Original Paper

Disassembly of Organosolv Lignin in Supercritical Fluid —Phenol as a Suppressor for Repolymerization—

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Supercritical fluid has been expected to solubilize high-molecular biomass materials by a conversion to low molecules. In this study, we attempted to solubilize an organosolv lignin at 673 K in a mixture of phenol and water, and that of benzene and water. The formation of insoluble particles, called char, which result from polymerization of organosolv lignin, was decreased to 12 wt% of supplied lignin in a mixture of 1.75g phenol (0.35g/cm³) and 0.75g water (0.15g/cm³), while the char formation in a benzene-water solution was more than that in the phenol-water solutions at any mixture ratios. The soluble products from decomposed organosolv lignin in the phenol-water solution at the appropriate mixture ratio were analyzed by gel permeation chromatograph; the average molecular weight from the phenol-water solution was 388, while 1690 from a benzene-water solution. These results indicate that phenol can function as an inhibitor of polymerization of organosolv lignin, but do not benzene. Further, the chemical compounds produced from the decomposed organosolv lignin were characterized by GC-FID; GC-FID detected several low molecular compounds only from the decomposed organosolv lignin in a phenol-water solution. The inhibition mechanism of organosolv lignin polymerization by phenol at supercritical conditions was discussed.

Key Words

Benzene, Biomass, Char, Organosolv lignin, Phenol, Polymerization, Supercritical water

1. Introduction

Advances in supercritical technique have enabled us to produce micro/nano particles¹⁾ and extract useful components from biomass material²⁾. In the view of green chemistry, the thermal decomposition of the high-molecular compounds in super/sub-critical condition is noteworthy because biomass materials are considered to be a renewable resource and a CO₂ sink. The decomposition can lead highly-polymerized biomass materials to alternative energy resources for fossil fuels^{3)~10)}, but also for chemicals and materials¹¹⁾.

In this study, we attempted the disassembly and conversion of the highly-polymerized biomass materials to low molecules in supercritical water using organosolv lignin. The liquefaction of organosolv lignin has been often performed in subcritical water^{12) 13)}, because the application of supercritical condition, which can convert organosolv lignin to more low molecules, is considered to cause the

repolymerization of the low molecules. The repolymerization results in the formation of char and leads to low yield of chemicals decomposed from organosolv lignin material. Recently, we reported the conversion of organosolv lignin into low molecular compounds by hydrolysis in a water-phenol mixture at 673 K^{14) 15)}, suggesting a possible mechanism that phenol acts as a capping agent to suppress the repolymerization of decomposed organosolv lignin in supercritical water which results in the formation of char. Here, we compared the decomposition of organosolv lignin in a mixture of phenol-water and benzene-water to explain how the conversion from organosolv lignin to low molecular weight compounds can be achieved by use of phenol-water solvents at supercritical conditions.

2. Experimental

2.1 Materials

Organosolv lignin used here was purchased from Aldrich Chemicals (U. S. A). The organosolv lignin was extracted from a natural wood source (50 % from maple wood, 35 %

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birch wood, and 15 % poplar wood), using aqueous ethanol without any alkali and acid solutions. The weight-average molecular weight (M_w) and number-average molecular weight (M_n) of the organosolv lignin were 2100 and 620, respectively, and the weight fraction of carbon and hydrogen atoms were 67 % and 6 %, respectively. The sulfide atom was not detected, and the amount of ash was less than 1 %. The organosolv lignin sample can be completely soluble in tetrahydrofuran (THF). THF (HPLC grade), phenol (99.0 %), and benzene (99.0 %) were purchased from Wako Pure Chemical Industries (Japan) and were used without further purification.

