

Disassembly of Waste Lignin in Supercritical Water and *p*-Cresol Mixtures

Kazuhide Okuda, Satoshi Ohara, Mitsuo Umetsu, Seiichi Takami,
and Tadafumi Adschiri*

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University
2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
*E-mail: ajiri@tagen.tohoku.ac.jp

Depolymerization of waste lignin, namely sodium lignosulfonic acid and alkali lignin was performed without catalyst in a mixture of supercritical water and *p*-cresol. No char formation was found (~1wt%), in analogy with organosolv lignin which is insoluble in water. Gel permeation chromatography confirmed that the molecular weight distribution of original lignin shifted toward smaller molecular weight after the reaction at 400°C for 0.5h. With higher reaction temperature, the amount of the water soluble products decreased. The chemical species in the tetrahydrofuran soluble products were identified by gas-chromatography (GC)-flame ionization detector and mass spectroscopy (MS). GC-MS analysis indicated that the products were phenol, methyl (Me)-anisole, *o*-cresol, di-Me-phenol, ethyl-Me-phenol, 2-(hydroxyl-benzyl)-4-Me-phenol, and 2-(2-hydroxy-5-Me-benzyl)-4-Me-phenol. They, except *o*-cresol, were primarily produced in the presence of waste lignin.

1. Introduction

Plant biomass has recently attracted interest as a potential substitute for petroleum. Various conversion processes are proposed to use biomass as the alternative source of fuel [1-5]. In addition to the use as a fuel, biomass is also a rich source of chemicals [6]. Plant biomass consists of approximately 50 wt% cellulose, 20 wt% hemicellulose, and 30 wt% lignin. Lignin is a complex heteropolymer of trans-*p*-coumaryl, coniferyl, and sinapyl alcohols [7] and is a potential source of aromatic chemicals. Freudenberg *et al.* reported the production of vanillin from lignin by an alkali-nitrobenzene method [7]. One of the authors [8] also demonstrated the conversion of organosolv lignin, which is a soluble component of lignin in organic solvents, into chemicals in a water-phenol (2.5:0.75g) mixture at 400°C. However, prolonged reaction time results in uncontrolled polymerization during the decomposition process leading to low conversion/selectivity and the formation of char. We found that an increase in the ratio of phenol, which presumably serves as a capping agent to prevent unfavorable polymerization, decreased the formation of char [9]. Recently, we have succeeded in the complete dissolution of organosolv lignin in a water-*p*-cresol (1.8:2.5g) mixture at 400°C

without formation of char and in selective conversion of lignin into a few chemicals with low molecular weight [10].

In this study, we disassembled waste lignin excreted in pulp manufacturing process, namely sodium lignosulfonic acid and alkali lignin, in supercritical water and *p*-cresol mixtures.

2. Experimental Methods

2.1. Materials Sodium lignosulfonic acid (the weight-average molecular weight (M_w): ca.54000) and alkali lignin (M_w : ca.28000) were purchased from Aldrich Chemicals (U.S.A) and used as the waste lignin samples. They were soluble in water and insoluble in *p*-cresol and Tetrahydrofuran (THF). The weight fractions of carbon and hydrogen atoms were 44.05% and 4.94% for sodium lignosulfonic acid, 53.00% and 4.95% for alkali lignin, respectively. THF (HPLC grade) and *p*-cresol (99.0%) were purchased from Wako Pure Chemical Industries (Japan) and were used without further purification.

2.2. Depolymerization of Lignin All Experiments were conducted using pressure-resistant vessels (SUS316) whose inner volume was 5 mL. 0.1g of either sodium lignosulfonic acid or alkali lignin and either distilled water (2.5g) or a mixture of distilled water (1.8g) and *p*-cresol (2.5g) were confined in

the vessel without purge by an inert gas. The vessel was heated in an electric furnace whose internal surface temperature was maintained at 250°C~400°C. In preparatory experiments, the temperature inside the vessel was measured by a thermocouple. The vessel was heated up from room temperature to 250°C~400°C within about four minutes irrespective of the temperature and after that the vessel temperature was found to be the same as the furnace temperature within the accuracy of 1°C. Reaction time in this study includes this heat-up period. The pressure inside the vessel has not been measured. The reaction was conducted for 6~30 min and ended by quenching the vessel in a water bath at room temperature. After the reaction, products were collected by rinsing the vessel with 50mL of THF and separated into THF insoluble and THF soluble components using a 1.6 µm glass-fiber membrane filter. The THF insoluble components were dried *in vacuo* at 313K for 1 day and then weighed. Further, the THF insoluble components were washed by water and separated into water soluble and insoluble components using a 1.6 µm glass-fiber membrane filter. The THF and water insoluble components were defined as char.

