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Efficient conversion of lignin into single chemical species by solvothermal reaction in water–*p*-cresol solvent

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Abstract

Lignin was selectively converted into single chemical species in water–*p*-cresol mixtures at 673 K. Complete depression of char formation was realized in a mixture of 1.8 g of water and 2.5 g of *p*-cresol. The frame structure of lignin was efficiently decomposed within a reaction time of 4 min. The species obtained had a molecular weight of 214 (M^+) assigned by gas chromatography–mass spectroscopy and was identified as hydroxylphenyl-(hydroxyltolyl)-methane (HPHTM) by ^1H and ^{13}C nuclear magnetic resonance. Its yield approached the maximum of 80% C at ~ 30 min of reaction time. HPHTM was presumably produced by the addition of *p*-cresol at the most active $C\alpha$ position of the hydroxyphenylpropane derivative that was formed by the hydrolysis of lignin.

1. Introduction

Biomass has been noted as a renewable resource that is essential to realize a sustainable development of the world. A variety of conversion [1–7] and liquefaction [8, 9] processes have been proposed for using biomass as energy and chemicals resources alternative to fossil resources. Plant biomass consists of 50 wt% of cellulose, 20 wt% of hemicellulose and 30 wt% of lignin, approximately. Lignin is a biopolymer in which hydroxyphenylpropane units connect with ether and partial carbon–carbon bonds [10–12] in a helical structure [13]. Therefore, phenolic chemicals can be obtained from lignin by chemical disassembly processes. Freudenberg *et al* [14] has reported that vaniline was produced from lignin by the alkali–nitrobenzene method.

Recently, some researchers converted lignin into chemicals in supercritical water ($T_c = 647.3$ K and $P_c = 22.1$ MPa). Johnson *et al* [12] found that the yield (maximum 4.4%) of hydrolysis products including catechol from lignin increased with reaction time in supercritical water when using Pt catalysts at 648 K under 27.6 MPa of hydrogen. Yokoyama *et al* [15]

reported that higher water density increased the yield (maximum 40%) of oil and products containing hydroxyl groups, and decreased the yield (minimum 30%) of char in subcritical and supercritical water at 623–693 K up to 40 MPa. These results indicate that supercritical water can be used for disassembly of lignin. However, the formation of char due to repolymerization occurs at the same time. This seems a main reason that the yield of chemicals is so low in the lignin conversion. Recently, Saisu *et al* [16] demonstrated the conversion of organosolv lignin into chemicals with water–phenol mixtures at 673 K. They suggested that phenol acted as a capping agent to prevent char formation in supercritical water. Nevertheless, the suppression of char formation could not have been achieved by their method. Longer reaction time increased the formation of char.

In this study, we aimed to convert lignin into single chemical species at high efficiency. We examined mixtures of water and *p*-cresol for selectively producing chemicals from lignin without the formation of char.

2. Experimental details

Organosolv lignin was purchased from Aldrich and used as a lignin sample. The average molecular weight of the lignin was 2100 and its carbon and hydrogen contents were 66.54% and 5.85%, respectively. The organosolv lignin was completely soluble in tetrahydrofuran (THF). THF (HPLC grade) and *p*-cresol (99.0%) were purchased from Wako chemicals and were used without further purification.

Experiments were conducted using pressure-resistant vessels (SUS316) whose inner volume was 5 cm³. The vessel was loaded with 0.1 g of lignin and a solvent without purging by an inert gas. The solvents used were water, *p*-cresol and their mixtures. The vessel was heated in an electric furnace whose temperature was maintained at 673 K. The time required to heat up the reactor from room temperature to 673 K was a few minutes. Reaction times reported include these heat-up periods. The reaction was conducted for 3–60 min and ended by quenching the vessel in a water bath at room temperature. Figure 1 shows the analytical procedure. The products were collected by rinsing the vessel with 50 mL of THF and separated into THF insoluble and THF soluble components using a 1.6 μm glass-fibre membrane filter. The THF insoluble components were dried *in vacuo* at 313 K for one day and then weighed. The insoluble components were defined as char. The yield of the THF soluble components was defined as follows:

