

Formation of *p*-Unsubstituted Phenols in Base-catalyzed Lignin Depolymerization

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Abstract Lignin valorization is one of the biggest challenges for developing biomass-based chemical industry. Recent innovative works has enabled depolymerization of lignin to the monomers with the yield close to theoretical maximum. The main product is a mixture of phenols derived from the cleavage of β -O-4 linkages between phenylpropanoid units. However, the obtained highly functionalized phenols are not common in current industry and, therefore, needs further processing for the utilization in intended applications. The present study shows that simple phenols without functional groups at *para*-position form selectively in base-catalyzed depolymerization of lignin. The yield is not sufficiently high, up to 6.9% on a carbon basis under the examined conditions, but the selectivity among released lignin monomers reaches 80%. The study also discusses the mechanism of *p*-unsubstituted phenols formation.

1 Introduction

Lignocellulosic biomass is a renewable source of chemicals and fuels. The development of technologies for efficiently converting biomass to a variety of chemicals is a key to sustainable society with less dependency on fossil fuels. Studies on bio-renewable chemicals production so far mostly focussed on cellulose, a main component of biomass. On the other hand, to reach biochemical industry with economic feasibility, we need to consider valorization of the other portion of biomass.

Lignin accounts for 16–31 wt% of woody biomass. Although the detailed structure is different by the origin, lignin is a phenolic polymer with β -O-4 as the most abundant linkage. Different from cellulose and hemicellulose, lignin is thus has a potential to be abundant direct source of bio-aromatics. However, the complex and recalcitrant structure inhibits the depolymerization to mono-aromatics. In fact, until several years ago, it was generally accepted that available yield of lignin monomers was limited to less than 10% (Beauchet *et al.*, 2012). In recent years, triggered by key findings on the depolymerization chemistry (Song *et al.*, 2013; Rahimi *et al.*, 2014; Shuai *et al.*, 2016), a rapid advancement has been made in this research field. There have been many studies that report near-complete lignin depolymerization. For example, Van den Bosch *et al.* (2017) showed that treatment of birch wood with Ni/Al₂O₃ in methanol under pressurized hydrogen produced phenolic monomers with 44% yield, which was close to the theoretical maximum yield. Cellulose and hemicellulose in the residue were hardly damaged in the treatment and could be converted into bio-ethanol with 73% yield. This type of biorefinery

strategy is called lignin-first fractionation, where depolymerization of native lignin from biomass and their quick stabilization are important for achieving high monomer yield. The depolymerization technology is thus being established at a high level. Whilst, the immediate utilization of obtained lignin oil is generally difficult because of their undesired properties consisting of a variety of highly functionalized phenols (Rinaldi *et al.*, 2016). There are studies on downstream processing of the oil, but it often results in the utilization as a low-value added liquid fuel.

Hydrothermal base-catalyzed depolymerization is another approach to the lignin valorization (Vigneault *et al.*, 2007; Beauchet *et al.*, 2012; Katahira *et al.*, 2016). Because it is a type of reaction occurring in traditional kraft process, chemistry behind the reaction has attracted attention for researchers. Brønsted basicity derived from base in water causes alteration of electronic structure of lignin and facilitates the dissolution and depolymerization (Otromke *et al.*, 2019). Different from lignin-first strategy, depolymerized lignin is generally unstable, leading to the condensation and relatively low yields of soluble products (sulfide ion suppresses the condensation in kraft process). Even with the low yields, this approach is still attractive because of similarity to existing processes in paper industry. High dissolution power of basic water enables facile lignin extraction and downstream processing. In our previous studies, a process scheme for valorization of lignin utilizing base-catalyzed reaction was proposed, which consisted of three steps: lignin dissolved in basic water was depolymerized, lignin monomers were extracted from the aqueous phase with water-insoluble solvent, and the lignin left in aqueous phase was

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completely reformed to combustible gas consisted mainly of methane (Kudo *et al.*, 2014; Nishioka *et al.*, 2014). Valorization of 78% lignin as monomers and fuel gas was demonstrated, and the basic water at the outlet could be fully recycled to the process.

