

Research article

Modeling pyrolytic behavior of pre-oxidized lignin using four representative β -ether-type lignin-like model polymersWeikun Jiang^a, Jiangyong Chu^a, Shubin Wu^{a,*}, Lucian A. Lucia^b^a State Key Lab of Pulp & Paper Engineering, South China University of Technology, Guangzhou 510640, PR China^b Key Laboratory of Pulp & Paper Science and Technology, Qilu University of Technology, Jinan 250353, PR China

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ABSTRACT

A better understanding of the pyrolytic characteristics of pre-oxidized lignin in which $C_{\alpha}H-OH$ was oxidized to $C_{\alpha}=O$ group was obtained through four selected β -ether-type lignin-like model polymers containing the H- and G-type subunits. These models were depolymerized in closed ampoule reactor system and interrogated using *in-situ* FTIR. The results show that their degradation products differ significantly in species and yield due to $C_{\alpha}H-OH$, $C_{\alpha}=O$, and aryl- OCH_3 . The yield of phenolic monomers from oxidized G-type polymer rose to 27.87 wt%, almost twice that of initial G-type polymer. Nevertheless, as for H-type polymer, oxidation of the $C_{\alpha}H-OH$ to $C_{\alpha}=O$ group lead to decreases in phenolic monomers yield by $\sim$ half. The *in-situ* FTIR indicates that oxidation of the $C_{\alpha}H-OH$ to $C_{\alpha}=O$ accelerates cleavage of interunit linkages and simplifies depolymerization pathways resulting in better selectivity of phenolic monomers, especially at low pyrolysis temperatures (< 500 °C). Several important transformation pathways are proposed that clearly explain the pyrolytic behavior of pre-oxidized polymers.

1. Introduction

Although oil refinery operations are the main source of chemicals in society today, a worldwide energy crisis and environmental concerns dictate consideration of alternative feedstocks for chemicals such as renewables [1]. Lignocellulosic biomass is the only renewable organic carbon resource in nature [2], which is mainly composed of hemicelluloses, cellulose, and lignin. For hemicellulose and cellulose, several mature utilization technologies have been adopted industrially for biofuels and platform chemicals [3]. Lignin, the most abundant and only renewable source composed of aromatic units in nature [4], is quite valuable for producing value-added aromatic chemicals. Annually, millions of tons of alkali-soluble lignin are produced by the pulp and paper industry [5]. All but a small percentage of the lignin is used in low-value commercial applications, such as fuel for heat and power applications [6].

Selective, high yield transformations of lignin into low molecular weight value-added chemicals have been studied recently [7–10], but little progress has been made toward industrialization. This is likely because of a lack of systematic theory to guide lignin depolymerization arising from the complexity of the lignin macromolecule [11]. A representative lignin structure is illustrated in Fig. 1a. It is mainly composed of three primary precursors: sinapyl (S), coniferyl (G), and *p*-

coumaryl (H) alcohols (see Fig. 1b), which differ in the number of methoxyl groups [12]. All these monomeric units contain a phenyl nuclei and a propyl side chain. Monolignols couple with each other but, more importantly, endwise cross-couple in a combinatorial fashion with evolving oligomers to produce complex, branched, lignin polymers [13]. Interunit linkage types are defined by the way a monomer or preformed oligomer cross-couples with another monolignol; common ones involve ether bonds (β -O-4, α -O-4, α -O- γ , etc.) or carbon-carbon bonds (5-5, β - β , etc.) (Fig. 1a), which can be present in varying amounts depending on the relative proportion of monolignols present in the plant source and lignin isolation methods [14]. Additionally, lignin is an amorphous tri-dimensional polymer which has a wide range of molecular weight distributions from $\sim$ 5000 to 40,000 Da [15]. Depolymerization methods typically afford ill-defined products in low yields (that is, < 10 –20 wt%) and poor selectivity (individual yield of most of the compounds are < 1 wt%) [16–18].