$$\text{Yield (wt\%)} = (1 - \text{char (g)/lignin loaded (g)}) \times 100.$$

The molecular weight distributions of THF soluble components were measured by a gel permeation chromatograph (GPC-900, JASCO) equipped with a refractive index detector, double Shodex KF-803L columns and a single Shodex KF-801 column. Naphthalene was added as an internal standard in solutions of THF soluble components, and the THF soluble components were analysed by a gas chromatograph–mass spectroscope (GCMS Saturn 2000, VARIAN) with a CP-SIL 8 CB Low Bleed column and a gas chromatograph–frame ionization detector (GCFID CP-3800, VARIAN) with a CP-SIL 8 CB Low Bleed column. A nuclear magnetic resonance spectroscope (DRX-500, Bruker Avance) with ¹H and ¹³C was used to identify the chemical species obtained.

3. Results and discussion

The reactant, namely, organosolv lignin, is completely soluble in THF. Therefore, the formation of insoluble components implies unfavourable repolymerization between lignin

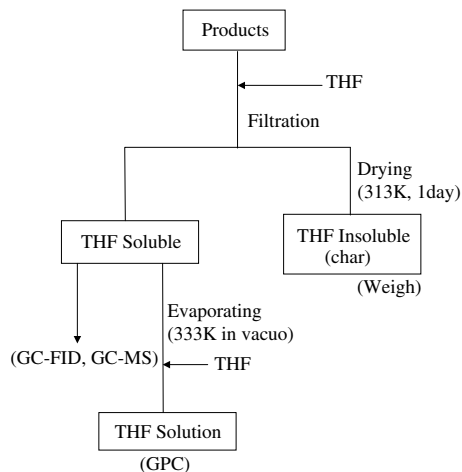


Figure 1. The analytical procedure.

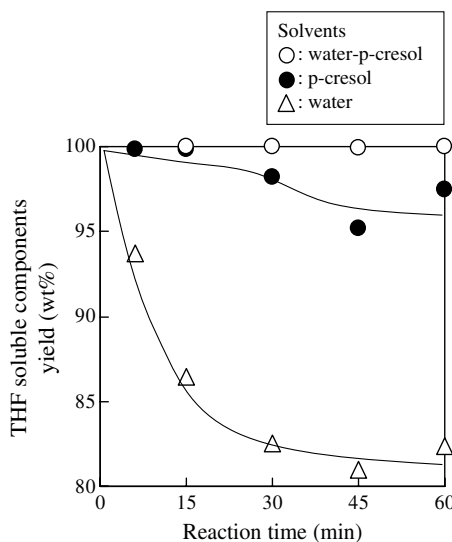


Figure 2. The effect of solvent and reaction time on the yields of the THF soluble components produced by reactions in three solvents at 673 K. Solvents: water, *p*-cresol (2.5 g) and water-*p*-cresol mixture (1.8:2.5 g).

and decomposed fragments to form products with large molecular weight. Figure 2 shows the effect of solvent on the yields of the THF soluble components produced by the reactions at 673 K in three kinds of solvent, namely, 2.5 g of water, 2.5 g of *p*-cresol and a mixture of 1.8 g of water and 2.5 g of *p*-cresol. In both water and *p*-cresol solvents, repolymerization occurred to some extent and gave the THF insoluble components. The yield of the THF soluble components decreased as reaction proceeded and the yields were about 82% after 60 min and 97% in water and *p*-cresol, respectively. On the other hand, the products in the mixture were completely soluble in THF throughout the reaction. On the basis of this result, we then examined the effect of composition of the solvent on the decomposition of lignin. Figure 3 shows the yield of char as a function of loading of water into 2.5 g of *p*-cresol. The yield of char decreased with increasing amount of water although it slightly increased at low water composition. This result indicates that depolymerization and repolymerization occurred simultaneously in mixtures. The yield of char became negligible after the reaction in 1.8 g of water and 2.5 g of *p*-cresol (total 4.3 g of solvent). The mixture of 1.8 g of water and 2.5 g of *p*-cresol is excellent as a solvent for lignin disassembly.