2.2 Hydrothermal reaction in supercritical condition

All the hydrothermal experiments were conducted using pressure-resistant vessels (SUS316) with 5 mL of inner volume. The vessels were heated and shaken in an electric furnace which controlled external surface temperature of the reactors at 673 K. In preparatory experiments, the temperature inside the vessel was measured by a thermocouple inserted in the vessel. The vessel was heated up from room temperature to 673 K within four minutes and after that the vessel temperature was the same as the furnace temperature within the accuracy of 1 K. Reaction time in this study includes this heat-up period. In a series of experiments, the thermocouple has not been used to accurately define the inner volume of vessels and to avoid unnecessary reactions on the surface of the thermocouple.

2.3 Decomposition of lignin

0.1 g of organosolv lignin was dissolved in a mixture of phenol and distilled water or that of benzene and distilled water at the following ratio; organic solvent / water = 0 g / 2.5 g, 0.25 g / 2.25 g, 0.75 g / 1.75 g, 1.25 g / 1.25 g, 1.75 g / 0.75 g, 2.25 g / 0.25 g, and 2.5 g / 0 g. Each organosolv lignin solution was confined in the vessel without purge by an inert gas, as the effect of oxidation by air contained in a space on the conversion of organosolv lignin was estimated negligibly small because of a low oxygen / carbon molar ratio of the feed (below 0.001).

Fig. 1 shows the experimental procedure in this study. In all the experiments, produced gas was too little to analyze the products. The vessels have been heated and shaken for 1 hour, and then the reaction was quenched by cooling the vessels 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 μ m glass-fiber membrane filter. The THF-insoluble products were washed for several times and dried in vacuo at 313K for 1 day, and then

Fig. 1 Experimental procedure

were weighed. The insoluble product was defined as residual solid (char). The yield of residual solid was calculated as the equation below:

$$\text{Residual solid yield (weight \%)} = \frac{\text{residual solid (g)}}{\text{lignin loaded (g)}} \times 100\%$$

2.4 Analytical instruments

The molecular weight distribution of THF soluble products was measured by gel permeation chromatography (GPC, GPC-900 JASCO, Japan) equipped with a refractive index detector and double Shodex KF-803L columns and one Shodex KF-801 column. In order to remove redundant water, the THF-soluble decomposed organosolv lignin fragments were dried at 333K and then re-dissolved in THF before GPC analysis. The characterization of the THF-soluble products was performed by gas chromatography-mass spectroscopy (GC-MS Saturn 2000, VARIAN) with a CP-SIL 8 CB Low Bleed column and gas chromatography-frame ionization detector (GC-FID CP-3800, VARIAN) with a CP-SIL 8 CB Low Bleed column. Recovery ratio of phenol could not be evaluated, because of the accuracy of the GC-FID. Naphthalene was used as an internal standard for this quantitative analysis.

3. Results

Fig. 2 shows the effect of phenol-water (open square) and benzene-water (closed circle) ratios on the yields of THF-insoluble residual particles (char) formed by the hydrothermal reaction at 673 K for 1 hour. The increase of water in the phenol-water solutions led to a slight decrease in the formation of insoluble particles (char), but the yield was increased on reaching the ratio of 1.75 g phenol / 0.75 g water. Whereas, there was formed more char in the ben-

Fig. 2 The yield of char from reactions in a phenol-water (a: open squares) and benzene-water (b: closed circles) mixture as a function of the amount of organic solvents. The weight of the mixture was maintained to 2.5 g.

zene-water solutions at the ratios of 0.75 g benzene / 1.75 g water and 1.25 g benzene / 1.25 g water than in the phenol-water solutions at the same ratios, and then the increase of water resulted in the comparable yield of char to that in the phenol-water solutions. We also treated each organic solvent-water solution without organosolv lignin in order to confirm that the char is made from organosolv lignin. All the organic solvent-water solutions formed no char (data not shown), which indicates that the char formed in the phenol-water and benzene-water solutions does not contain the compounds made from only solvent. In addition, we estimated the amount of phenol and benzene in the reacted solutions. The amounts of them in all the cases were decreased only a little (1-5%), which supports no insoluble particles formed from only solvents.

