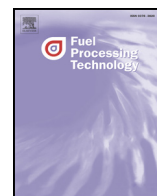




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Research article

Effect of functional groups on hydrogenolysis of lignin model compounds<sup>☆</sup>Guodian Zhu<sup>a</sup>, Xinping Ouyang<sup>a,\*</sup>, Linfeng Jiang<sup>a</sup>, Yuan Zhu<sup>a</sup>, Dongxue Jin<sup>a</sup>, Yuxia Pang<sup>a</sup>, Xueqing Qiu<sup>a,b,\*\*</sup><sup>a</sup> School of Chemistry & Chemical Engineering, South China University of Technology, Guangzhou 510640, China<sup>b</sup> State Key Laboratory of Pulp & Paper Engineering, South China University of Technology, Guangzhou 510640, China

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## ABSTRACT

Lignin is a future feedstock for the production of low molecular weight aromatics, and hydrogenolysis is probably the most promising process for lignin depolymerization. Effect of the benzylic alcohol group, aromatic methoxyl and phenolic hydroxyl groups on the hydrogenolysis of  $\beta$ -O-4 bonds in lignin model compounds was investigated in Pd/C hydrogenolysis system. It was found that the  $\beta$ -O-4 bonds in compounds with no a benzylic alcohol group were cleaved directly and quickly to form two aromatic monomers in near-quantitative yield. However, both dehydrogenation and dehydroxylation occurred for the model compounds containing a benzylic alcohol group, and resulted in more complicated products distribution. The dehydrogenation of a benzylic alcohol group hindered the cleavage of  $\beta$ -O-4 bonds to form aromatic monomer products. The results also indicated that both the aromatic methoxyl and phenolic hydroxyl groups had no impact on products distribution. The aromatic methoxyl group in non-phenolic and phenolic compounds promoted the cleavage of  $\beta$ -O-4 bonds, while the phenolic hydroxyl group had a slightly negative impact on cleavage of  $\beta$ -O-4 bonds.

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## 1. Introduction

With the rapid depletion of fossil resources and increasing demand for energy, lignocellulosic biomass is an alternative renewable resource for the production of liquid fuels and chemicals [1–3]. Lignin contributes to 15–30% by weight and 40% by energy content in lignocellulosic biomass [4], but its highly random and branched three-dimensional polyphenolic structure leads to its resistance to depolymerization [5]. Therefore, it has so far mainly been burnt for power generation, only less than 2% is used efficiently for producing high-valued products [6]. Efficient conversion of lignin into small aromatic molecules is still a huge challenge [7], so it is important to investigate the mechanism to address the principle of lignin depolymerization.

Lignin is mainly composed of p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) phenylpropanoid units linked by C–O and C–C bonds, and  $\beta$ -O-4 linkage is the predominant linkage in lignin [8,9]. Therefore, the investigation of  $\beta$ -O-4 bond cleavage has received the greatest attention. Typically, in order to better understand the lignin depolymerization mechanism and to control the depolymerization behavior for the production of aromatic monomers, lignin model compounds

containing  $\beta$ -O-4 bond were used to represent the most common sub-structure of lignin [10].

