Study on the Mechanism of the Pyrolysis of a Lignin Monomeric Model Compound by *in situ* FTIR

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The *in situ* Fourier transform infrared (FTIR) spectroscopy technique was used as an online method for fundamental mechanistic studies of the pyrolysis of a lignin monomeric model compound. The formation of important reaction intermediates was revealed. Three major decomposition routes were shown: P1, dehydration at approximately 270 °C; P2.1, demethylation at approximately 350 °C; and P2.2, H-abstraction at approximately 430 °C. A free reaction of the pyrolysis of the lignin model compound was suggested based on the results. The comparative results showed that the methyl group was the initiator of many secondary reactions.

Keywords: in situ FTIR; Pyrolysis; Lignin model compound; Bio-oil

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INTRODUCTION

Currently the utilization of biomass resources has attracted increasing worldwide interest, and thermochemical conversion is of greater interest as a potential method for converting raw biomass into new green energy (Chu *et al.* 2013; Lou and Wu 2011). Lignocellulose consists mainly of plant cell wall materials and is a complicated natural composite with three main biopolymers, cellulose (40% to 50%), hemicellulose (15% to 25%), and lignin (15% to 35%) (Singh *et al.* 2014). Pyrolysis of biomass has been studied by many researchers over the decades. Most research has focused on the product identification or kinetic studies, while some has been dedicated to biomass model compounds as materials for mechanistic (Britt *et al.* 2000; Chu *et al.* 2013; Nakamura *et al.* 2008; Shin *et al.* 2001) or computational (Wang *et al.* 2013) studies.

In situ Fourier transform infrared (FTIR) spectroscopy, which was initially developed in 1992 (Moser *et al.* 1992), is becoming increasingly important for fundamental kinetic and mechanistic studies and process development, as well as process control in chemical, biochemical, and pharmaceutical industries (Pintar *et al.* 2004). Used for *in situ* FTIR, the mid-infrared spectrometer has proven to be extremely valuable in detecting transient chemical species that cannot be captured for off-line analysis. *In situ* FTIR spectroscopy is one of the most widely used spectroscopic techniques in catalysis to analyse reaction mechanisms of the catalysed processes. These studies are usually performed on heterogeneous catalysis applied either in gas phase, solid surface, or liquid phase reactions (Dubois *et al.* 2012; Hu *et al.* 2013; Martins *et al.* 2008; Mul *et al.* 2004). It is a powerful tool for studying the reaction mechanisms of electrooxidation of small organic molecules (Chen *et al.* 2003). Change in the surface functional groups under pyrolysis condition of biomass can be observed by using this method (Kirtania *et al.* 2014;

Uchimiya *et al*. 2013). The hydrodeoxygenation process of liquefied biomass over catalyst can also be investigated by *in situ* FTIR spectroscopy (Grilc *et al*. 2014; Veryasov *et al*. 2014).

The route of depolymerisation of lignin in the pyrolysis process has been much less frequently investigated with *in situ* FTIR spectroscopy. Conventional analysis methods are based on end products, with the use of coupled techniques such as pyrolysis gas chromatography mass spectrometry (Py-GC/MS), GC-MS, thermogravimetric analysis coupled with Fourier transform infrared analysis (TG-FTIR), and TG-MS. These techniques aim to identify liquid or gas products, since direct analysis of the reaction intermediates is not possible.

This investigation combines the py-GC/MS and *in situ* FTIR methods for the first time. The purpose of the former is to detect the qualitative pyrolysis products, and the latter is to observe the reaction process of the lignin monomeric model compound (4-hydroxy-3-methoxy-α-methyl benzyl alcohol, designated as "compound G"). A monomeric model compound was chosen since it is relatively simple, has a constant boiling point, and the specific functional group is fairly obvious using FTIR. Three main free radical pathways are put forward with respect to the pyrolysis mechanism of compound G.

EXPERIMENTAL

Materials

Compound G, purchased from Sigma-Aldrich Corporation (purity 97%), was used without further purification. The boiling point of compound G is 301 °C at 760 Torr.