Fig. 3 shows the GPC spectra for untreated organosolv lignin (solid line) and the THF-soluble products from the decomposed organosolv lignin in the phenol-water (dotted line) and benzene-water (chained line) solutions which were mixed at the ratio of 1.75 g organic solvent / 0.75 g water. In comparison with the original organosolv lignin (solid line), both the THF-soluble products from the decomposed organosolv lignin in the phenol-water (dotted line) and benzene-water (chained line) solutions were distributed in lower

Fig. 3 Gel permeation chromatograph of untreated organosolv lignin (solid line), the product generated in 1.75g phenol-0.75g water (dotted line), and the product generated in 1.75g benzene-0.75g water (chained line).

molecular weight than the original organosolv lignin, indicating that most of organosolv lignin was converted to the compounds with the molecular weights of 100-1000 by the solvothermal reactions in both the mixture solutions. However, the GPC spectrum for the THF-soluble products formed in the phenol-water solution had the clear signals corresponding to the molecular weight of 130 and 275, while the products from the benzene-water solution did not show the signal for the molecular weight of 275 and the spectrum seemed to be more widely distributed than that of phenol-water solution.

Table 1 lists the weight-average molecular weight (M_w) and molecular weight distribution (M_w/M_n) for the decomposed organosolv lignin in the phenol-water and benzene-water solutions. M_w and M_w/M_n were calculated from the GPC results. M_w of the THF-soluble products was shifted from 2100 to 388 after the solvothermal reaction in the phenol-water solution, while the benzene-water solution caused a smaller shift of M_w to 1690 than that for the phenol-water solution and M_w/M_n was larger than that in the phenol-water solution. Therefore, both the phenol-water and benzene-water solutions converted organosolv lignin to low molecules in supercritical condition, but the phenol-water solution was apt to produce lower molecules than the benzene-water solution.

Fig. 4 shows the characterization of the THF-soluble products from the decomposed organosolv lignin in the phenol-

Table 1 The average weight molecular weight (M_w) and molecular weight distribution (M_w/M_n).

	THF-soluble products	
	1.75 - 0.75 (g) mixture solvent	
	M_w	M_w/M_n
Organosolv lignin	2100	3.1296
Phenol-water	388	4.4713
Benzene-water	1690	6.3400

Fig. 4 GC-FID chromatogram of THF-soluble products generated in (a) 1.75g phenol-0.75g water, and (b) 1.75g benzene-0.75g water.

water (a) and benzene-water (b) solutions by chromatography frame ionization detector (GC-FID). All the peaks in the chromatograms were identified with GC-MS. For the products in the phenol-water solution, several outstanding peaks corresponding to the compounds such as anisole, o-cresol and catechol, and products of alkylphenol and xanthene, could be found. The compounds have been confirmed as the products from organosolv lignin or the products made from phenol and the decomposed organosolv lignin¹⁵. On the other hands, the GC-FID chromatogram for the benzene-water solution had little peaks corresponding to the products from lignin. This indicates that the phenol-water solution converts organosolv lignin to low molecules which can be detected by GC-FID, but the benzene-water solution does not (see discussion).

4. Discussion

Previously, we have proposed a possible disassembly mechanism of organosolv lignin in a supercritical water-phenol mixture^{14) 15)}, where phenol functions as a capping agent to suppress re-polymerization from decomposed lignin fragments in supercritical water. In a supercritical water, the decomposition of organosolv lignin by hydrolysis and dealkylation is considered to occur and form reactive low molecular weight fragments (formaldehyde, etc.) and compounds (syringols, guaiacols, catechols, etc). The fragments and compounds can be cross-linked through the active molecules and sites, but phenol suppresses the re-polymerization by reacting to the active site.

