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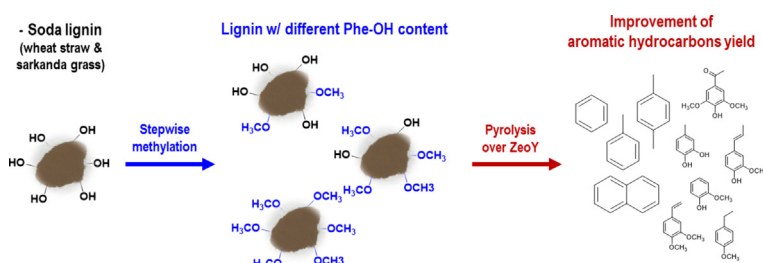
## Effects of phenolic hydroxyl functionality on lignin pyrolysis over zeolite catalyst



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## GRAPHICAL ABSTRACT



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## ABSTRACT

The phenolic hydroxyl group (Phe-OH), a representative functional group in the lignin macromolecule, was found to play an important role in lignin pyrolysis in the presence of zeolite catalyst. We prepared lignin samples with different Phe-OH content by chemoselectivity controlled stepwise methylation. These methylated lignins had almost the same structures as the original lignin except for their Phe-OH content. However, the instantaneous decomposition rate of methylated lignins by exposure to heat increased with increasing degree of methylation due to restriction of intermolecular hydrogen bonding of the Phe-OH. It suggested that Phe-OH content changed the thermal decomposition behavior of lignin. Upon pyrolysis in the absence of catalyst, methoxylated aromatics compounds such as *p*-methy-, *p*-ethyl-, and *p*-vinylanisole (evidence of methylation) were released from methylated lignins. Pyrolyzing methylated lignins with zeolite Y catalyst produced benzene, toluene, xylenes, and naphthalenes as main aromatic hydrocarbons, and their yields showed. A positive correlation with the degree of methylation. In addition, oxygenated functional groups in pyrolysis products were completely decomposed with zeolite Y catalyst. We obtained 39% enhanced aromatic hydrocarbons yield in totally methylated lignin compared with the original lignin. In this study, we propose plausible pathways for methylated lignin pyrolysis over zeolite Y on the basis of our observations.

## 1. Introduction

Lignin, the second most abundant natural polymer on Earth, consists of three phenylpropane units (*p*-coumaryl, coniferyl, and sinapyl alcohol) with various interunit linkages such as  $\beta$ -O-4 (40–60%),  $\beta$ -5 (4–10%), and biphenyl (3.5–25%) [1]. Lignin has been considered a

potential feedstock candidate for phenolic chemical production because of its inherent aromatic structure. According to previous studies, only 1–2% of the 50–70 million tons of lignin produced each year from the pulp and paper industries are commercialized [2–4]. In addition, the US Department of Energy predicts that approximately 225 million tons of lignin will be generated from the lignocellulosic bioethanol industry by

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2030 [5].

Catalytic pyrolysis is a thermochemical conversion process that enables the production of valuable aromatic hydrocarbons or other phenolics from lignin. To date, numerous studies on lignin pyrolysis have been conducted in various aspects involving process optimization, catalyst development, and diversification of lignin feedstocks [6–14]. Zeolite is the most widely used solid acid catalyst for catalytic pyrolysis because it can efficiently remove oxygen derived from biomass, resulting in a final liquid product with low O/C and high H/C ratio [15]. It has both Brønsted and Lewis acid sites, which possibly convert oxygenated compounds to aromatic hydrocarbons via cracking, dehydration, decarbonylation, decarboxylation, aromatization, dealkylation, dehydrogenation, and oligomerization [16]. Furthermore, zeolites have a unique microporous structure that enables them to control product distribution and enhance product selectivity toward specific aromatic hydrocarbons or phenolics.

Lignin is the most difficult biomass constituent to deoxygenate because of its structural complexity [17]. Mullen et al. obtained approximately 5–6 wt% of aromatic hydrocarbons from four kinds of lignin at 650 °C with HZSM-5 catalyst [6]. Wang et al. reported that the yield of aromatic hydrocarbons from switchgrass milled wood lignin was 2–9<sub>Carbon</sub>% within a temperature range of 400–800 °C. Our earlier study produced only 3.6 wt% of aromatic hydrocarbons from milled hardwood lignin under various pyrolysis conditions using HZSM-5 catalyst [11]. One of the reasons for low conversion efficiency may be the presence of Phe-OH in the lignin structure. It has been previously reported that Phe-OH in lignin or lignin-derived phenolics forms tight bond interactions with oxygen atoms in a zeolite framework, which gives rise to phenolate ions [18]. These ions were strongly adsorbed on acidic sites and led to a reduction in catalyst activity. Recently, Rezaei studied the effect of lignin-derived phenolics on zeolite deactivation by comparing catalyst properties before and after pyrolysis [16]. In addition, the Phe-OH in lignin could participate in the condensation reaction during pyrolysis [19,20]. It can be inferred that the Phe-OH of lignin would play a deleterious role in conversion efficiency and aromatic hydrocarbon selectivity during zeolite-catalyzed pyrolysis. However, few studies have proved this issue using lignin macromolecules.

In this study, we investigated the role of Phe-OH on the catalytic pyrolysis of lignin over zeolite catalyst using chemically modified lignins with different levels of Phe-OH content. We selectively blocked the Phe-OH site using dimethyl sulfate (DMS). After the methylation process, several analyses such as phosphorus-31 nuclear magnetic resonance (<sup>31</sup>P NMR), two-dimensional heteronuclear single quantum coherence spectroscopy nuclear magnetic resonance (2D-HSQC-NMR), and thermogravimetric analysis were performed to elucidate the structural change of the lignins. These methylated lignins were pyrolyzed using a pyroprobe pyrolyzer with zeolite, and pyrolysis products were quantitatively analyzed by gas chromatography-mass spectroscopy/flame ionization detector (GC-MS/FID). Based on these results, the impact of Phe-OH on the pyrolysis feature of lignin over zeolite catalyst is discussed in detail.