Methods

Py-GC/MS method

The Py-GC/MS systems was performed on a CDS5200 series pyrolyser (CDS, USA). The gas chromatography-mass spectroscopy (GC/MS) analysis of the pyrolysis products was conducted with an Agilent 6890N gas chromatography equipped with a 5973N mass selective detector (Agilent Technologies, USA) with an ion source of electron impact (EI) at 70 eV. Approximately 0.1 mg of sample was dried at 80 °C for 5 s, then it was pyrolyzed at 500 °C at a heating rate of 10 °C/ms for 5 s, and the gaseous products were then purged by high purity helium (99.9995%) into the gas chromatograph *via* a transfer line preheated at 270 °C. The flow rate of the carrier gas was 45 mL/min with a split ratio of 40:1 and the injection temperature was 250 °C. The pyrolysis products were separated in an Agilent DB-35MS capillary column (30 m × 0.25 mm × 0.25 μm). The temperature programming was as follows: the GC oven was kept at 50 °C for 1 min and programmed to 180 °C at an increment of 15 °C/min, holding for 1 min; then 4 °C/min to 210 °C, holding for 2 min; then 20 °C/min to 280 °C with a final hold time of 5 min. The mass range m/z 33-500 was scanned. Identification of the pyrolysis compounds was achieved by comparison of their mass fragment with the NIST 08 Mass Spectral Library.

In situ FTIR spectroscopy

The *in situ* FTIR spectroscopy was carried out on a Nicolet IS50 spectrometer (Thermo Fisher Scientific, USA) with a DTGS detector combined reactor-spectrometer system using a low-volume *in situ* cell with water-cooled CaF_2 windows. A thermocouple

was placed inside the *in situ* cell to measure the pyrolysis temperature. Approximately 0.1 mg of the sample was placed in a stainless steel sample boat. Before heating, the *in situ* cell was purged with high purity nitrogen (99.999%) at a flow rate 1 L/min for 15 min to ensure an oxygen-free system, and the valves from both ends were closed to ensure a hermetic system. The sample was heated from 30 °C to 590 °C at a heating rate 40 °C/min and held at 590 °C for 15 min. The IR spectra of the gaseous phase were collected throughout the experiment. The background was scanned in a N_2 atmosphere at 100 °C.

RESULTS AND DISCUSSION

Analysis of the Pyrolysis Products from Py-GC/MS of Compound G

The major pyrolysis products of compound G were identified by Py-GC/MS, as described by the data in Table 1.

Table1. Pyrolysis Products Detected by Py-GC/MS

Rt/min	Compound	Major peaks	A^p
1.427	carbon dioxide	44	2.82
1.757	acetic acid	60,45,43	1.03
2.217	benzene	78,52,39	0.98
5.914	phenol	94,66,65	0.60
6.858	2-methylphenol	108,107,79	0.35
7.524	guaiacol	124,109,81	4.91
8.185	4-ethylphenol	122,107,77	0.24
8.668	1,2-benzenediol	110,92,64	1.00
8.945	4-vinylphenol	120,91,65	0.90
9.500	4-ethyl-2-methoxylphenol	152,137,91	1.08
10.113	2-methoxy-4-vinylphenol	150,135,107	83.10
10.691	4-ethylcatechol	138,123,77	0.87
11.416	eugenol	164,149,131,77	0.38
11.475	4-vinylcatechol	136,110,77	0.68
12.265	acetovanillone	166,151,123	1.27
A^p designates peak area percent of the compounds			

It can be seen from Table 1 that there were two abundant products in this reaction, 2-methoxy-4-vinylphenol and guaiacol, which implies that these two products were easier to produce and more stable in this system compared to other possible compounds.

Analysis of the *in situ* FTIR Spectrum

With the increase of temperature, the *in situ* FTIR spectrum not only shows the change of functional groups but also provides strong evidence of the appearance of small molecules and non-condensable gases. It can be seen from Fig. 1 that the IR band of –OH (alcoholic hydroxyl group, from ~3250 cm^{-1} to 3580 cm^{-1}; centered at 3500 cm^{-1}) decreased with the increase of temperature, while the band of gaseous water molecules (~3734 cm^{-1}) (Weng 2010) increased; the peak at 2969 cm^{-1} became split into two peaks, which indicated that a dehydration reaction took place before 400 °C. The band at 1030 cm^{-1}, which can be reasonably assigned to symmetrical stretching vibration between the methyl group and oxygen atom in the structure of C–O–CH_3, decreased (especially from 400 °C to 450 °C) while the CH_4 band (~3017 cm^{-1}) (Weng 2010) increased. Similarly, the band located at

1369 cm^{-1}, which should be assigned to the symmetric deformation vibration of $–CH_3$, decreased with the increasing temperature. This implies that CH_4 originated mainly from the breakage of the methoxy group and methyl group. The most striking observation is the appearance of an intense absorption band around 1677 cm^{-1} when the temperature is 400 °C, which can be assigned to –C=O stretching vibration of aldehyde (Pretesch *et al.* 2012); the intensity of the band continued increasing at 450 °C. However, when the pyrolysis temperature reached 500 °C, the peak at 1677cm^{-1} almost vanished, while a new peak at 1654 cm^{-1}, which can be assigned to –C=O stretching vibration of ketone conjugate with the benzene ring (Pretesch *et al.* 2012), appeared. These observations provide strong evidence that pathway 2.1 (P2.1) occurs before pathway 2.2 (P2.2) as shown in Scheme 1. The intensity of the band at 1270 cm^{-1}, which can be assigned to the ar-OH stretching vibration, decreased progressively with the increasing temperature. The reason for this result may be the breakage of the ar-OH structure in the formation of phenol oxygen free radicals, which may be attributed to polycyclic-aromatic hydrocarbons in bio-oil (Chu *et al.* 2013; McGrath *et al.* 2001). The three bands at 1604 cm^{-1}, 1515 cm^{-1}, and 1454cm^{-1}, which can be reasonably assigned to aromatic ring vibration, changed little. This implies the benzene ring was very stable in the present situation.

