

Solubilization of D-Grade Wood Wastes in Subcritical Water

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ABSTRACT

Solubilization of D-grade wood waste (branch and bark of Japanese cedar) was investigated in subcritical water (150 °C to 350 °C) under saturated pressure for 10 min or 60 min. To know the solubility of the wood waste in subcritical water, particularly lignin solubility at that conditions, two batch reactors connected together in a row were used for solubilization in a first batch reactor and recovery of the soluble components in a second batch reactor. The soluble components were separated into water solubles, acetone solubles, and acetone insolubles. As a result, 80wt% of the wood waste was solubilized and recovered in the second batch reactor. Over 250 °C, the yield of toluene solubles, which were probably lignin, in the recovered solution increased remarkably. The GPC measurement of the acetone soluble told us that the increase of the solubility was due to high molecular weight lignin solubilization in subcritical water. To understand the phenomena, solubility parameter and severity analysis were employed.

INTRODUCTION

Low-grade woods such as branch, root and bark have no use for materials and chemical resources and, although their amount was quite huge, they are wasted by landfill and incineration. In sub- and supercritical water, almost all the components of wood (such as lignin, hemicellulose and cellulose) are miscible and the combustion of dissolved woody component is expected because it is known that oxidation of organic components is rapidly developed in supercritical water. To design energy production process by solubilization and oxidation of wood in sub- and supercritical water, an optimum condition for each step has to be revealed.

Solubilization of several woody biomass has been investigated at subcritical water [1]-[5]. To know the solubility, the reactivity of components must be also taken into account. At hydrothermal treatment, not only solubilization but also hydrolysis occurs, particularly, acetyl group in hemicellulose is easily hydrolyzed to form acetic acid and the acid promotes autocatalytic hydrolysis [5]. The solubilization is not only dissolution in hydrothermal water but also resulted in the acid formation and hydrolysis. The key parameters of the solubilization are temperature, reaction time and acid concentration. To simplify solubilization phenomena, severity analysis, of which a single parameter (severity factor) including these parameters is introduced, has been employed [2]-[5]. At lower severity, solubilization well described the experimental phenomena, but at high severity, the simple

severity model was not applicable. One of the reasons is assumed to progress carbonization. In the presence of high-pressure oxygen at hydrothermal condition Solubility of woody biomass increased: solubility of pine wood at 200 °C was 38% without high-pressure oxygen, while that was 83% by adding of high-pressure oxygen [1].

For evaluation of solubility, solubility parameter, in particular, Hansen solubility parameter is quite useful. Lignin solubility parameter was reported [6] and solubility parameter of water at hydrothermal condition is also available [7].

In this study, by small batch experiments, D-grade wood were treated in subcritical water (at 160 ~ 350 °C and 9 wt% slurry concentration for 60 min) to know the solubility of these biomass and the effect of oxygen on the solubility. For the comparison, the solubilization of rice straw was also examined. To know the solubility of the wood waste in subcritical water, particularly lignin solubility at that conditions, two batch reactors connected together in a row were used for solubilization in a first batch reactor and recovery of the soluble components in a second batch reactor.

MATERIALS AND METHODS

D-grade wood, branch and bark of Japanese cedar, that was used in this study consists of 48 % lignin (Klason lignin). The D-grade wood was crashed and sieved under 5 mm.

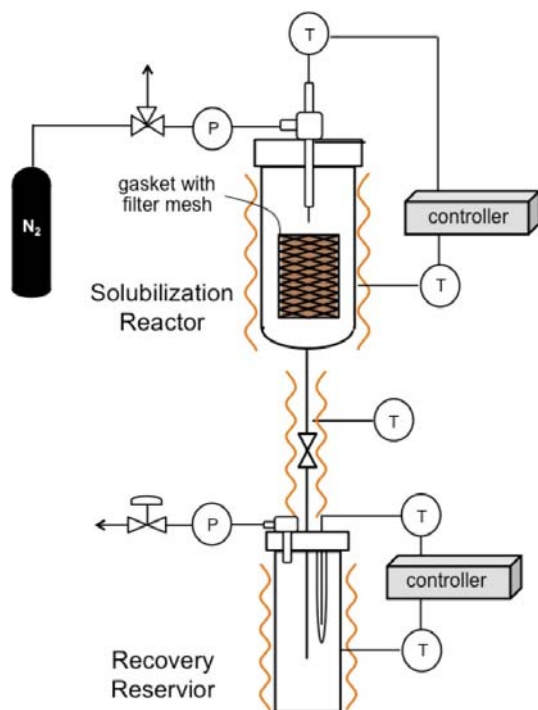


Figure 1 Schematic diagram and digital camera picture of two-reactor experiment apparatus

