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Lignin-based resin production from lignocellulosic biomass combining acidic saccharification and acetone-water treatment

Yosuke Muranaka[a]*, Hiroyuki Nakagawa[a], Isao Hasegawa[b], Taisuke Maki[a], Junji Hosokawa[a], Junya Ikuta[c], and Kazuhiro Mae[a]

[a] Department of Chemical Engineering, Kyoto University, Kyoto, 615-8510, Japan

[b] Department of Chemical, Energy and Environmental Engineering, Kansai University, Osaka, 564-8680, Japan

[c] Ube Industries, Ltd., Yamaguchi, 755-8633, Japan

*Corresponding author. Email: muranaka@cheme.kyoto-u.ac.jp

Abstract: The structure of lignin is formed by the cross-linking of phenolic compounds. Taking advantage of this structural property, the conversion method of lignin into resin material was developed in this study. Depolymerization of lignin is one of the most important factors for utilizing the basic frameworks of phenylpropanoids. Lignin is extractable from lignocellulosic biomass using acetone-water binary solution. Therefore, the simultaneous extraction and depolymerization of lignin under high temperature and high pressure from Japanese cedar was examined. Prior to the extraction process, cedar was treated with 50 wt% formic acid at 175 °C for the saccharification of hemicellulose and part of cellulose which could be contaminants in resin material. Next, the lignin extraction was conducted using 30 wt% of acetone at the higher temperature of 295 °C and 0.82 g/(g-lignin in material) was obtained. The curing property of the obtained sample was evaluated by differential thermal analysis and the detected exothermic energy during resinification was 18.2 μV/mg. In addition, it was confirmed by visual observation that the obtained sample resinified uniformly by heating at 150 °C. Thus, the effective production method of usable lignin-based resin was developed. Lastly, this treatment method was applied to eucalyptus, another type of lignocellulosic biomass, and was validated as effective.

Keywords: depolymerization, lignin-based resin, two-step treatment.

1. Introduction

Biomass conversion has been a hot topic in recent years. For the feasible biorefinery process, all the components of biomass are required to be efficiently utilized [1][2][3]. Among the main components of biomass, cellulose and hemicellulose have a relatively clear structure, and many conversion methods have been developed [4][5][6][7][8][9][10][11][12][13][14]. The cellulose and hemicellulose derivatives include many important chemicals which can be converted further into valuable chemicals or valuable products [15][16][17]. On the other hand, the structure of lignin is very complicated and rigid so that the conversion of lignin into specific chemicals is difficult, and the utilization of lignin is mostly limited in energy use through combustion. Although the structure of lignin is complex, it is known that the basic compounds consist of the following three types of phenylpropanoids: *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol [18][19][20]. When the structures of these basic compounds were focused on, they possess the active sites which phenol also possess for the production of phenolic resin. Therefore, in this study, the production method of lignin-based phenolic resin material from lignocellulosic biomass was examined. In this case, the products have not necessarily to be pure chemicals or components. As a resin material, products are required to possess many active sites for resinification in each weight. To satisfy this requirement, it is important to depolymerize lignin compounds as similarly to basic phenylpropanoids as possible. In our previous research [21], lignin-based resin material was successfully produced from lignocellulosic biomass, through the selective extraction of lignin with an acetone and water binary solution and sequential depolymerization by hydrothermal treatment. The produced resin showed fine mechanical durability which was measured by pressurizing the product until it was bent. The measured pressure at the resin was bent was 164 MPa, and that was 172 MPa for conventional phenolic resin. These results meant that the produced resin showed competitive mechanical durability with conventional phenolic resin. However, in the method, hemicellulose and a part of cellulose may also be extracted at this step, which seems to be undesirable because the contamination by hemicellulose or cellulose derivatives (*i.e.* saccharides) may decrease the lignin content in each weight and the produced resin becomes unusable. If the extraction was conducted at a low temperature to avoid this undesirable extraction, it results in the low lignin extraction yield. Therefore, it was difficult to increase the yield of usable resin material. Based on these facts, this study aimed to remove hemicellulose and a part of cellulose in advance when they were in the form of saccharides by acidic saccharification using formic acid, which is one of the organic acids obtainable from biomass. Our group has also previously reported on biomass saccharification using formic acid [22] and clarified that hemicellulose and a part of cellulose could be recovered as saccharides at good yield. After the saccharification process, the simultaneous extraction and depolymerization of lignin was conducted using the acetone and water binary solution at a high temperature. The proposed reaction process is summarized in **Figure 1**. The major challenges for the production of usable lignin-based resin material from lignocellulosic biomass were to achieve the selective extraction of lignin at high yield without the contamination by saccharides and to improve the curing activity of extracted lignin by deplymerization. To overcome these challenges, the removal of saccharides beforehand from lignocellulosic biomass through the saccharification with formic acid was examined at first. The various concentrations of formic acid were examined to achieve the effective removal of saccharides without extracting lignin, and to obtain a lignin-rich fraction as the residue. The obtained lignin/cellulose-rich fraction is defined as residue 1 and the obtained saccharides-rich fraction is defined as soluble 1 in this article. The next examination was to obtain depolymerized and usable lignin-based resin material selectively from residue 1 through the extraction with acetone. This treatment was conducted at high temperature for simultaneous depolymerization of lignin and extraction of depolymerized lignin at high yield. The obtained soluble fraction which ideally consists of pure depolymerized lignin is defined as soluble 2 and the obtained cellulose-rich fraction is defined as residue 2 in this article. The various concentrations of acetone were examined to obtain a high performance lignin-based resin material selectively. The curing property of soluble 2 was evaluated quantitatively by measuring the exothermic energy during resinification. Lastly, the adaptability of the proposed method to other types of lignocellulosic biomass was examined.

