it is more difficult to cook and bleach softwood as compared with hardwood. The structural unit of softwood lignin is mainly guaiacol propane, whereas hardwood lignin contains both guaiacol propane and syringyl propane.

<table>
<thead>
<tr>
<th>Tree species</th>
<th>Fir lignin</th>
<th>Commercial lignin</th>
<th>Larch lignin</th>
<th>Poplar lignin</th>
<th>Eucalyptus lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td>TG/wt%</td>
<td>80</td>
<td>90</td>
<td>80</td>
<td>70</td>
<td>60</td>
</tr>
<tr>
<td>Temperature/°C</td>
<td>0</td>
<td>100</td>
<td>200</td>
<td>300</td>
<td>400</td>
</tr>
</tbody>
</table>

Table 1 Kinetic parameters of pyrolysis of lignin separated from different tree species.
The residue yield of pyrolysis of lignin is 43%~55% owing to the high content of carbon elements in lignin, and they are the main material forming char residue. The maximum weight loss temperature and char residue yield of softwood lignin are higher than those of hardwood lignin, and the activation energy of softwood lignin is also slightly higher than that of hardwood lignin, which indicates that the thermal degradation of softwood lignin is more difficult to achieve as compared with that of hardwood lignin. Compared with lignin made by Klason method, the decomposition of commercial alkaline lignin is easier with lower maximum weight loss temperature and lower activation energy. Notably, the pyrolysis of commercial lignin during the TG process produces more residue char, probably because of its high metal content, which is believed to contribute to the char-forming reactions during the pyrolysis process. The results obtained herein are similar to those obtained by Liu et al.\(^\text{[14]}\), who also determined that the main pyrolysis sections and the maximum weight loss rates were different for lignin separated from different wood species. In general, wood lignin undergoes three consecutive stages, corresponding to the evaporation of water, formation of primary volatiles, and subsequent release of small molecular gases.

### 3.2 Infrared spectrum analysis of the evolution of pyrolysis steam

Fig.2 shows the 3D infrared spectra illustrating the evolution process of the pyrolysis vapor obtained from commercial lignin and lignin separated from different tree species (eucalyptus as the typical example of hardwood, fir as the typical example of softwood).

From Fig.2, the spectral change of pyrolysis vapors can be observed with the variation of pyrolysis temperature in each period. The infrared absorption intensity corresponds to the thermal derivative thermogravimetric curve of pyrolysis vapor. The strength is weak at the beginning of the thermal cracking. The average intensity of infrared absorption reaches the highest at the maximum weight loss rate. After severe thermal cracking, the release of the gaseous product gradually decreases, and the infrared absorption intensity of the vapors becomes weak.

According to the IR spectrum in Fig.2, characteristic peaks corresponding to the typical gases can be observed around the maximum weight loss of the lignin sample. The large peak corresponding to water vapor is represented by the wave number range 3566~3791 cm\(^{-1}\). The wave number range 2118~2164 cm\(^{-1}\) corresponds to the characteristic peak of CO. The wave numbers 2217~2391 cm\(^{-1}\) and 700 cm\(^{-1}\) correspond to the characteristic peak of CO\(_2\). The stretching vibration absorption peaks of C—H (methyl, ethyl) at 2820 and 2931 cm\(^{-1}\), the stretching vibration peak of the carbonyl C=O and the bending vibration peak in the C—H plane at 1743 cm\(^{-1}\), the skeleton vibration peaks of C—O and C—C at 1370 cm\(^{-1}\), the stretching vibration peaks of C=C at 664–670 cm\(^{-1}\), and the benzene ring stretching vibration peaks within the range of 600–1500 cm\(^{-1}\) indicate the existence of various alkanes, aldehydes, ketones, phenols, carboxylic acids, and alcohols, respectively\(^\text{[15-17]}\).