Small batch experiments over 200 °C were conducted with stainless steel (SS 316) tube bomb reactors (6 cm³). A 0.3 g of D-grade and 3 g (10 wt% of D-grade wood) were loaded. Air in the reactor was purged with N₂ gas. The loaded reactor was submerged in a molten salt bath whose temperature was controls to be 200 °C to 350 °C. Heat-up time required was around 90 s. After a reaction time up to 60 min, the reactor was taken out of the bath and rapidly cooled in a cold-water bath. Under 200 °C, high-pressure glass reactor was also used under microwave heating. The detail of the glass reactor heated up by microwave heating can be seen in elsewhere [8].

For the experiments by the small size reactors, solubilisation in water was evaluated by filter separation at room temperature after cooling. In this case, relative large size of lignin can be classified into water insoluble, if it was solubilized in subcritical water. To know the solubilisation at high temperature more correctly, two-reactors experiments were also performed.

It is suggested that relative large molecular weight of lignin could be mobilized over 200°C. As shown in **Fig. 1**, two batch reactors connected together in a row. Upper reactor was solubilisation reactor and lower reactor was recovery reservoir. The solubilisation reactor and the line between the two reactors were heated up to the reaction temperature (200 °C to 270 °C). The reservoir was heated at 200 °C. The size of the solubilization and the reservoir was 300 mL. The experimental procedures of the two-reactor experiments are introduced briefly as below:

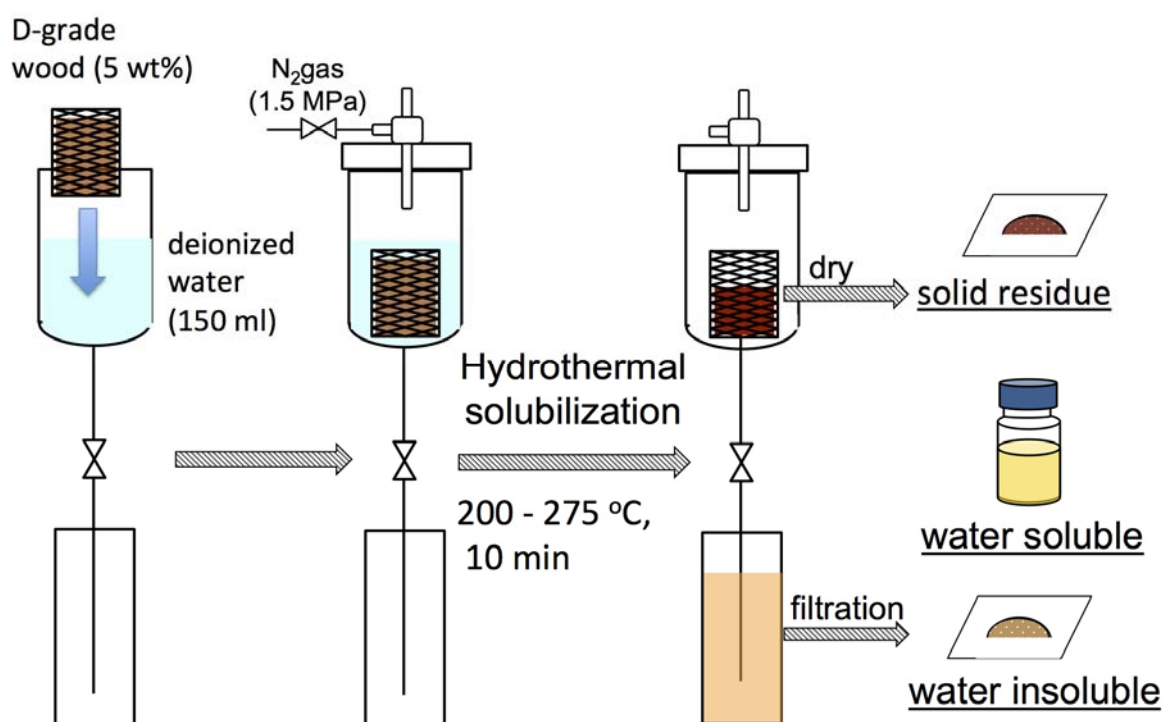


Figure 2 Schematic diagram of procedures of two-reactor experiment apparatus

A 7.5 g of D-grade wood was surrounded with stainless steel mesh and loaded in the solubilisation reactor with 150 mL of pure water. After purging air inside the solubilisation

reactor with 1.5 MPa N₂, the reactor loaded the samples was heated up to 200 to 275 °C and kept for 10 min at the temperature. Then the stop valve between the two reactors was opened and the solubilized components in the subcritical water were recovered by the reservoir. The residue in the solubilisation reactor remaining in the stainless steel mesh was weighted after drying at 60 °C for overnight. The recovered solution consisted of water soluble and insoluble, which was separated by vacuum filtration. The water insoluble was further separated into toluene soluble and insoluble.