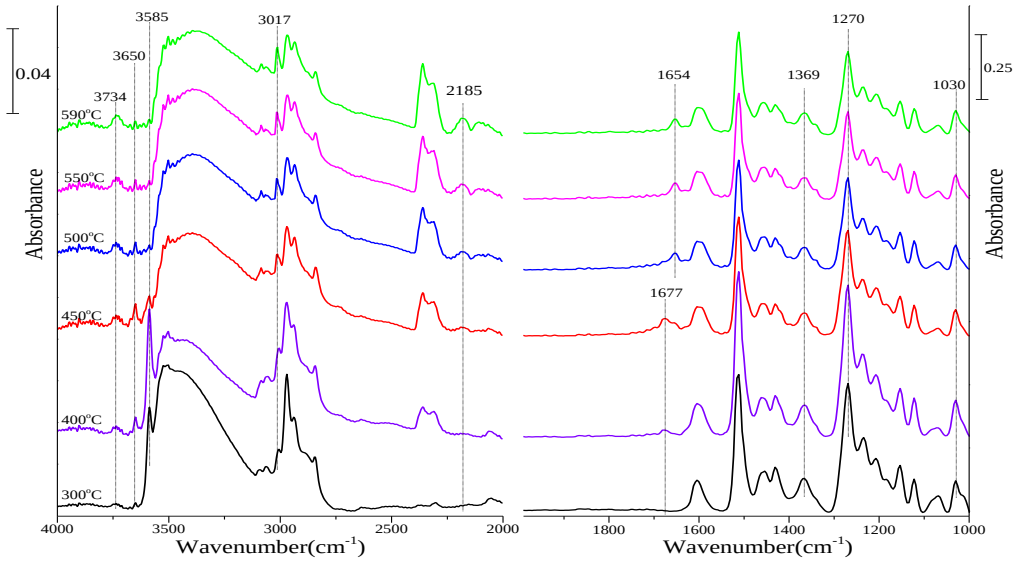


Fig. 1. FTIR spectra of the compound G at different pyrolysis temperatures

The change in the intensity of absorbance at seven major wavenumbers relative to the pyrolysis time was also explored, as shown in Fig. 2. The band of 1677 cm^{-1} appeared at about 8 min when the temperature was about 350 °C, which suggests pathway 2.1 (P2.1, in scheme 1) reaction starting at about 350 °C. With the decrease of 1677 cm^{-1}, the intensity of 1654 cm^{-1} and 2185 cm^{-1} started to increase. When the temperature reached 550 °C, the band at 1677 cm^{-1} nearly vanished, which indicates that vanillin is an intermediate product in this system. This is in agreement with the pyrolysis products shown in Table 1. The band of CO (~2185 cm^{-1}) (Weng 2010) appeared in parallel with that of 1654 cm^{-1}, and increased with the decrease of 1654 cm^{-1}. These observations provide strong evidence that CO is formed by the breakage of the C=O structure. The band -COOH at 3658 cm^{-1} increased from 300 °C to 400 °C then decreased, while the peak at 2359 cm^{-1} began to increase. This gives direct evidence that CO_2 was produced by carboxylic acid.