A family of thermochemical methods, such as pyrolysis, oxidation, hydrogenolysis and so on, had been employed to convert lignin into aromatic monomers. Both the linkages between the phenylpropanoid units and lignin benzene rings are cracked by pyrolysis or oxidation. It usually gave higher oxygen content of products which mainly include aromatic aldehydes and carboxylic acids by oxidation methods [11]. Due to the higher yield of aromatic monomers, hydrogenolysis is probably the most promising process for lignin depolymerization, and Yan group has put lot of efforts on the novel catalysts design to improve lignin hydrogenolysis [12–14]. Pd/C, a common heterogeneous catalyst, has received attentions in lignin hydrogenolysis [15–17]. In order to better convert lignin into aromatic monomers via hydrogenolysis, it is important to understand the mechanism of such depolymerization. The Fan et al. reported that benzyl phenyl ether as a lignin model compound was decomposed through a free-radical reaction mechanism to 71.6% of phenol and 50.4% of toluene with Pd/C as a catalyst in the presence of Na<sub>2</sub>CO<sub>3</sub> and N-methyl-2-pyrrolidone [18]. To understand the role of hydrogen atom at C $\alpha$ -position in lignin hydrogenolysis with Pd/C, the effect of benzylic alcohol, ketone, ether and alkane on  $\beta$ -O-4 bond cleavage rate and yield was investigated with  $\beta$ -O-4 model compounds [19]. It was found that a critical role of a benzylic hydrogen atom for  $\beta$ -O-4 bond cleavage was the formation of the intermediate  $\beta$ -phenoxyalkyl palladium hydride. Galkin et al. [20] reported that the dehydrogenation of a benzylic alcohol group in  $\beta$ -O-4 model compounds, the first step of decomposition, was a slow reaction step with Pd/C, and that  $\beta$ -O-4 bond cleavage proceeded through enolate

<sup>☆</sup> Notes: The authors declare no competing financial interest.<sup>\*</sup> Corresponding author.<sup>\*\*</sup> Correspondence to: X. Qiu, School of Chemistry & Chemical Engineering, South China University of Technology, Guangzhou 510640, China.E-mail addresses: [ceouyang@scut.edu.cn](mailto:ceouyang@scut.edu.cn) (X. Ouyang), [xueqingqiu66@163.com](mailto:xueqingqiu66@163.com) (X. Qiu).

isomerization which showed that hydrogen atom at C $\beta$ -position was also necessary to cleave  $\beta$ -O-4 bond. The benzylic alcohol group in lignin may play an important role in lignin hydrogenolysis process, so it is important to address how a benzylic alcohol group controls the products distribution and  $\beta$ -O-4 bond cleavage.

In addition, Hanson and coworkers reported that the phenolic hydroxyl group was required for C–C bond cleavage of lignin model dimer [21]. It was found that S unit-rich lignin was easier to be solubilized in the delignification process compared to G unit-rich lignin [22], because G unit-rich lignin made resistant to the depolymerization [23]. Therefore, it is also important to understand how aromatic methoxyl and phenolic hydroxyl groups in lignin affect the behavior of lignin hydrogenolysis.

In the present work, nine  $\beta$ -O-4 lignin model compounds in Scheme 1 used in previous studies [19,20,24] were chosen to explore the effect of functional groups (a benzylic alcohol group, aromatic methoxyl and phenolic hydroxyl groups) on hydrogenolysis of  $\beta$ -O-4 lignin model compounds in Pd/C hydrogenolysis system. The results may provide insights into lignin hydrogenolysis, and help to develop better catalytic system for producing aromatic monomers from lignin.

## 2. Experimental

### 2.1. Materials

Methanol, ethylbenzene, acetophenone and 1-phenylethanol were purchased from Aladdin Industrial Inc. (China). 4-Ethylphenol, 4'-hydroxyacetophenone, phenol, guaiacol and 2,6-dimethoxyphenol were purchased from Alfa Aesar Co. Inc. (China). 10%Pd/C and formic acid (99%) were purchased from J&K Scientific Ltd. (China). All chemicals were used without further purification.

Lignin model compounds 1–9 (Scheme 1) were prepared according to the published methods [25,26] with partial modification, and the structures of all model compounds were confirmed by MS,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and elemental analysis (Supporting Information).

### 2.2. Hydrogenolysis of model compounds

Because microwave irradiation can dramatically accelerate decomposition rate of lignin model compounds [25], the Pd/C hydrogenolysis of model compounds was carried out in a 100 mL vessel of microwave reactor (Ethos One, Milestone Inc., Italy). 0.10 mmol of lignin model compound, 0.0165 g of 10%Pd/C, 10 mL of methanol and 1.0 mmol of formic acid were added into the vessel. The vessel was purged three times with nitrogen to remove oxygen before sealed. The hydrogenolysis was carried out at 50–180 °C for 2.0–120 min under microwave irradiation with an initial power of 400 W. The average output power was 150 W (recorded by software installed in the microwave reactor). After reaction, the reaction vessel was cooled down to room temperature with ice water. Subsequently, the mixture was filtered by 0.45  $\mu\text{m}$  filter membrane, and the products from the filtrate were analysed by gas chromatography–mass spectrometry (GC–MS, GCMS-

QP2010, Shimadzu Co., Japan) and high performance liquid chromatography (HPLC, LC-20AT, Shimadzu Co., Japan).