2.3. Analytical Methods The THF soluble products were analyzed by a combination of gas chromatography and mass spectroscopy (GC-MS Saturn 2000, VARIAN) with a CP-SIL 8 CB Low Bleed column and a combination of gas chromatography and flame ionization detector (GC-FID CP-3800, VARIAN) with a CP-SIL 8 CB Low Bleed column. Injector and detector temperature was 300 °C. Oven temperature was increased to 300 °C at the rate of 5 °C/min after 50 °C was kept for 5 min and then the temperature was maintained for 15 min. Naphthalene as an internal standard was added in the THF soluble products for quantitative analysis. In a series of experiments, gaseous products have not been analyzed.

The molecular weight distribution of the water soluble-THF insoluble products (the water soluble products) were measured by gel permeation chromatography (GPC-900, JASCO) equipped with a refractive index detector and TSK-GEL α-3000 column (Tosoh Co.) and TSK-GEL α-5000 column (Tosoh Co.) at 40°C of oven temperature.

3. Results and Discussion

Table 1 summarizes the yields (wt%) of char formed from each lignin by the reaction in water

(2.5g) and a mixture of water (1.8g) and *p*-cresol (2.5g) for 0.5h. The original waste lignin, that is, sodium lignosulfonic acid and alkali lignin are soluble in water and insoluble in THF. On the other hand, organosolv lignin (Mw: ca. 2000, Aldrich Chemicals) is soluble in THF and insoluble in water. The yields of char formed from each lignin were 1.3~27.8wt% after the reaction in water for 0.5h at 250°C and 400°C. Char was formed in water due to polymerization. This result suggests the polymerization in water as Saisu *et al.* reported in Energy & Fuels [8]. However, for the mixture of water-*p*-cresol, the yield of char drastically decreased up to ~1wt%. The formation of char was nearly completely depressed in the mixture of water-*p*-cresol even at high temperature and pressure. It is interesting that the yield of char after the reaction with sodium lignosulfonic acid in water at 250°C was higher than that at 400°C. This result is similar to that with organosolv lignin which is insoluble in water. It is probably indicated that the solubility of sodium lignosulfonic acid varies in water at higher temperature, and so on.

Table 1. The yields (wt%) of char formed from each lignin by the reaction in water (2.5g) and a mixture of water (1.8g) and *p*-cresol (2.5g) for 0.5h.

Lignin	Water		Mixture	
	250°C	400°C	250°C	400°C
Lignosulfonic acid Na	20.1	13.9	0.1	0.8
Alkali lignin	1.3	9.9	0.2	0.5
Organosolv lignin	27.8	17.5	0.0	0.0

Fig. 1 shows the molecular weight distribution of the water soluble products after the reaction with waste lignin in a mixture of water and *p*-cresol. The wt% in parentheses indicates the yield of the water soluble products. The weight-average molecular weight of the original lignin had ca.54000 for sodium lignosulfonic acid, and ca.28000 for alkali lignin, respectively. The molecular weight distribution curves of the water soluble products after the reaction were shifted to lower molecular weights compared with that of the original lignin. Char can be regarded as cross-linked higher molecular weight compounds. Therefore, the conversion in water solvent produced cross-linked higher molecular weight compounds. On the other hand, the reaction in the mixture of water and *p*-

cresol effectively decomposed lignin without producing the cross-linked higher molecular weight compounds. Higher reaction temperature was decreased the amount of the lower molecular weight compounds of the water soluble products and decreased the total amount of the water soluble products.

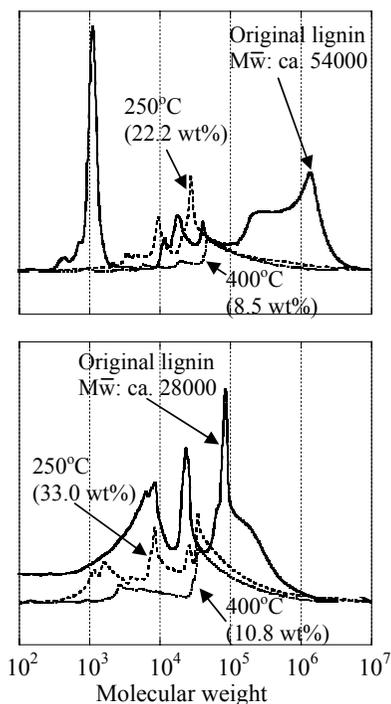


Fig. 1. The molecular weight distribution of the water soluble products after the reaction with waste lignin in a mixture of water and *p*-cresol. Lignin: lignosulfonic acid Na (upper panel), alkali lignin (lower panel).

Fig. 2 shows GC-FID chromatogram of the THF soluble products formed by the reaction in the mixture of water and *p*-cresol at 390°C for 0.1h. The peaks were identified with GC-MS. The chromatogram had several sharp peaks including *p*-cresol (solvent) and naphthalene (standard). Negligible peaks were found from the reaction with solvent only (c). For the reaction with waste lignin (a-b), the peaks with a retention time of 21.2, 23.1, 23.8, 26.9, 29.3, 49.6, and 50.2 min correspond to fragments that have a molecular weight of 94 (M^+), 122 (M^+), 108 (M^+), 122 (M^+), 136 (M^+), 214 (M^+), and 228 (M^+), respectively. They were identified as

phenol, methyl (Me)-anisole, *o*-cresol, di-Me-phenol, ethyl (Et)-Me-phenol, 2-(hydroxyl-benzyl)-4-Me-phenol (BMP) [10] and 2-(2-hydroxy-5-Me-benzyl)-4-Me-phenol (MBMP), respectively. These results are also verified by GC-FID.