Fortunately, the β -aryl-ether linkages that are highlighted in blue color in Fig. 1a are ubiquitous, and constitute $\sim$ 50–65% of the various interunit linkages. Their chemical reactivity determines the reactivity of lignin. Hence, a number of efforts including the present [19–21], have used β -ether model compounds to model lignin degradation mechanism. It was found that $C_{\alpha}H-OH$ group within the β -O-4 structure highlighted in red color in Fig. 1a played a key role in β -O-4 cleavage

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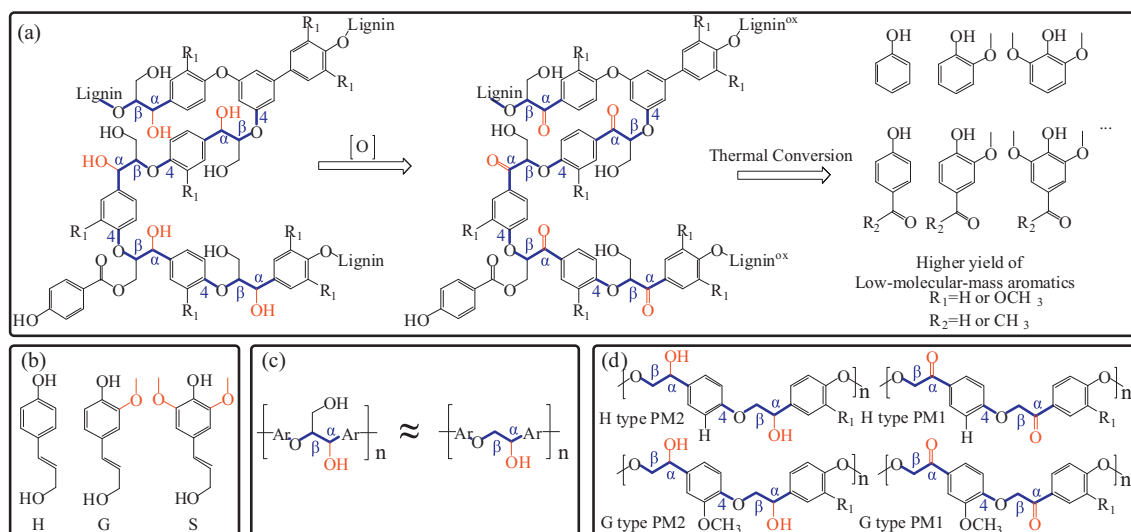


Fig. 1. Strategies for oxidation depolymerization and the structure of original lignin and selected β -ether-type lignin-like polymers used in this study.

reactions, while significantly affecting products distribution and yields. Many atypical methods on preprocessing or modification of the benzylic alcohol group have therefore been explored, such as acetylation [22], methylation [23], and oxidation [24–27]. Among them, the oxidation of $C_{\alpha}H-OH$ to $C_{\alpha}=O$ is one of the most promising methods due to its low cost and technological simplicity [28]. Simultaneously, the bond dissociation enthalpy (BDE) of $C_{\beta}-O$ bond of β -O-4-ketones is ~ 40 – 50 $\text{kJ}\cdot\text{mol}^{-1}$ lower than that of β -O-4-alcohols; in addition, β -O-4-ketones contain active $C_{\beta}-H$ and $C_{\alpha}-C_{\beta}$ bonds for further transformations [29], making subsequent interunit linkage bond cleavage easier. Oxidation methods for benzyl alcohol in lignin or its model compounds are well-established given the importance of the resultant aldehydic structure [24,30,31]. A number of efforts from the PIs have been devoted to lignin degradation via fast pyrolysis [21,31–33] and have revealed that a two-step methodology (pre-oxidation of $C_{\alpha}H-OH$ and degradation) is suitable for dissociating lignin interunit linkages. However, the pyrolytic reactivity of pre-oxidized lignin is still unknown and little studied. Furthermore, attention on the theoretical aspects of the pyrolysis pathways of $C_{\alpha}=O$ type lignin dimers have emerged from the current PI efforts [31] to determine that oxidation of the $C_{\alpha}H-OH$ group to $C_{\alpha}=O$ facilitated cleavage of the $C_{\alpha}-C_{\beta}$ bond and, as a result, allowed access to high-value aromatics via inhibition of subsequent condensation of the formed fragments. Additionally, a study of the secondary pyrolysis pathway of monomeric aromatics resulting from oxidized β -O-4 lignin dimeric model compounds verified that the polymerization reaction of unstable reaction intermediates led to a diminution of monomeric aromatics [32]. However, due to limitations in structure and molecular weight of β -O-4 lignin dimeric model compounds, dimeric model compound results do not necessarily imply that an operating framework that applies to dimeric model compound will apply to lignin fragments. Meanwhile, β -ether-type lignin-like model polymers are more similar to lignin fragments than monomeric and dimeric model compounds. Yet, to date, little research has been done on their pyrolysis behavior.