A main focus of the present study is on the characteristics of lignin monomers from the base-catalyzed depolymerization. The monomers from lignin-first fractionation consists mainly of phenols with propane, propylene, or propanol chain at *para*-position because of selective cleavage of β -O-4 linkage. On the other hand, the monomers from base-catalyzed depolymerization tend to contain more *p*-unsubstituted phenols such as phenol, guaiacol, and syringol (R = H in Figure 1). Those phenols have established market or high potential to be readily used in industry because of the simple structure. However, the formation of *p*-unsubstituted phenols is unusual because it generally involves C-C bond (α -1 linkage) cleavage, which needs much higher bond-dissociation energies than that of β -O-4 linkage (Galkin and Samec, 2016). Studies on chemistry of kraft pulping (Gierer, 1980) have evidenced the cleavage of α -1 linkage but described that the C-C bond cleavage accounts for only small portion of lignin depolymerization. In this study, the selective formation of *p*-unsubstituted phenols is demonstrated using two types of technical lignin in the base-catalyzed depolymerization, and discussion is made for providing insight into the mechanism of their formation.

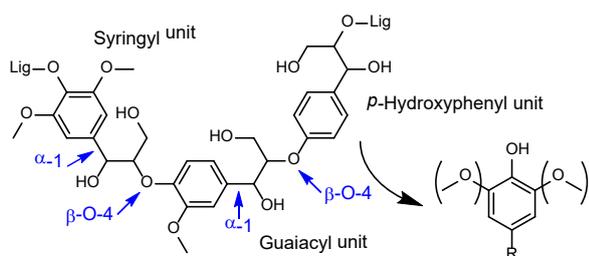


Figure 1. Simplified structure of lignin and lignin monomer

2 Experimental

2.1 Materials

Two types of lignin were used as feedstock. Lig-A was purchased from Sigma-Aldrich (lignin, alkali), and Lig-B was kindly supplied by Sanuki Kasei Co., Ltd., Japan. The ratio of aromatic nuclei, analysed by a common nitrobenzene oxidation method (Rodrigues *et al.*, 2011), was syringyl/guaiacyl/*p*-hydroxyphenyl (mol%) = 1/94/5 and 25/48/26 for Lig-A and Lig-B, respectively.

2.2 Reaction and product analysis

Experiments of base-catalyzed lignin depolymerization were carried out mainly with a flow type reactor (Figure 2). Na_2CO_3 was used to make basic solution. NaOH is often used for the base-catalyzed depolymerization, but it reacts with generated carbonate ion during the reaction to form Na_2CO_3 . For the direct reuse to the process, Na_2CO_3

would be a better choice (Kudo *et al.*, 2014). 0.1 M Na_2CO_3 aqueous solution was fed to the tubular reactor (SUS316, i.d. 2.17 mm, volume 9 mL) at 11 MPa, and the reactor was heated to a prescribed temperature. Then, the feed was switched to a solution containing lignin at 5,000 ppm (mg-C/L) in 0.1 M Na_2CO_3 aqueous solution. The reaction time was controlled by feeding rate of the lignin solution. The depolymerization experiment was also carried out with a batch reactor. A container (10 mL) consisting of Swagelok fittings was loaded with lignin, 5 mL of 0.1 M Na_2CO_3 aqueous solution or water, and nitrogen (ambient pressure), and submerged in a fluidized sand bath heated at a reaction temperature. After a prescribed reaction time, the reaction was quenched by immersing the reactor in an iced water.