## 2. Materials and methods

### 2.1. Preparation of lignins with different Phe-OH contents

Soda lignin (Protobind 1000, SL) extracted from a mixture of sarkanda grass and wheat straw by the soda pulping process was purchased from Granit Research and Development SA. This lignin was selectively methylated using dimethyl sulfate (DMS) as described in Scheme 1 [21]. A total of 1.0 g of SL was dissolved in 50 mL of aqueous 0.7 M NaOH at room temperature. A different amount of DMS (0, 1, 3, 5 mL) was added to each 1.0 g of lignin, and the mixture was heated to 80 °C for 2 h. After the reaction, the mixture was acidified with 2 M HCl until the pH was below 2, and the solid precipitate was washed with

deionized water and freeze-dried. Methylated lignin samples were subsequently described as DMS0, DMS1, DMS3, and DMS5 depending on the amount of DMS added.

### 2.2. Zeolite catalyst preparation

Zeolite Y (CBV500, ZeoY) purchased from Zeolyst International was used in this experiment because its pore size was  $7.4 \times 7.4 \text{ \AA}$ , which is similar or slightly bigger than the diameter of monomeric phenols [22]. ZeoY was calcined in air for 5 h at 550 °C in order to convert to the H-form before use. The surface properties were measured with an ASAP 2010 analyzer (Micrometrics), and the acid property was determined by NH<sub>3</sub>-TPD measurements (BEL Japan, BELCAT B) [11]. The physical characteristics of ZeoY are presented in Table S1.

### 2.3. Lignin characterization

<sup>31</sup>P NMR was used to quantify the hydroxyl group content in lignins [23]. Lignin (25 mg) was phosphitylated with 70 μL of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP), and cyclohexanol was used as an internal standard (IS). This mixture was analyzed by a Bruker AVANCE 600 MHz instrument (Bruker, Germany) with an inverse-gated decoupling pulse sequence using a 45-degree pulse angle and 5.0 s relaxation delay. The resulting <sup>31</sup>P NMR spectra were integrated using MestReNova v10.0 software.

The weight percentages of carbon, hydrogen, nitrogen, and sulfur of lignins were measured by an elemental analyzer CHNS-932 from LECO Corp. The oxygen content was calculated by subtraction.

Gel permeation chromatography (GPC) analysis was performed to investigate the molecular weight information of the lignins. All lignins were acetylated with acetic anhydride/pyridine (1:1 v/v) at 70 °C for 6 h to dissolve in tetrahydrofuran (THF). Dissolved lignins were analyzed by a Spectra System P1000 apparatus (Thermo Separation Products, USA) equipped with PL gel 5.0 μm MIXED-C and MIXED-D columns (Polymer Laboratories). The effluents were detected by a Viscotek LR125 laser refractometer (Viscotek, USA).

2D-HSQC-NMR was performed with a Bruker AVANCE 600 MHz spectrometer (Bruker, Germany). Lignin (20 mg) dissolved in 0.75 mL DMSO-*d*<sub>6</sub> was analyzed by a standard Bruker pulse sequence “hsqcetgpsisp2.2” with a 90° pulse, 0.08 s acquisition time, 2.0 s pulse delay, 1JC-H of 150 Hz, 48 scans, and an acquisition of 1024 data points (for 1H) over 512 increments (for 13C). The 1H and 13C pulse widths obtained were p1 = 11.43 μs and p2 = 10.00 μs, respectively. HSQC data processing was carried out using MestReNova v10.0 software. Two regions were considered: (1) the aliphatic oxygenated side chain region ( $\delta_C/\delta_H$  50–90/2.5–5.9) and (2) the aromatic/unsaturated region ( $\delta_C/\delta_H$  100–140/5.5–8.0). In this study, C<sub>2,6</sub>-H<sub>2,6</sub> in H units ( $\delta_C/\delta_H$  127.9/7.19), C<sub>2</sub>-H<sub>2</sub> in G units (110.9/6.98), and C<sub>2,6</sub>-H<sub>2,6</sub> in S units (103.8/6.71) signals were chosen as an internal standard. The number of linkages, expressed as number per 100 aromatic units, was determined based on the corresponding signal ( $\beta$ -O-4:  $\delta_C/\delta_H$  71.9/4.9,  $\beta$ -5:  $\delta_C/\delta_H$  87.7/5.5, and  $\beta$ - $\beta$ :  $\delta_C/\delta_H$  85.5/4.6) [24].

Thermogravimetric analysis (TGA) was performed with a TGA/DSC 3 + STARE System (Mettler Toledo Corporation, Switzerland) to study the thermal decomposition behavior of the methylated lignins with and without ZeoY catalyst. In the former case, a mixture of lignin and catalyst 1:1 w/w was used. TGA was carried out at a constant heating rate of 10 °C/min up to 600 °C within an inert atmosphere under a 25 mL/min N<sub>2</sub> flow.

### 2.4. Catalytic pyrolysis of lignin

A coil-type CDS Pyroprobe 5000 (CDS Analytical Inc., Oxford, PA, USA) was used in this study. Before catalytic pyrolysis, lignin and ZeoY were mixed in a 1:1 w/w ratio, and then 2.0 mg was introduced to a quartz tube. When lignin was pyrolyzed alone, 1.0 mg of lignin was

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