In this study, we compared the decomposition of organosolv lignin in a phenol-water and benzene-water solution in order to verify the capping effect of phenol. The char formation and GPC result clearly showed that the conversion of organosolv lignin to low molecules is more accelerated by the present of phenol than benzene (Figs. 2 and 3, Table 1); char was produced in a benzene-water solution at most of the ratios than in a phenol-water solution (Fig. 2), and M_w for the THF-soluble products in the benzene-water solution was larger than that in the phenol-water solution (Table 1). Phase state for each organic solvent-water solution was estimated by the method of Heidenmann¹⁶⁾. The estimation suggests that all the conditions except the phenol / water solutions of 2.5 g / 0 g, 2.5 g / 0.25 g lead to supercritical state. Therefore, the difference of char formation between phenol-water and benzene-water mixtures, which is observed in the solutions containing more than 0.75 g water, is probably not due to the change of phase state. Considering that benzene has no reactive site relative to phenol, the comparison between the results of phenol and benzene supports the suggestion that the acceleration of decomposing organosolv lignin by phenol is due to the suppression of re-polymerization to huge molecules by the capping effect of phenol. In the organic solvent / water solutions of 0.75 g / 1.75 g and 1.25 g / 1.25 g, the yield of char in the benzene-water solution surpassed that in neat organic solvent in contrast to the phenol-water solution (Fig. 2). The low amount of water might product active molecule or site which cause re-polymerization before the hydrothermal decomposition to low molecules; The formation of char might be accelerated in the benzene-water solutions because benzene does not have a capping effect for the active site.

Fig. 5 shows the reaction pathway of organosolv lignin conversion in supercritical water on the basis of the GC-FID results. The organosolv lignin is considered to mainly have the structure where guaiacyl glycerols are polymerized¹⁷⁾. The organosolv lignin is dissociated at the α carbon by hydrolysis and dealkylation, so that active molecules such as formaldehyde and low molecular weight fragments having reactive functional groups and phenolic structure compounds (anisoles, guaiacols, catechols, and so on) can be produced (scheme 1 in Fig. 5). The formaldehyde can react with phenolic compounds by cross-linking interaction to form higher molecular weight fragments corresponding to huge residual lignin molecules (char), but phenol would react the formaldehyde so that xanthene, 22' diOH-phenylmethane (22' OPM) and 44' diOH-phenylmethane (44' OPM) might be formed (scheme 2 in Fig. 5). The xanthene, 22' OPM, and 44' OPM were not pro-

Scheme 1 **Scheme 2**

Fig. 5 Reaction pathway and low molecular weight compounds production mechanism. Scheme 1: Main hydrolyzed products from organosolv lignin. Scheme 2: Products of reaction between phenols and formaldehyde.

duced from only phenol and water, but the three molecules were made from phenol, water and formaldehyde (data not shown). This supports the reaction in the scheme 2 in Fig. 5. In the case of the benzene-water solution, little methyl/ethyl-benzene derivatives and products from formaldehyde and benzene were detected by GC-FID (Fig. 4b). The reaction of the intermediates from organosolv lignin might be more active to methyl / ethyl ions and formaldehydes than benzene so that the intermediate would be led to repolymerization.

The thermal decomposition of guaiacylglycerol-b-guaiacyl ether (GG) as a lignin compound in phenol solution at subcritical condition has been reported; the products are various but many of them have three aromatic rings^{18)~20)}. Although the structure of the organosolv lignin used in this study is different from GG, there are fewer varieties of the products formed from organosolv lignin in the phenol-water solution at supercritical condition than those from GG at subcritical condition. In the organosolv lignin conversion, the products with two aromatic rings were detected (xanthene, 22' OPM, 44' OPM), but one of two is at least derived from phenol as a result that phenol suppressed formaldehyde which causes the formation of char (Scheme 2 in Fig. 5). Therefore, the application of supercritical condition in the phenol-water solution results in more decomposition than subcritical condition due to a capping effect of ethanol on the active sites which cause the formation of char.

In conclusion, the comparison between the thermal reaction of organosolv lignin in a phenol-water and benzene-water solution supports that the high-efficiency conversion of lignin to low molecules by solvothermal reaction in a mixture of phenol and water is due to a capping effect of phenol to the active molecules or sites in the decomposed

lignin. Especially, the trapping of formaldehyde by phenol would be contributed to little formation of char.

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