The product solution was acidified to pH = 1–1.5 with HCl, and separated by PTFE membrane filter (pore size: 0.45 μm) into acid-soluble and -insoluble fractions. The acid-soluble fraction was extracted by ethyl acetate and subjected to gas chromatography–mass spectrometry (GC–MS) analysis with a PerkinElmer Clarus SQ8 for the quantification of lignin monomers. Details for the analytical method can be found elsewhere (Kudo *et al.*, 2014). The acid-insoluble fraction (acid-insoluble lignin: AIL) was dried in vacuo at 40°C overnight. AIL was analysed by thermogravimetry (TGA), Fourier transform infrared spectroscopy (FT-IR), and gel permeation chromatography (GPC). TGA was performed on a SII Nano Technology EXSTAR TG/DTA 7200. 2–2.5 mg of AIL was heated at 5°C/min under nitrogen flow (200 mL/min). The conversion (X) was calculated with a relative mass on a basis of the mass at 110°C. FT-IR spectra were measured on a PerkinElmer, Spectrum two equipped with an attenuated total reflectance (ATR) cell at 4 cm^{-1} resolution. GPC analysis was carried out with a Shimadzu LG-20 prominence series equipped with three columns connected in series (Tosoh TSKgel G3000HXL, G2000HXL, and G1000HXL) using tetrahydrofuran (THF) as mobile phase. Before GPC analysis, AIL samples were acetylated with acetic anhydride in pyridine to be soluble in THF.

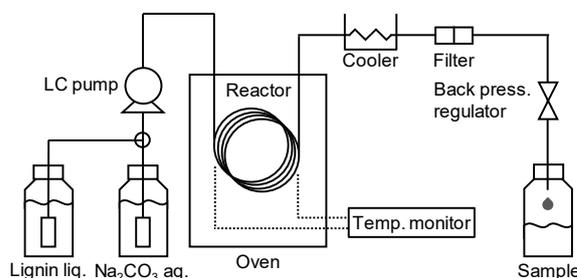


Figure 2. Schematic diagram of experimental setup for base-catalyzed lignin depolymerization in a flow type reactor

3 Results and Discussion

3.1 Effect of base-catalysis on depolymerization

To investigate the effect of base-catalysis, hydrothermal lignin depolymerization was carried out in 0.1 M Na_2CO_3

and water. The batch reactor was employed for this experiment because lignin was little soluble in water to feed into the flow reactor. The difference of depolymerized products was apparent from GC-MS chromatograms (Figure 3). Both products contained phenol, guaiacol, and syringol, but the depolymerization in water also produced phenolic compounds (Phs) with substituent at *para*-position. Figure 4 shows the yields of Phs from Lig-A and Lig-B. The main Phs from base-catalyzed depolymerization were guaiacol for Lig-A and phenol, guaiacol, and syringol for Lig-B. The compositions agree with their aromatic nuclei structure. Lig-A is from softwood and consists mainly of guaiacyl unit. Lig-B is from bamboo and has all three units (syringyl, guaiacyl, *p*-hydroxyphenyl). *p*-Substituted Phs (= other Phs) accounted for only a minor portion of the lignin monomers. Moreover, the total yield of Phs was much higher for the depolymerization under base-catalysis, reaching 6.9–8.4% on a carbon basis (%-C), although it is not necessarily high, compared to that in recent studies, which achieved near-complete lignin depolymerization (Song *et al.*, 2013; Rahimi *et al.*, 2014; Shuai *et al.*, 2016). It was thus confirmed for two types of lignin that base-catalyzed depolymerization selectively produces *p*-unsubstituted Phs.

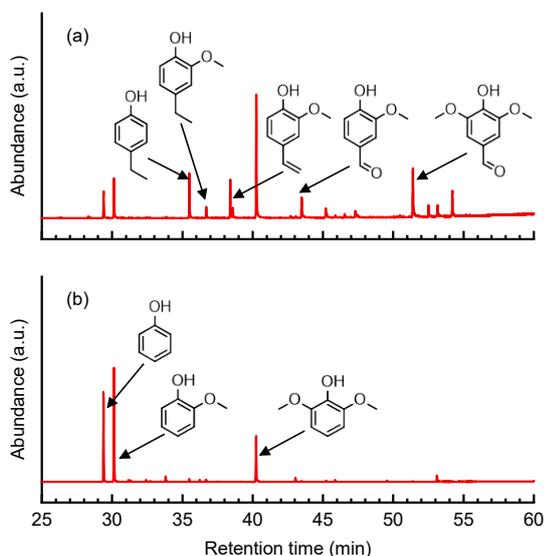


Figure 3. GC-MS chromatograms of acid-soluble fraction of Lig-B after depolymerization in (a) water and (b) 0.1 M Na₂CO₃ at 300°C for 20 min in batch reactor