### 2.3. Analysis of products

The products were identified by comparing their mass spectra in GC–MS with computer library (National Institute of Standards and Technology) in the instrument, and comparing their retention time in GC–MS and HPLC spectra with those of authentic compounds. The typical GC total ion chromatogram and HPLC chromatogram are shown in Fig. S1 and S2, respectively. The decomposed products were quantified by using HPLC equipped with UV detector and Zorbax SB-C18 reverse-phase column (4.6  $\times$  250 mm, 5.0  $\mu\text{m}$ ). The column temperature was set at 40 °C. The mobile phase consisted of HPLC grade degassed water (A) and methanol (B). The separation was performed by gradient elution at a total flow rate of 0.8 mL/min. The gradient program was as follows: from 20% B to 30% B in 10 min for 10 min, from 30% B to 40% B in 1 min for 10 min, from 40% B to 50% B in 1 min for 10 min, from 50% B to 60% B in 1 min for 10 min, from 60% B to 90% B in 2 min for 10 min. The detection and quantification of all decomposed products were done at 254 nm. The injection volume was 20.0  $\mu\text{L}$ . The yield of decomposed products was determined by standard curves. The conversion of model compounds and yields of products were calculated by:

$$\text{Conversion (\%)} = (1 - n_u/n_m) \times 100\% \quad (1)$$

$$\text{Molar yield of product } i(\%) = n_i/n_m \times 100\% \quad (2)$$

where  $n_u$ ,  $n_m$  and  $n_i$  were moles of unreacted model compounds, initially added model compounds (0.10 mmol) and product  $i$ , respectively. The measurement errors in three replicate tests were less than 1.0%.

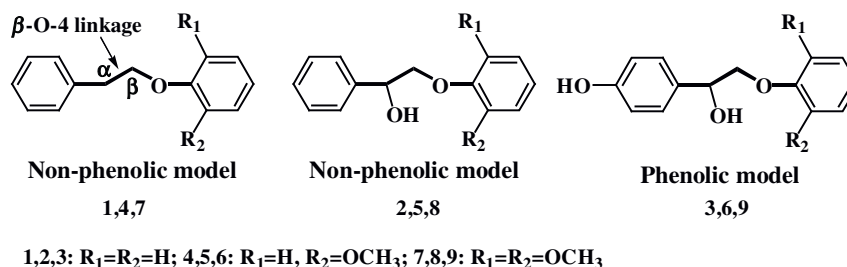
## 3. Results and discussion

### 3.1. Effect of a benzylic alcohol group

It is generally considered that lignin contains alcoholic hydroxyl group at C $\alpha$ -position [27], and the effect of a benzylic alcohol group on hydrogenolysis is shown in Fig. 1.

It was found that 11.8% of conversion was observed for compound 1 with no a benzylic alcohol group at 50 °C for 10 min, and 12.1% of phenol (10) and 10.8% of ethylbenzene (11) were produced. When reaction temperature increased to 180 °C, products 10 and 11 increased to 65.0% and 64.6%, respectively, which showed that the cleavage of  $\beta$ -O-4 bond was more favorable at an elevated reaction temperature. In addition, the decomposed products from compound 1 only contained products 10 and 11, in which the molar yield nearly equaled to the conversion at any reaction temperature. It was suggested that compound 1 with no a benzylic alcohol group was directly decomposed by only  $\beta$ -O-4 bond cleavage in hydrogenolysis system.

However, five products were produced when compound 2 containing a benzylic alcohol group was used, and it showed that the



Scheme 1. Lignin model compounds 1–9.

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