After confirming complete suppression of the THF insoluble products, we studied the molecular weight distribution of the THF soluble products. Figure 4 shows the molecular weight distribution of the original lignin and the THF soluble products. The original lignin had a broad peak around 4×10^3 , whereas the products had a sharp peak at around 3×10^2 . This figure clearly shows that the original lignin was decomposed into fragments with smaller molecular weight as the reaction time increased. The distribution curves had a sharp peak at around 3×10^2 , indicating that one small species is selectively obtained. We also note that the time required to decompose the frame structure of lignin is very fast. In our reactor, the time required to heat up the reactor from room temperature to 673 K was a few minutes. Therefore, original lignin was not well depolymerized within 3 min and the curve for 3 min of reaction

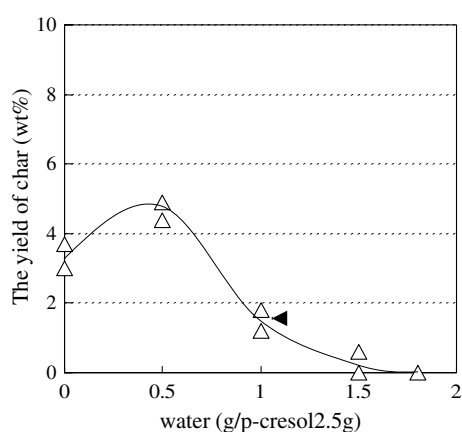


Figure 3. The effect of loading of water and *p*-cresol in the reactor on the yields of char produced by reaction for 60 min at 673 K.

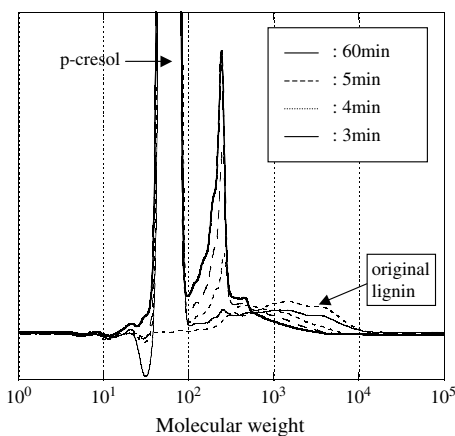


Figure 4. The effect of reaction time on the molecular weight distribution of the THF soluble components produced by reaction in the mixture (1.8:2.5 g) at 673 K.

time still had a small peak at $\sim 4 \times 10^3$. However, the large molecular weight components of the original lignin were almost depolymerized within 4 min to form molecular weight compounds at $\sim 3 \times 10^2$. These results indicate that the frame structure of original lignin was rapidly depolymerized at around 673 K. The longer reaction time decreased the amount of compounds at $\sim 1 \times 10^3$ and increased that of the compounds at $\sim 3 \times 10^2$. These results suggest that the decomposition rate of the frame structure of lignin is very fast; also further decomposition of the fragments followed.

To identify the product of the reaction in the mixture of 2.5 g of water and 1.8 g of *p*-cresol, we performed GC-FID analysis. Figure 5 shows GC-FID chromatogram for the products of the reaction (a) with and (b) without lignin. The products of the reaction with lignin had a large peak at a retention time of 49 min, while the products of the reaction without lignin did not. Therefore this peak originates from the decomposition of lignin. GC-MS study indicated that the peak was identified as having a molecular weight of 214 (M^+). We also performed ^1H and ^{13}C NMR analysis and the peak was identified as hydroxyphenyl-(hydroxyltolyl)-methane (HPHTM) (^1H NMR (in d_8 -THF): δ 2.18 (3H, s, CH_3), 3.82 (2H, s, CH_2), 6.63 (2H), 6.78 (2H), 7.05 (3H) (7H, aromatic H), 7.92 (2H, s, OH); ^{13}C NMR (in d_8 -THF): δ 19.7 (CH_3), 34.6 (CH_2), 114.4, 114.7, 126.9, 129.4, 130.7 (aromatic C), 152.9 (COH), 155.7 (COH)).

Figure 6 shows the yield of HPHTM as a function of reaction time. The yield was evaluated on the basis of the mass balance of benzene rings using the following equation: $\text{yield (\% C)} = [(\text{carbon of HPHTM}/2)/(\text{carbon of lignin loaded} \times 7/9)] \times 100$. The yield reached a maximum of 80% C at 30 min of reaction time. Therefore we can conclude that our procedure decomposed lignin with complete suppression of char formation and selectively produced one compound whose yield is as high as 80% C.