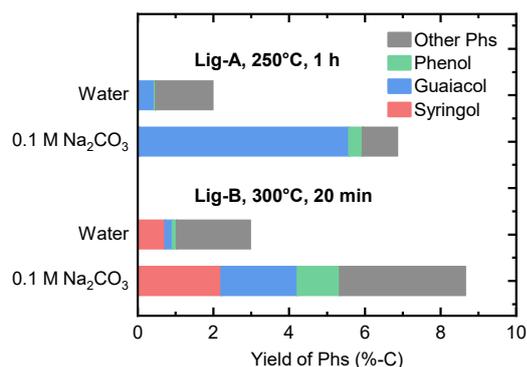


Figure 4. Yield of lignin monomers (Phs) from Lig-A and Lig-B after depolymerization in batch reactor

3.2 Base-catalyzed lignin depolymerization in flow type reactor

The base-catalyzed depolymerization was carried out in the flow type reactor for investigating the effect of reaction time on the products in detail. The total Phs yields are presented in Figure 5. The yield increased with reaction time and reached the maximum at 4–9 min in the reaction at 300°C. As with the batch experiment, Phs consisted mainly of phenol, guaiacol, and syringol. Their yields were 5.5 and 6.9%-C, and selectivities among Phs were 61.0 and 80.0% for Lig-A and Lig-B, respectively, at the maximum. The proportion of aromatic carbon, analysed by solid state ¹³C NMR, in the total carbon of Lig-B was 54.1%. Therefore, the yield showed substantial portion of aromatics in Lig-B, more than 10%, was released as *p*-unsubstituted Phs.

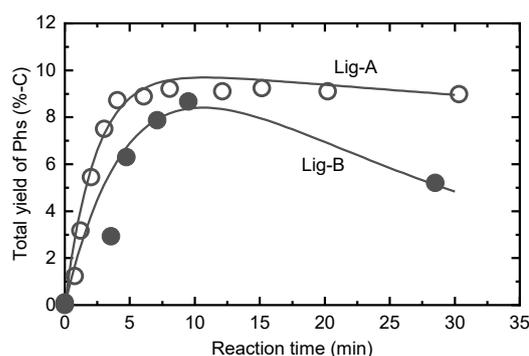


Figure 5. Total yield of Phs at different reaction time: lignin 5,000 ppm, 0.1 M Na₂CO₃, 300°C, 11 MPa, flow reactor

After showing the maximum, the total yield decreased for Lig-B in particular. To investigate the reason for the decreasing trend, the stability of main phenols under base-catalyzed condition was investigated (Figure 6). In the reaction at 325°C, phenol was relatively stable, losing only 13% of its portion even at 11 min. On the other hand, major portion of guaiacol and syringol were converted to degradation products. A linear increase in the conversion presented independency of kinetics on the concentration and indicated the influence of base-catalysis. Under the basic condition, guaiacol undergoes hydrolysis of methoxyl group to form catechol (Beauchet *et al.*, 2012). Similarly, syringol is demethoxylated to form guaiacol and then catechol. However, this does not explain the decrease in the total yield of Phs at a long reaction time. A plausible reason is condensation of the phenols, but the formation of condensed solid material was not visually observed in the experiment of Figure 6.

Detected Phs from the reaction were 21 and 37 types for Lig-A and Lig-B, respectively. Figure 7 summarizes temporal change in the yield of Phs, which showed the highest yield over 0.2%-C, for Lig-A. As seen from the result, ether linkage or hydroxyl groups at *Ca* and *Cγ* position did not survive the reaction. Even including other Phs, no Phs contained hydroxyl group in *p*-substituents. This was because of catalysis induced by Brønsted basicity for the deprotonation. Because the catalysis was active toward a wide variety of linkages in lignin, many types of Phs were formed as primary products. Therefore,

the most Phs were produced at an early stage of the reaction excepting catechol that was formed from guaiacol. In kraft process, sulfidolytic cleavage also helps the depolymerization, making the composition of Phs more complicated (Gierer, 1980).