The molecular weight distribution of the toluene soluble was measured by GPC. The GPC was measured at the condition as follows: column: KF-804L (the same column is connected, that means 2 KF-804L columns are used), column oven temp: 40°C (constant), flow rate of carrier (THF): 1 mL/min, detector: UV at 254nm.

For all the experiments, solubilization rate was defined as below:

$$\text{Solubilization rate [wt\%]} = \frac{\text{Residue [g]}}{\text{Starting material [g]}} \times 100 \quad (1)$$

Namely, the solubilization rate was defined as the ratio of unrecovered solid weight to the loaded amount of solid biomass. We also evaluated lignin recovery in the two-reactor experiments. The definition of the lignin recovery is as below:

$$\text{Lignin recovery [wt\%]} = \left(1 - \frac{\text{Klason lignin in the residue [g]}}{\text{Klason lignin in Starting material [g]}} \right) \times 100 \quad (2)$$

RESULTS

Figure 3 shows temperature dependence of solubilization rates of the two biomass (D-grade wood and rice straw) at 1.2 MPa N₂ atmosphere. The solubilization rate increased with increasing reaction temperatures. For the both biomass, the solubilization rate achieved to 70% over 300 °C. As shown in **Fig. 3**, the rice straw was a little more easily dissolved in subcritical water. This was probably due to the amount of polysaccharides: the amount of lignin is around 30% in rice straw, while that is around 48%

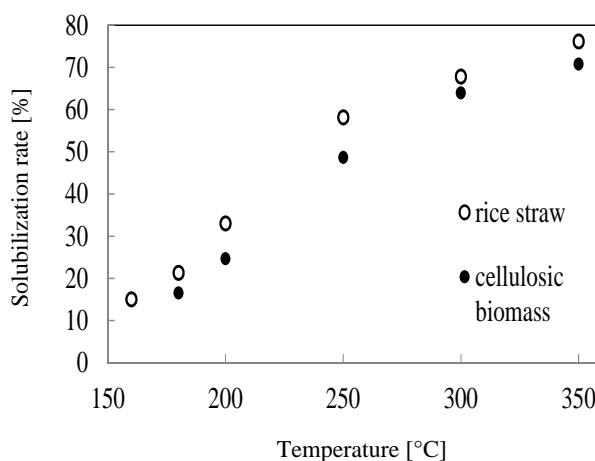


Figure 3 temperature dependence of solubilization rate of two kinds of biomass

in the D-grade wood.

To know the effect of O₂ on the solubilization, 0.8 MPa air was loaded instead of 1.2 MPa N₂. The solubility rate of the rice straw was slightly enhanced in the presence of O₂, on the other hand, that of the D-grade wood was insensitive to the existence of O₂. The reason of small effect of O₂ on the solubilisation was probably the concentration of O₂ (namely partial pressure in the reactor) is too low. Further investigation concerning the effect of O₂ is required.

To compare the results by the small batch reactor with the two-reactor experiments, **Figure 4** shows the results. As shown in the figure, the differences between the two experiments were negligible. The advantage of the two-reactor experiments was to increase scale and to obtain the samples to analyse in more detail, for example, lignin recovery and molecular weight distribution of the recovered lignin.

Figure 5 shows temperature dependence of the lignin recovery. Almost all the lignin in the D-grade wood was recovered over 250 °C, as shown in this figure. **Figure 6** shows the molecular weight distribution of the toluene soluble in the recovered lignin. The peak area reflects the lignin recovery at each temperature shown in **Fig. 5**. As shown in **Fig. 6**, up to 250 °C, relative low molecular weight lignin components was dissolved in high-temperature water. Over 250 °C, large size of lignin was soluble in water.