2. Experimental Section

2.1 Samples

Japanese cedar (*cryptomeria japonica*) and eucalyptus (*eucalyptus globulus*) were used as lignocellulosic biomass samples. The contents of lignin, cellulose, and hemicellulose for each sample were summarized in **Table 1**. Both of the samples were purchased from Kobo Mokuyo-Daiku (Tokyo, Japan), ground into particles under 500 µm, and dried in vacuo for 24 h at 70 °C prior to use. At the resinification step, hexamethylenetetramine (assay > 99.5 %, Kishida Chemical, Osaka, Japan) was used as the curing agent. Preparations of 50, 75, and 90 wt% of formic acid along with 30, 40, and 50 wt% of acetone were prepared by mixing distilled water and each reagent (formic acid: assay > 98.0 %, acetone: assay > 99.0 %, Wako Pure Chemical Industries, Ltd., Tokyo, Japan).

2.2 Acidic saccharification using formic acid (1st treatment)

Both types of biomass were treated under the acidic hydrothermal condition.

The experiments were performed using a Swagelok (316 stainless steel) batch reactor with an internal volume of 30 cm^3. In total, 1.0 g of sample biomass and 10 g of formic acid, which was prepared at the concentration of 50, 75, or 90 wt%, were mixed in a sealed batch reactor. The reactor vessels were plunged into an oil bath preheated to 175 °C for 2 h, and then cooled in a water bath. The products were filtered by suction, and the residues (residue 1) were dried in vacuo at 70 °C for 24 h and then used as the samples for the following extraction step.

2.3 Extraction of depolymerized lignin from residue (2nd treatment)

In total, 1.0 g of residue 1 and 10 g of acetone solution, which was prepared at concentrations of 30, 40, or 50 wt%, were mixed in a sealed batch reactor. The reactor vessels were plunged into an oil bath preheated to 295 °C for 1 h and then cooled in a water bath. The treatment condition was determined according to our previous work [21]. The products were filtered by suction, and the residues were dried in vacuo at 70 °C for 24 h. A small amount of filtrate was collected from each batch for the analysis of molecular weight distribution

(**MWD**) by gel permeation chromatography. The rest of the filtrates were heated on a hot plate at 80 °C to evaporate the solvent and the obtained samples (soluble 2) were dried in vacuo at 70 °C for 24 h. The solubles 2 were then analyzed by a CHNS elemental analysis and then evaluated through the following resinification step. The yield of soluble 2 was calculated according to **Equation 1**.

Yield of soluble 2 [g/g-lignin] = (Residue of 1st treatment [g] – Residue of 2nd treatment [g]) / Lignin content of material [g] — **Equation 1**

2.4 Resinification of extracted-depolymerized lignin

Obtained soluble 2 was resinified using hexamethylenetetramine as a curing agent. At first, a varnish, which was the mixture of soluble 2 and a curing agent, was prepared. All the amounts of the obtained soluble 2, 10 g/100g-sample of hexamethylenetetramine, 10 mL of methanol, and 10 mL of acetone were mixed in a glass bottle (internal volume of 50 cm^3), and the glass bottle was put in an ultrasonic wave disperser for 5 min for complete dissolution. Next, the mixture was poured into an evaporating dish and heated at 60 °C for the evaporation of methanol and acetone, and then dried in vacuo at 60 °C for 1 h. This prepared sample was defined as varnish. The thermal curing properties of all varnishes during resinification were evaluated by differential thermal analysis (DTA). In addition, the thermal curing property of varnish prepared by a certain method was visually observed by heating set amounts of varnish on a hotplate preheated at 150 °C.