Finally, we propose a mechanism for the formation of HPHTM during reaction (figure 7). HPHTM is produced by elimination of glycolaldehyde from HPHTP via the formation of hydroxyphenylpropane derivative (HPHTP) by hydrolysis of lignin with the addition of *p*-cresol at the most active α position and release [17] of formaldehyde from guaiacol units.

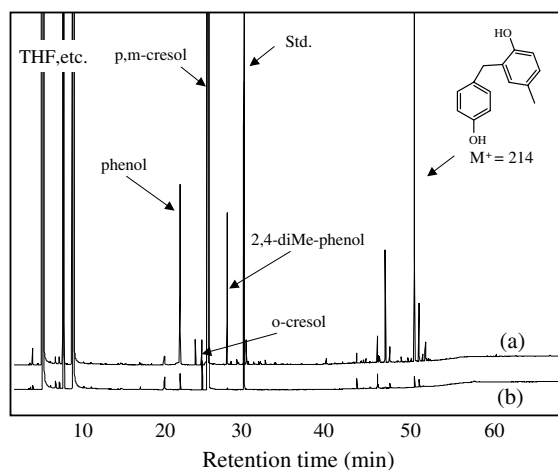


Figure 5. GC-FID chromatograms of the THF soluble components produced by reaction in the mixture (1.8:2.5 g) for 60 min at 673 K. (a) with lignin, (b) without lignin.

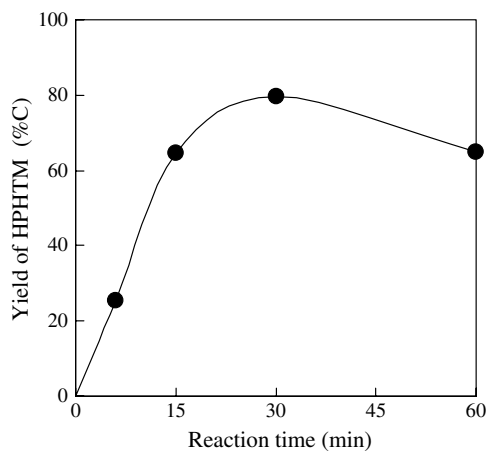


Figure 6. The effect of reaction time on the yield of HPHTM with reaction in the mixture (1.8:2.5 g) at 673 K.

4. Conclusion

The conversion of lignin was performed in water-*p*-cresol mixtures at 673 K. It was found that the yield of THF soluble components drastically increased up to 100% at 60 min of reaction time in a mixture of 1.8 g of water and 2.5 g of *p*-cresol. The molecular weight distribution curve of the product was remarkably shifted to lower molecular weights compared with that of the original lignin. Within a reaction time of 4 min, lignin, whose average molecular weight was 2×10^3 , was selectively converted into a compound. The compound has the molecular weight of 214 (M^+) assigned by gas chromatography-mass spectroscopy and identified as hydroxylphenyl-(hydroxyltolyl)-methane (HPHTM) by ^1H and ^{13}C NMR. Its yield approached a maximum of 80% C around 30 min of reaction time. HPHTM is produced via the formation

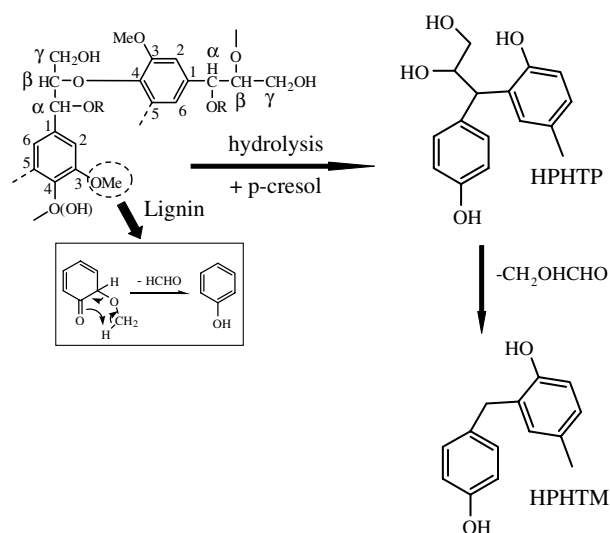


Figure 7. The mechanism of HPHTM formation.

of hydroxyphenylpropane derivative by hydrolysis of lignin with the conduction of *p*-cresol at the most active C α position.

Acknowledgments

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