When the pyrolysis reaction proceeds to the later stage of carbonization, the main occurrence is the expansion of C—H and the C—O stretching vibration. The process of further breakage of C—H bond and C—O bond, respectively, corresponds to the formation of CH\(_4\) and CO\(_2/\)CO, respectively. At this stage, the water absorption peak is extremely weak, and disappears at approximately 550°C. Aldehydes mainly

### Table 1 Kinetics parameters of lignin pyrolysis process

<table>
<thead>
<tr>
<th>Samples</th>
<th>Residue yield (wt%)</th>
<th>Maximum weight loss temperature/°C</th>
<th>Activation energy (kJ mol(^{-1}))</th>
<th>Frequency factor/min(^{-1})</th>
<th>Correlation coefficient (R(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fir lignin</td>
<td>45.7</td>
<td>405</td>
<td>53.82</td>
<td>6.82×10(^7)</td>
<td>0.9920</td>
</tr>
<tr>
<td>Larch lignin</td>
<td>45.4</td>
<td>405</td>
<td>47.19</td>
<td>1.87×10(^3)</td>
<td>0.9933</td>
</tr>
<tr>
<td>Poplar lignin</td>
<td>43.3</td>
<td>378</td>
<td>50.57</td>
<td>7.35×10(^6)</td>
<td>0.9900</td>
</tr>
<tr>
<td>Eucalyptus lignin</td>
<td>44.1</td>
<td>378</td>
<td>41.50</td>
<td>3.19×10(^5)</td>
<td>0.9866</td>
</tr>
<tr>
<td>Commercial lignin</td>
<td>54.5</td>
<td>330</td>
<td>31.72</td>
<td>1.08×10(^3)</td>
<td>0.9902</td>
</tr>
</tbody>
</table>
derived from the scission of the side chain of hydroxymethyl (—CH₂OH) in phenyl-propane unit correspond to the peak of 1747 cm⁻¹. Owing to the complexity of the structure of lignin, functional groups such as methoxyl and alkyl groups are frequently incorporated in the phenolic structural monomers during the process of thermal cracking, resulting in the formation of various complicated phenolic substances.

3.3 Analysis of the releasing rule of typical gases

The releasing profiles of typical gaseous products H₂O, CO, CO₂, and CH₄ during the pyrolysis process of lignin at different temperatures are shown in Fig.3. The reactions responsible for the release of volatile compounds during the pyrolysis process of lignin are mostly due to the instability of the propyl chains and of some linkages between monomer units and the methoxyl substituents of the aromatic rings. After this step, a charring process, which consists of the rearrangement of the char skeleton in a polycyclic aromatic structure, occurs and is responsible for the main release of primary volatiles.[18]

The maximum releasing peaks of these gases are mainly formed near the area of the strongest thermal weight loss. Among the four typical gases, CO₂ has the largest yield, followed by CH₄, H₂O, and CO in that order. In other words, the order of the amount is CO₂>CH₄>H₂O>CO. This result is different from that obtained with the sample of larch timber and holo cellulose.[10-11]. The yield of CH₄ from lignin pyrolysis is higher compared with those of other components. Therefore, it can be judged that CH₄ is mainly formed from the lignin component during the wood pyrolysis process.

CO₂ is the leading gas among the gaseous products of pyrolysis, and the amount of CO₂ generated is significantly higher than that of the other three gases. CO₂ is mainly formed by the decarboxylation and carbonyl fracture[7] of the lignin structure. Throughout the pyrolysis reaction process, CO₂ is released in every reaction stage and its precipitation concentration is relatively high. Notably, CO₂ is produced not only from the first pyrolysis reaction but also from the second pyrolysis cleavage of the volatile compounds. CH₄ is mainly formed by the fracture of —OCH₃ with weak bond energy.[19-20]. Moreover, the breakage of —CH₃— may also produce methane but the bond
energy is relatively high, which is not the main method to produce CH$_4$. The formation of water contains both the separation of free water inside the biomass and the condensation reaction of intermediate products in the process of thermal conversion. Water is formed in the main pyrolysis process with different degrees and a large distribution. CO is also separated over the entire temperature range but the yield is relatively low. CO mainly originates from the fracture of a large number of phenolic hydroxyl groups in lignin and unstable carbonyl groups$^{[7,14]}$ formed by the dehydration reaction generally occurring during the pyrolysis process of lignin.

4 Conclusions

TG-FTIR method was used to study the thermal degradation and product release process of lignin obtained from fir, larch, poplar, and eucalyptus wood in comparison with commercial alkaline lignin. Thermal decomposition kinetics showed that the rate and activation energy of lignin in softwood were higher than that of lignin in hardwood, and hence, the pyrolysis of the former is more difficult. Apparent characteristic peaks corresponding to H$_2$O, CO, CO$_2$, CH$_4$ and others, phenols, acids, aldehydes, alcohols, and other oxygen-containing compounds were observed in the stage with the maximum weight loss rate using the 3D IR spectrum. The possible formation pathways of typical gaseous products were analyzed, and the order of yields was CO$_2$$>$CH$_4$$>$H$_2$O$>$CO.

References


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