2.5 Analyses of products

The elemental compositions of samples were analyzed using a CHNS elemental analyzer (BEL Japan, Inc., ECS4010). The thermal curing properties of varnishes during resinification were evaluated using a differential thermal analyzer (Shimadzu, DTA-50) by elevating the temperature to 250 °C at the temperature rising rate of 10 °C/min under nitrogen. The softening point of the product was examined using a thermomechanical analyzer (Shimadzu, TMA-50) at the temperature rising rate of 20 °C/min. The gel permeation chromatography was used to estimate the MWD of soluble 2. The packed column used was Shodex Asahipak GF-310HQ (SHOWA DENKO), and an eluent of acetone was supplied at the flow rate of 0.7 mL/min to the high performance liquid chromatography equipped with a charged aerosol detector (Dionex, Corona). The intensity of the obtained chromatogram was standardized according to **Equation 2**.

Intensity [a.u.] = Intensity / Σ(Intensity・Mw) — **Equation 2**

3. Results and discussion

3.1 Production of lignin-based resin materials from Japanese cedar

The requirement for the 1st treatment was the selective solubilization of cellulose and hemicellulose. **Figure 2** shows the yield of residue 1 after the 1st treatment. The yield of residue 1 decreased with increasing concentration of formic acid. It is because stronger acid cleaves glycoside bonds of hemicellulose or cellulose more effectively. However, the yield of residue 1 was higher than the lignin content in the material, regardless of formic acid concentration. The lignin content in the material was 33.5 wt% according to **Table 1**. When 50 wt% of formic acid was used, 0.19 g/g-material of saccharides were recovered as soluble 1. Thus, some of hemicellulose or cellulose derivatives were recovered as valuable saccharides beforehand instead of being contaminants. Subsequently, residues 1 were used as the samples of the 2nd treatment. **Figure 3** summarizes the yield of soluble 2 from cedar. The yield tended to increase as the concentration of acetone increased. This was because the different concentrations expressed the different solubility parameters, so that the higher concentration of acetone enabled the solubilization of more types of components. The yield was relatively low when 90 wt% of formic acid was used for the 1st treatment. This was because hemicellulose and a part of cellulose were successfully solubilized when 50 or 75 wt% of formic acid was used. However, when 90 wt% of dense formic acid was used, some amounts of lignin were solubilized along with them as Imai et al. [23] reported that acidic condition promotes lignin solubilization. In addition, lignin also has a feature that it forms condensates which are difficult to solubilize when it was treated with strong acid [24]. Therefore, the yields of solubles 2 after the treatment with 90 wt% of formic acid were lower than the yields of solubles 2 after the treatment with 50 or 75 wt% of formic acid. **Figure 4** shows the elemental composition of soluble 2 obtained when 75 wt% of formic acid was used for the 1st treatment along with those of organosolv lignin and cellulose for comparison. The composition profiles were similar to lignin, which indicated that the obtained soluble 2 mainly consisted of lignin. The carbon content of soluble 2 increased with acetone concentration. This could be also explained by the difference of the solubility parameters, and the higher concentration of acetone could solubilize more amounts of carbon rich components. These results indicated that specific extract fractions could be obtained by controlling the concentration of acetone. Because the carbon contents of basic frameworks of lignin (three types of phenylpropanoids with different amounts of active sites) range in 60 - 75 wt%, the differences in carbon contents of the samples probably result in the differences of thermal curing properties. Subsequently, the thermal curing properties were analyzed by DTA, which could measure the exothermic energy while the samples were heated. This analysis was conducted because the phenolic resin materials were generally cured by forming cross-links between themselves and curing agents. This reaction is exothermic, therefore, the curing reaction proceeds better when higher exothermic energy is detected. **Figure 5** shows the results of DTA. All the varnishes delivered peaks of exothermic energy within the range of 100 - 150 °C. The results showed that higher exothermic energy was detected when lower concentrations of acetone were used. Judging from the results shown in **Figure 4** and **Figure 5**, lower concentrations of acetone extracted more active and low carbon content compounds selectively, whereas higher concentrations of acetone extracted undesirable, less active compounds, such as compounds consisting of long carbon side chains. The highest exothermic energy was detected when 75 wt% of formic acid was used for the 1st treatment and 30 wt% of acetone was used for the 2nd treatment. However, judging from the yield of soluble 2 shown in **Figure 3**, the proper reagent concentration among samples was determined as 50 wt% for formic acid and 30 wt% for acetone. This reaction resulted in a yield of 0.82 g/g-lignin and 18.2 µV/mg of exothermic energy. **Figure 6** shows the MWDs of soluble 2 obtained through 50 wt% formic acid treatment. The result also confirmed that the lower concentration of acetone was desirable for the reaction process, showing that soluble 2 was recovered with the smaller molecular weight fractions by the lower concentration of acetone. When the 2nd treatment was conducted at the different temperatures of 220 °C and 245 °C using 50 wt%