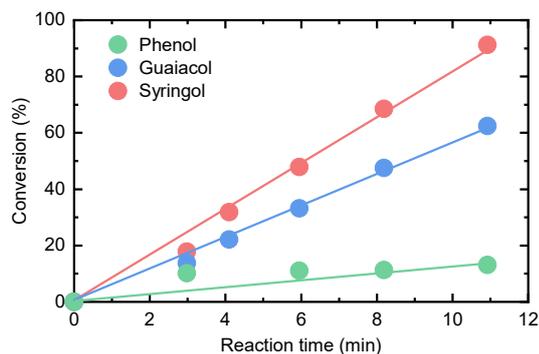


Figure 6. Stability of phenol, guaiacol, and syringol under base-catalyzed condition: phenols 500 ppm, 0.1 M Na₂CO₃, 325°C, 11 MPa, flow reactor

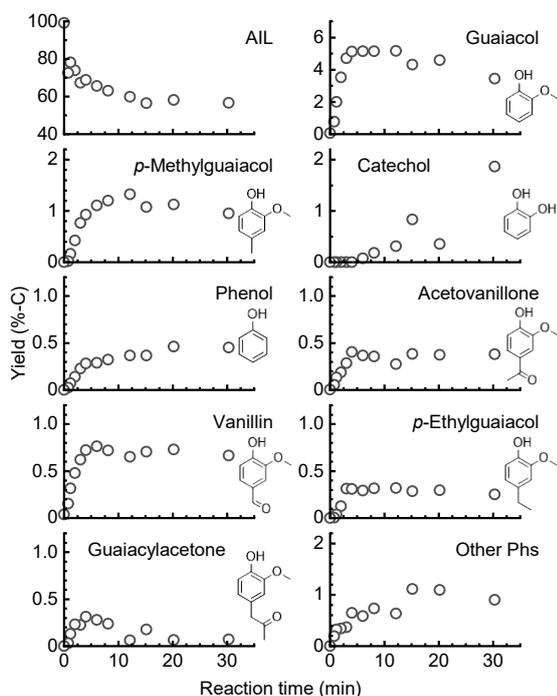


Figure 7. AIL yield and breakdown of Phs yield from Lig-A: lignin 5,000 ppm, 0.1 M Na₂CO₃, 300°C, 11 MPa, flow reactor

3.3 Analysis of AIL

Figure 7 also shows the yield of AIL. Raw Lig-A (reaction time = 0 min) consisted mostly of AIL with the recovery of 99.1%-C. The AIL recovery dropped to 72.5%-C at the initial stage of the reaction (0.8 min) and gradually decreased to 56.6%-C at 30 min. The sum of yields of AIL and Phs were in the range of 65.6–79.3%-C at 0.8–30 min, and thus indicated the presence of acid-soluble products that could not be detected in GC-MS analysis and had oligomeric structure. In other words, the oligomeric product, accounting for over 20%-C portion of Lig-A, was released even with the short reaction time of 0.8 min.

Because the yield of Phs more slowly increased, the fragmented oligomer was unlikely the source of *p*-unsubstituted Phs. This observation in turn suggested that the residual phase was gradually reformed to quinone methide intermediates, which was active to retrograde aldol reactions (Gierer, 1980), releasing *p*-unsubstituted Phs. Because the present reaction conditions were not sufficient for actively causing the cleavage of β -O-4 linkage, *p*-unsubstituted Phs accounted for major portion of Phs in the product.

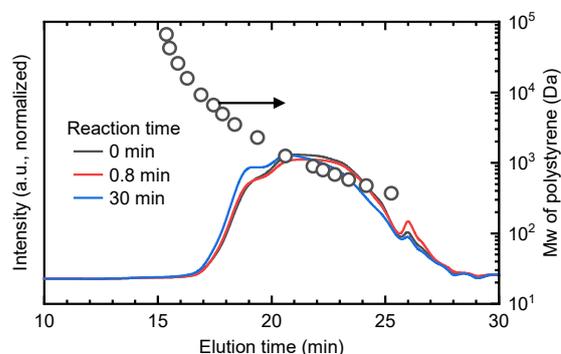


Figure 8. GPC chromatograms of AIL after base-catalyzed depolymerization for 0, 0.8, and 30 min.