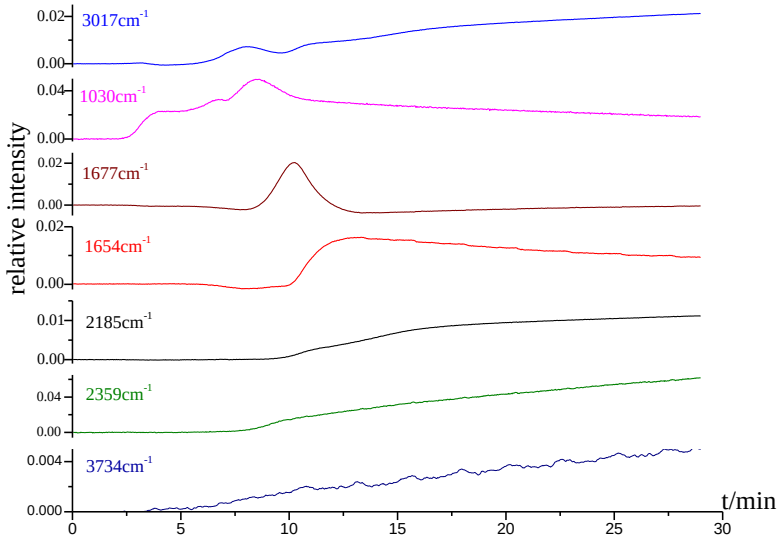
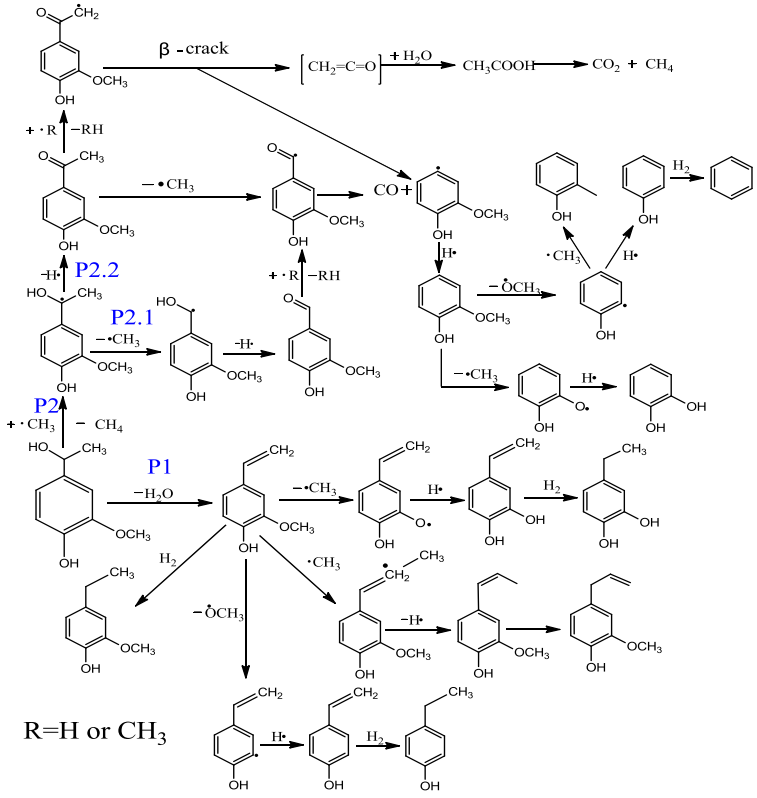


Fig. 2. Time-dependent relative intensity of seven main wavenumbers. The time resolution was 1.93 s

Taking the overall results summarized in Table 1, Fig. 1, and Fig. 2 into account, one can begin to consider the free radical reaction as the dominant pathway for the pyrolysis of this monomeric model compound, as shown in Scheme 1.



Scheme 1. Proposed reaction mechanism of pyrolysis of lignin monomeric model compound

Some of the reaction routes are based on the major products observed in Table 1. Radicals are generated after $–OCH_3$ homolysis cleavage, which can be confirmed by a flat peak at about 5 min in the curve of 1030 cm^{-1} (Fig. 2). This is believed to be the initiation step for a free radical chain reaction. The radicals can abstract the proton from other species that have weak C–H or O–H bonding and form products (Chu *et al.* 2013). 2-Methoxy-4-vinylphenol and guaiacol were the two most abundant products produced by dehydration and H-abstraction. Secondary reactions can also occur. H-abstraction, rearrangement, isomerization, and concerted reaction diversify the products distribution, such as the formation of vanillin (Shin *et al.* 2001) and 2-methoxy-4-propyl-phenol from the lignin model compound (Chu *et al.* 2013).

The formation of ethenone from the pyrolysis of methyl ketone was reported in a previous study (Sato *et al.* 2000). The formation of benzene, 4-ethylphenol, and 4-ethylcatechol requires hydrogen, similar to that shown in the study on the pyrolysis products of lignin model compounds (Liu *et al.* 2011).

CONCLUSIONS

1. In the pyrolysis of a lignin monomeric model compound, three major decomposition routes were revealed: P1, dehydration at about 270 °C; P2.1, demethylation at about 350 °C; and P2.2, H-abstraction, at about 430 °C.
2. Carbon monoxide mainly comes from the breakage of aldehyde groups, CO_2 is produced from acetic acid, and CH_4 is produced by the breakage of methoxy group and the pyrolysis of acetic acid.
3. The pyrolysis was very selective towards 2-methoxy-4-vinylphenol at the heating rate of 10 °C/ms, which indicated that α-H of the compound G was relatively more active.

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