of acetone after 50 wt% formic acid treatment, the yield of lignin decreased from 0.98 g/g-lignin at 295 °C to 0.57 g/g-lignin and 0.84 g/g-lignin, respectively. In addition, the DTA of these samples showed a very small peak, which demonstrated that a temperature of at least more than 245 °C was required for the 2nd treatment of this process.

3.2 Comparison of the results with the previous production method and thermal curing property

In our previous research, the production method of lignin-based resin consisted of two steps; the first step was the extraction of lignin with 50 wt% acetone at 220 °C, and the second step was the depolymerization of extracted lignin at 300 °C. The performances of previous product such as the thermal durability and the mechanical durability were quite compatible with conventional phenolic novolac resin [21]. The mechanical durability was measured by pressurizing the product until it was bent. The measured pressure was 164 MPa for our previous product, and that was 172 MPa for conventional phenolic resin. In this report, because the samples were not produced in large quantities (due to the small quantities of used materials), the thermal and mechanical durability were not evaluated. Therefore, the properties were evaluated by the visual observation of thermal curing property of varnish, the comparison of MWD of soluble 2, the comparison of softening profile of soluble 2, and the comparison of the values of exothermic energy during resinification with those of the previous product. The varnish used for the evaluation was the varnish prepared through the treatment with 50 wt% of formic acid and 30 wt% of acetone. **Figure 7** shows the thermal curing property of the varnish. The powder varnish was heated on the hot plate at 150 °C, and it started melting in 15 seconds of heating. Finally, it was confirmed that the varnish was successfully resinified uniformly in 1 minute. **Figure 8** shows the MWD of the cedar derivative soluble 2 in this study and the MWD of the produced available resin material in our previous report. The MWD of soluble 2 obtained by the new proposed method was narrower in the low molecular weight range, which indicated that the obtained material was more depolymerized and therefore could consist of more usable resin. **Figure 9** shows the thermal softening profiles of the cedar derivative soluble 2 in this study and those of the samples obtained in previous study. Because the previous production method consisted of two steps, the profiles of the products from the first step and the second step were shown in **Figure 9**. The softening temperature is desirable to be low for the useful resin, and it was reported in the previous study that the softening profile improved by the second step (depolymerization step). The softening profile of soluble 2 in this method was very similar to that of the fine product in previous study. Therefore, the product in this study was confirmed to be as easy to handle as the previous product. About the exothermic energy, it was 18.2 μV/mg for the new product (as described in Section 3.1) and 6.0 μV/mg for the previous product, which also confirmed the usability of the new obtained material. Thus, the product by the new method was indicated to be better product than the one by previous method. This proved that hemicellulose or cellulose derivatives were clearly undesirable components for the resinification. Therefore, the removal of hemicellulose or cellulose derivatives was clarified to be one of the important factors for the production of lignin-based resin material from lignocellulosic biomass.

3.3 Production of lignin-based resin materials from eucalyptus

As shown in **Table 1**, eucalyptus contains more hemicellulose than Japanese cedar. Because hemicellulose is the most degradable component, the 1st treatment was conducted only using 50 or 75 wt% of formic acid for eucalyptus. **Figure 10** shows the yield of soluble 2 from eucalyptus. When eucalyptus was used as a material, the yield was much lower when the formic acid concentration was 75 wt% compared with 50 wt%, indicating that even 75 wt% of formic acid was dense enough to degrade lignin. **Figure 11** shows the exothermic energy during the curing reaction of eucalyptus varnishes analyzed by DTA. All the peaks of exothermic energy were within the range of 100 - 150 °C. The trend was similar to that of cedar varnishes, and the higher exothermic energy was detected when lower concentrations of acetone were used. Thus, the proper reagent concentration among samples was determined as 50 wt% for formic acid and 30 wt% for acetone, which was the same as for the treatments on cedar. The yield of soluble 2 and measured exothermic energy for the determined condition were 1.11 g/g-lignin and 21.7 μV/mg. Both of the yield and the exothermic energy were higher than the values obtained from cedar sample. Thus, it was confirmed that the proposed method could be also adapted to other types of lignocellulosic biomass.