Four polymers (see Fig. 1d) were synthesized to represent β -ether-type lignin fragments (see Fig. 1c). These polymers model not only contained both the typical β -aryl-ether linkages and primary aromatic units, but also more closely resembled the molecular weight of lignin. Pyrolysis characteristics of four β -ether-type polymers were investigated by using a tube furnace reactor system and *in-situ* diffuse reflectance infrared pyrolysis system; the specific product distributions and migration patterns of volatile functional groups with temperature were analyzed and monitored in real time. Several important transformation pathways were proposed explaining the pyrolytic reactivity

of pre-oxidized lignin.

2. Materials and methods

2.1. Materials

The four β -ether-type lignin-like polymers (referred to as H type PM1, H type PM2, G type PM1 and G type PM2, respectively) were synthesized according to the published methods [34], whose specific synthesis reactions are shown in Fig. S1. Their characterization by ^{13}C NMR and ^1H NMR is in Figs. S2 and S3, respectively. More detailed characterization can be found in previous literature [35].

2.2. Tubular reactor pyrolysis system

Fast pyrolysis of samples was carried out with a tubular reactor using quartz U-tube. The detail of apparatus was described in Fig. S4. ~ 100 mg sample was added into the quartz U-tube as a methanol solution, and then the solution was evaporated in vacuum in an upright position. After purging with N_2 , the tube was sealed at atmospheric pressure. Pyrolysis was conducted by inserting the whole ampoule into a muffle furnace that was preheated to 400, 450, 500, 550 or 600 $^{\circ}\text{C}$. After 2 min, the U-tube was removed from the furnace and cooled with ice water for 2 min. The ampoule was opened and the mixture was collected by pouring it out and washing the reactor with ethyl acetate three times. The reaction mixture was filtered to separate the char from the liquid phase. The remaining char was then dried in an oven at 105 $^{\circ}\text{C}$ overnight before weighing for the yield calculation and subsequent analysis. Any adventitious water was absorbed by anhydrous Na_2SO_4 . Then the liquor mixture was separated using a filtration funnel. The liquor products remaining in the solvent phase were diluted with ethyl acetate to 100 mL (EA-soluble fractions) for further analysis.

The qualitative and quantitative analyses of EA-soluble fractions were carried out on a GC equipped with a mass selective detector (Agilent HP6890-5973 GCMS; quartz capillary column, $30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$). Helium was used as the carrier gas at a flow rate of 1 mL/min. Temperature program: 40 $^{\circ}\text{C}$, hold 1 min; 250 $^{\circ}\text{C}$ (rate 10 $^{\circ}\text{C}/\text{min}$), hold for 4 min; 280 $^{\circ}\text{C}$ (rate 5 $^{\circ}\text{C}/\text{min}$), hold for 5 min. The injector temperature was 250 $^{\circ}\text{C}$ with a split ratio of 10:1. The mass selective detector was operated with an electron impact (EI) ionization mode. Identification of the products was conducted by means of National Institute of Standards and Technology (NIST) library of mass spectra. The monomer yields were calculated by an external standard method. The yields of various products and selectivity were calculated

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