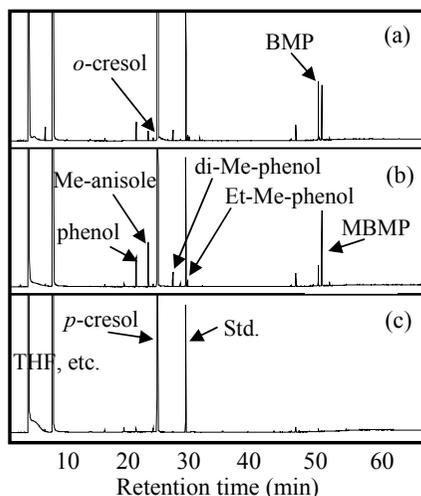


Fig. 2. GC-FID chromatogram of the THF soluble products after the reaction in the mixture of water and *p*-cresol at 390°C for 0.1h. (a) sodium lignosulfonic acid, (b) alkali lignin, and (c) solvent only without lignin.

As reported in our previous paper [11], the products except *o*-cresol were primarily derived in the presence of glycerol and guaiacol, that is, minimum unit of lignin. We evaluated the ratio (%C) of the carbon (mole) in products come from lignin to that in loaded lignin on the basis of the six assigned compounds except *o*-cresol, from the following equation,

$$\text{The recovery (\%C)} = \frac{\sum(C(p) - C(s))}{C(L)} \times 100$$

where $C(p)$, $C(s)$, $C(L)$ represent the carbons of the each product came from lignin, the carbons of each product after the reaction in solvent only without lignin, and the carbon in loaded lignin. This result represents the recovery of lignin. The recovery was 53%C for sodium lignosulfonic acid, 47%C for alkali lignin, respectively. The others were the water soluble products (7.8wt% for sodium lignosulfonic acid, 16.4wt% for alkali lignin,

respectively), and are probably the gaseous products and non-identified products.

4. Conclusions

Depolymerization of waste lignin, namely sodium lignosulfonic acid and alkali lignin in a mixture of supercritical water and *p*-cresol was investigated without added catalysts. No char formation was found (~1wt%), in analogy with organosolv lignin which is soluble in *p*-cresol. The molecular weight distribution for the water soluble products after the reaction at 400°C for 0.5h was smaller than that of original lignin. With higher reaction temperature, the amount of the water soluble products decreased. The THF soluble products were primarily produced in the presence of waste lignin.

Acknowledgements

This research was partially supported by the Ministry of Education, Science, Sports, and Culture, Grant-in-Aid for Scientific Research (B), 14350413, 2003. The authors also wish their thanks to Nissan Science Foundation for their financial support.

References and Notes

- [1] W.S.L. Mok, M. J. Antal, Jr., *Ind. Eng. Chem. Res.*, **31**, 1157 (1992).
- [2] H. Ando, T. Sakaki, T. Kokusho, M. Shibata, Y. Uemura, Y. Hatate, *Ind. Eng. Chem. Res.*, **39**, 3688 (2000).
- [3] M. J. Antal, Jr., S. G. Allen, D. Schulman, X. Xu, *Ind. Eng. Chem. Res.*, **39**, 4040 (2000).
- [4] M. Sasaki, B. Kabyemela, R. Malaluan, S. Hirose, N. Takeda, T. Adschiri, K. Arai, *J. Supercrit. Fluids*, **13**, 261 (1998).
- [5] M. Sasaki, Z. Fang, Y. Fukushima, T. Adschiri, K. Arai, *Ind. Eng. Chem. Res.*, **39**, 2883 (2000).
- [6] E. Dorrestijn, L. J. J. Laarhoven, I. W. C. E. Arends, P. Mulder, *J. Anal. Appl. Pyrolysis*, **54**, 153 (2000).
- [7] J. Nakano, *Chemistry of Lignin*, (Uni Publication, Japan, 1992), pp 503-508 (in Japanese).
- [8] M. Saisu, T. Sato, M. Watanabe, T. Adschiri, K. Arai, *Energy & Fuels*, **17**, 922 (2003).
- [9] K. Okuda, M. Umetsu, S. Takami, T. Adschiri, *Fuel Processing Technology*, **85**, 803 (2004).
- [10] K. Okuda, X. Man, M. Umetsu, S. Takami, T. Adschiri, *J. Phys. Condensed Matter*, **16**, S1325 (2004).
- [11] K. Okuda, S. Ohara, M. Umetsu, S. Takami, T. Adschiri, submitted for publication in *Bioresource Technology*.