4. Conclusions

The new production method of lignin-based resin material from lignocellulosic biomass was proposed and examined. By recovering hemicellulose and a part of cellulose as saccharides beforehand through formic acid saccharification, their potential as contaminants for resinification was removed. After a 50 wt% formic acid treatment, the simultaneous extraction and depolymerization of lignin was efficiently achieved using 30 wt% of acetone. The produced resin material from Japanese cedar was confirmed to be available in terms of its low MWD, high yield of 0.82 g/g-lignin, and high exothermic energy of 18.2 µV/mg during curing. These results were better than our previous resin product, which was very compatible with conventional phenolic novolac resin in thermal and mechanical durability. Thus, the importance of the removal of hemicellulose or cellulose derivatives was indicated. The proposed method was also conducted on eucalyptus, and the adaptability of the method to other types of lignocellulosic biomass was confirmed.

Table 1. Contents of biomass samples

	Cellulose	Hemicellulose	Lignin
		[wt% (dry ash free)]	
Japanese cedar	52.7	13.8	33.5
Eucalyptus	44.9	28.9	26.2

Figure 1. Proposed reaction flowchart in this study.

Figure 2. Yield of residue 1 from cedar after 1st treatment. (175 °C, 2 h, broken line - lignin content in cedar)

Figure 3. Yield of soluble 2 against the concentration of acetone after 2nd treatment. (Biomass - cedar; 1st treatment - 175 °C, 2 h, concentration of formic acid [wt%] - circle = 50, square = 75, triangle = 90; 2nd treatment - 295 °C, 1 h)

Figure 4. Elemental compositions of soluble 2 after 2nd treatment against concentration of acetone. (Biomass - cedar; 1st treatment - 175 °C, 2 h, 75 wt% formic acid; 2nd treatment - 295 °C, 1 h)

Figure 5. Exothermic energy during the curing reaction as detected by DTA

against the concentration of acetone for the 2nd treatment. (Biomass - cedar; 1st treatment - 175 °C, 2 h, concentration of formic acid [wt%] - circle = 50, square = 75, triangle = 90; 2nd treatment - 295 °C, 1 h; temperature rising rate for DTA - 10 °C/min)

Figure 6. MWDs of soluble 2 obtained using different concentrations of acetone. (Biomass - cedar; 1st treatment - 175 °C, 2 h, 50 wt% formic acid; 2nd treatment - 295 °C, 1 h)

Figure 7. The thermal curing property of the prepared varnish at 150 °C.

Figure 8. MWDs of soluble 2 and lignin solution from previous method. (Solid line - soluble 2 in this study, broken line - our previous method [21])

Figure 9. The softening profiles of soluble 2 and samples in previous report by thermomechanical analysis. (Black solid line - soluble 2 in this study, gray broken line - extracted sample at first step in previous method, gray solid line – depolymerized sample at second step in previous method [21])

Figure 10. Yield of soluble 2 against the concentration of acetone after 2nd treatment. (Biomass - eucalyptus; 1st treatment - 175 °C, 2 h, concentration of formic acid [wt%] - circle = 50, square = 75; 2nd treatment - 295 °C, 1 h)

Figure 11. Exothermic energy during the curing reaction as detected by DTA against the concentration of acetone for the 2nd treatment. (Biomass - eucalyptus; 1st treatment - 175 °C, 2 h, concentration of formic acid [wt%] - circle = 50, square = 75; 2nd treatment - 295 °C, 1 h; temperature rising rate for DTA - 10 °C/min)

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Abbreviations

Molecular weight distribution (MWD)

Differential thermal analysis (DTA)