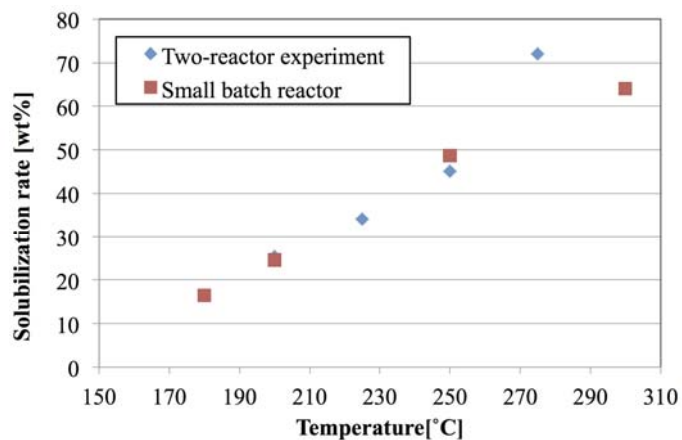


Figure 4 Comparison between small batch reactor and two-reactor experiments for D-grade wood solubilization

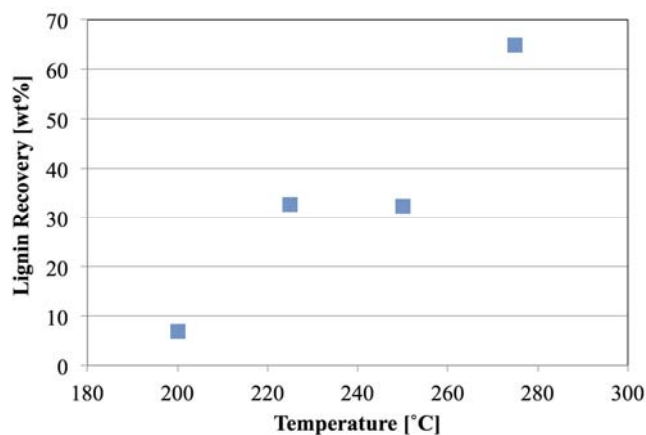


Figure 5 Temperature dependence of Lignin Recovery

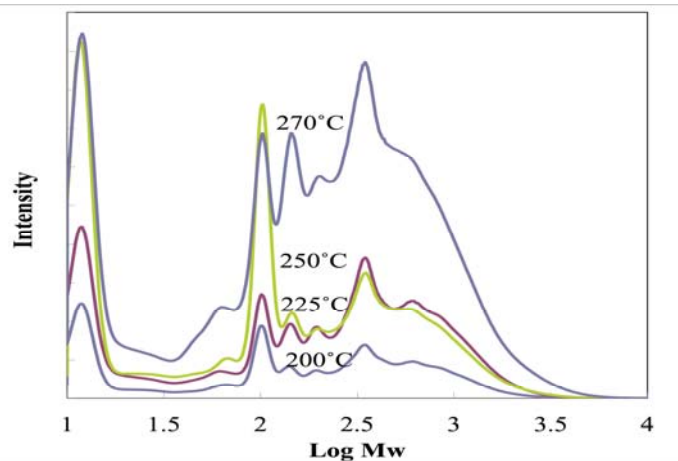


Figure 6 Molecular weight distribution of recovered lignin

Table 1 shows the solubility parameter of lignin [6] and hydrothermal water [7].

Table 1 Solubility parameters of lignin [6] and hydrothermal water [7]

	δd	δp	δh	δt
Lignin	21.9	14.1	16.9	31.0
200°C	11.2	14.0	25.8	31.4
220°C	10.8	13.8	24.4	30.1
240°C	10.3	13.6	23.0	28.7
260°C	9.9	13.4	21.6	27.3
280°C	9.3	13.1	20.2	25.8

Here Hansen solubility parameter is expressed by the below expression:

$$\delta t^2 = \delta d^2 + \delta p^2 + \delta h^2 \quad (3)$$

where δt is total solubility parameter, δd is dispersion, δp is polarity and δh is hydrogen bonding. On Hansen solubility parameter, any molecular substance can be represented by a point in a 3D space, so-called Hansen sphere. Good solvents for a solute must stay in the sphere and bad (poor solvents) should be outside. Now further investigation based on the solubility parameter is now being progressed. In addition, to express dynamics of the solubilisation, severity analysis based on the literature [2]-[5] is also now being performed.

CONCLUSION

Over 80% of D-grade wood was dissolved in hydrothermal water beyond 250 °C. The detail observation for lignin solubilization was conducted by two-reactor experiments. As a result, over 70% of lignin having high molecular weight can be recovered as soluble component in 270 °C hydrothermal water. To enhance the solubilization of woody biomass, the effect of O₂ will be performed as well as the investigation of effect of temperature, water/wood ratio, flow dynamics (mixing) and so on.

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