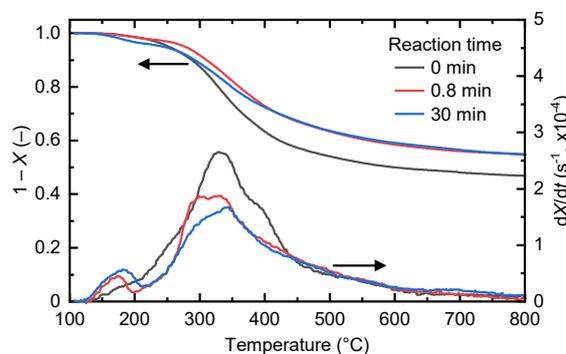


Figure 9. TG curves and dX/dt profiles of AIL after base-catalyzed depolymerization for 0, 0.8, and 30 min.

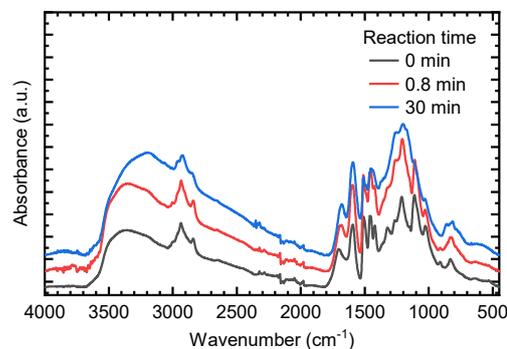


Figure 10. FT-IR spectra of AIL after base-catalyzed depolymerization for 0, 0.8, and 30 min.

Selected AIL samples were analysed by GPC, TGA, and FT-IR. There was little difference in GPC chromatograms of AIL after 0, 0.8, and 30 min of reaction (Figure 8). The base-catalysis depolymerizes lignin while promotes the condensation in parallel, which resulted in apparent similarity in the molecular size distribution. The carbon content, measured by elemental analysis, was 63.3, 70.2, 71.6 wt% for AIL with the reaction time of 0, 0.8,

and 30 min, respectively, supporting the progress of condensation. TGA also showed the effect of reactions induced by the base-catalysis (Figure 9). TG curves presented the decrease in volatile matter content. The concave in dX/dt profiles around 200–300°C was supposedly caused by the release of acid-soluble oligomeric fraction. On the other hand, FT-IR analysis (Figure 10) distinguished the structures of AIL with the reaction time of 0.8 and 30 min. All spectra contained IR absorbance at wavenumbers characteristic of lignin, but the peak at 1060–1160 cm^{-1} , corresponding to the ether linkage, was hardly observed only for AIL after 30 min of the reaction. This indicated that precursor of *p*-unsubstituted Phs still survived after the initial release of its large portion as acid-soluble fraction and gradually decreased along with the formation of Phs. According to the above mentioned mechanism of α -1 linkage cleavage (Gierer, 1980), the phenolic unit of *p*-unsubstituted Phs precursor needs to be phenolate anion with β -O-4 linkage at $C\beta$ position. Given the yield of *p*-unsubstituted Phs, the precursor-like structure dominated at least more than 10% of aromatic rings in Lig-A.

4 Conclusions

Base-catalyzed depolymerization experiments using two types of technical lignin demonstrated the effectiveness for selectively producing *p*-unsubstituted Phs such as phenol, guaiacol, and syringol. The yield reached 5.5–6.9%-C in the short reaction time of 5–9 min at 300°C, and the selectivity among lignin monomers was 61.0–80.0%. In the reaction, more than 20%-C of lignin was released as acid-soluble lignin oligomer at the initial stage. The residual phase retained abundant precursor of *p*-unsubstituted Phs, and presumably formed phenolate anion linked to lignin molecule, followed by the cleavage of β -O-4 linkage. Under the base-catalysis, the released phenol was relatively stable, but guaiacol and syringol were converted to degradation products with a long reaction time.

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