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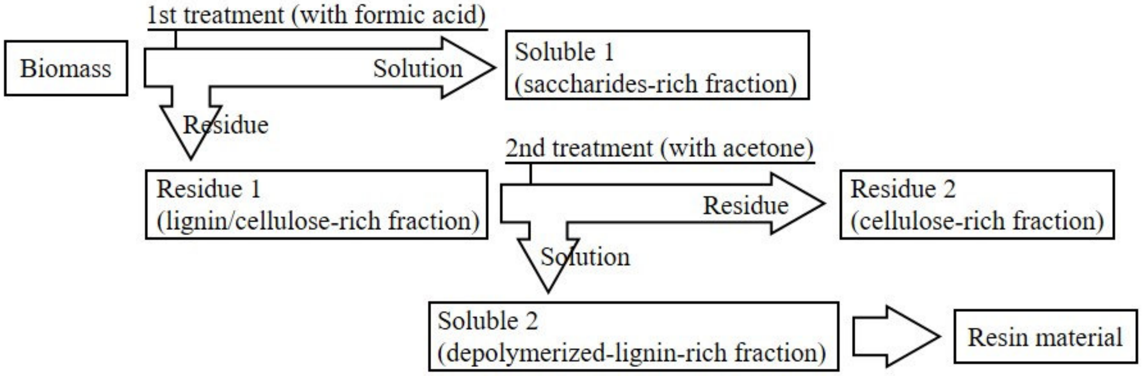
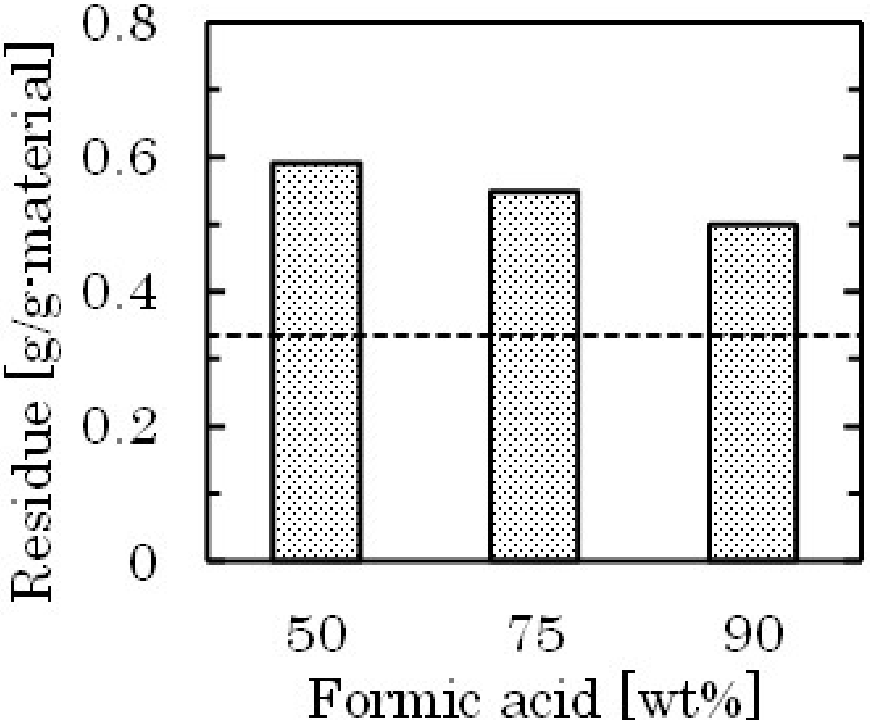
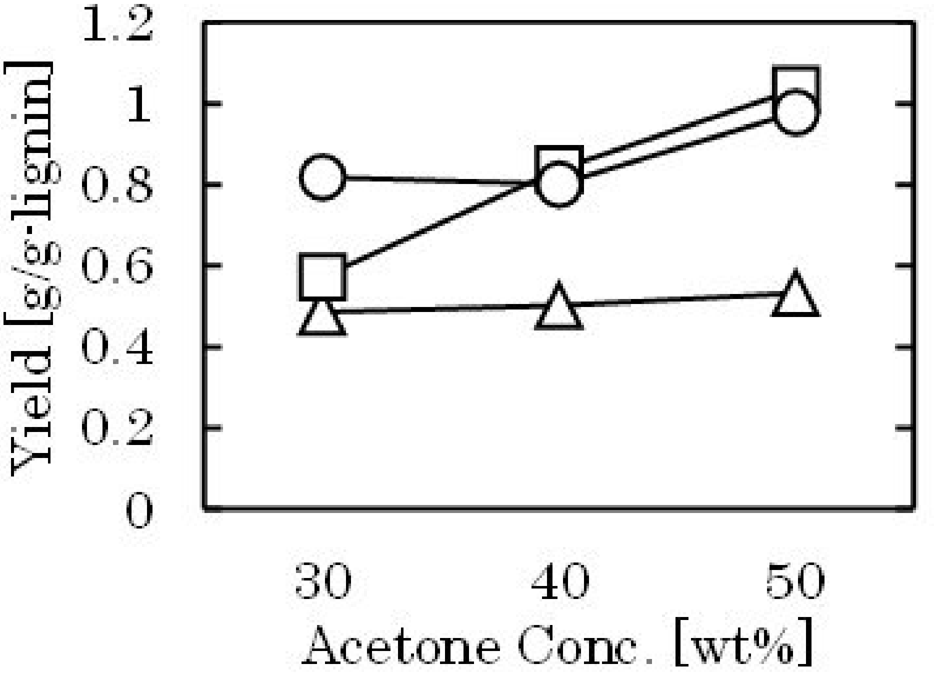
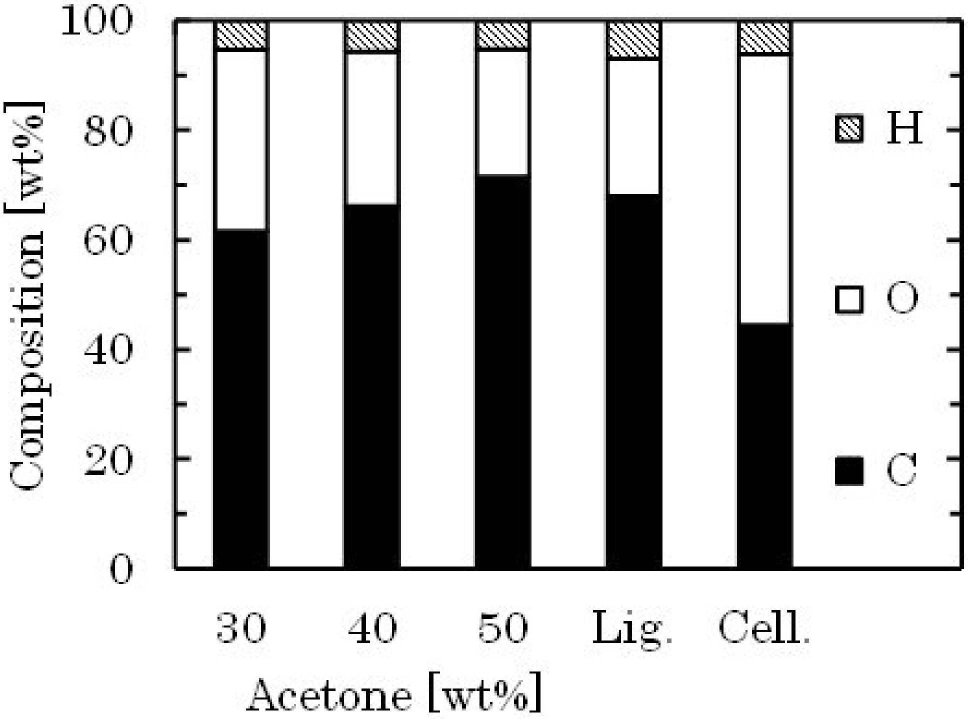
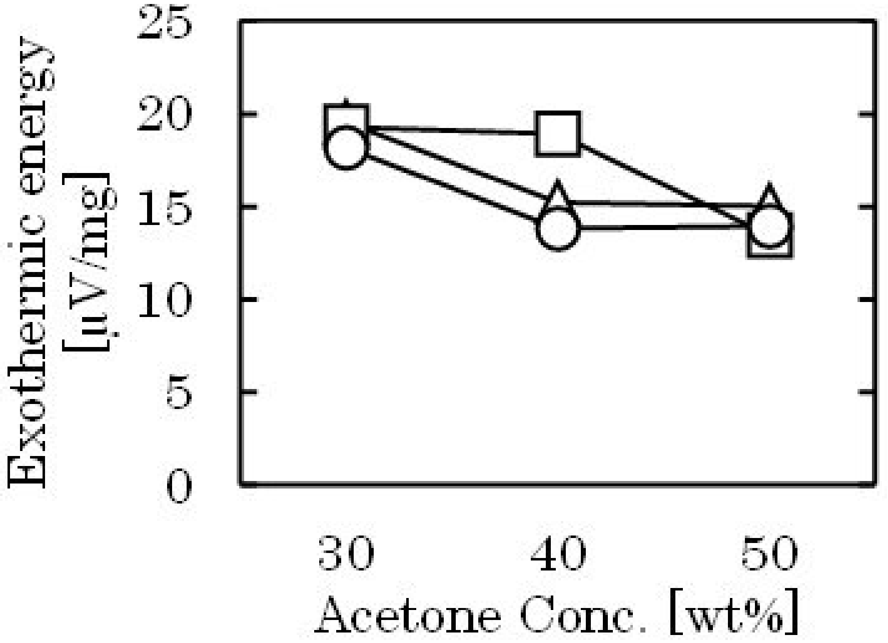
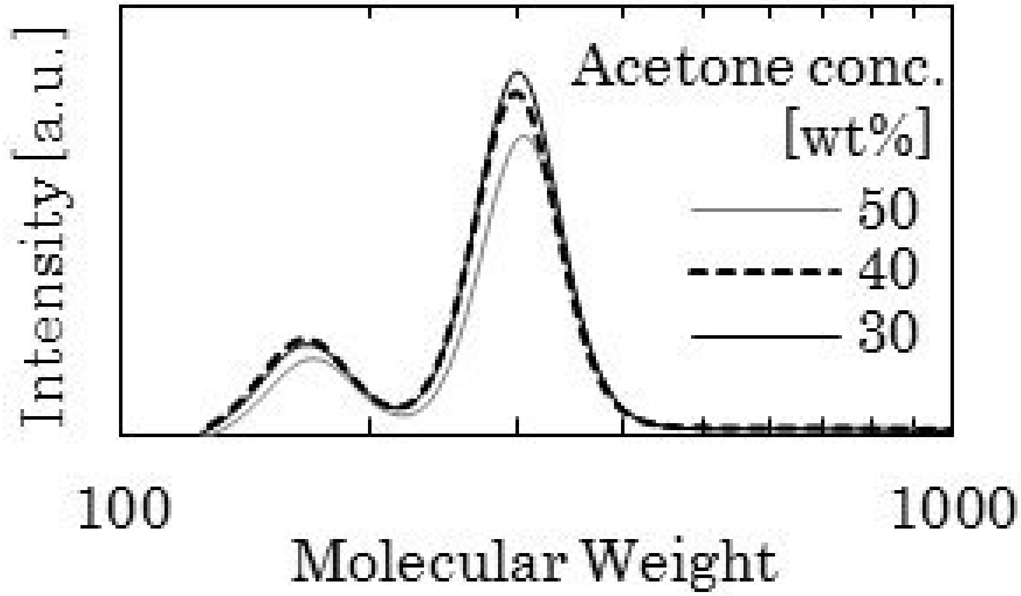

1st treatment (with formic acid)
Biomass
Solution
Soluble 1
(saccharides-rich fraction)
Residue
2nd treatment (with acetone)
Residue 1
(lignin/cellulose-rich fraction)
Residue
Residue 2
(cellulose-rich fraction)
Solution
Soluble 2
(depolymerized-lignin-rich fraction)
Resin material

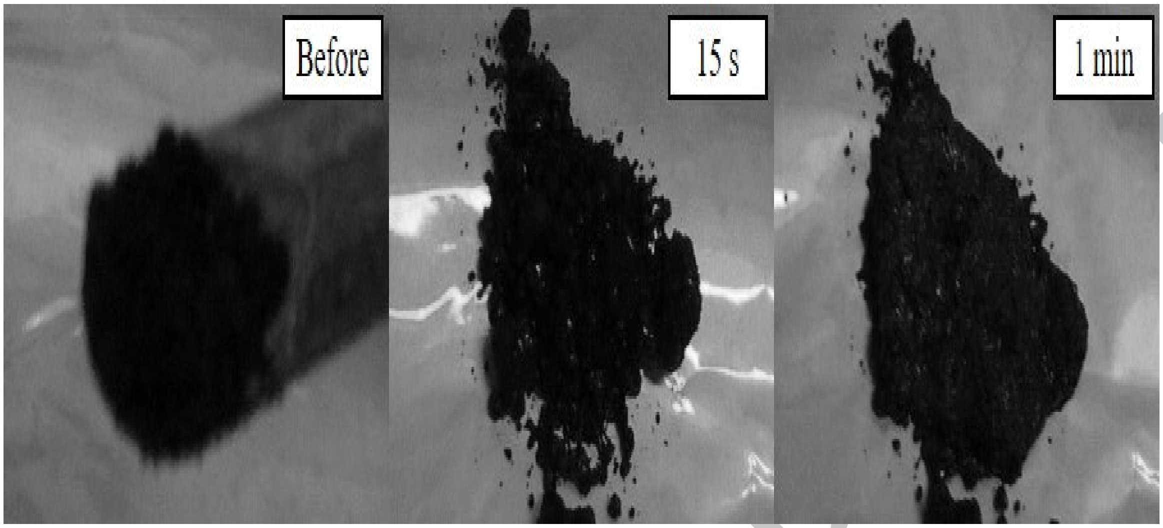

Residue [g/g·material]
0.8
0.6
0.4
0.2
0
50
75
90
Formic acid [wt%]

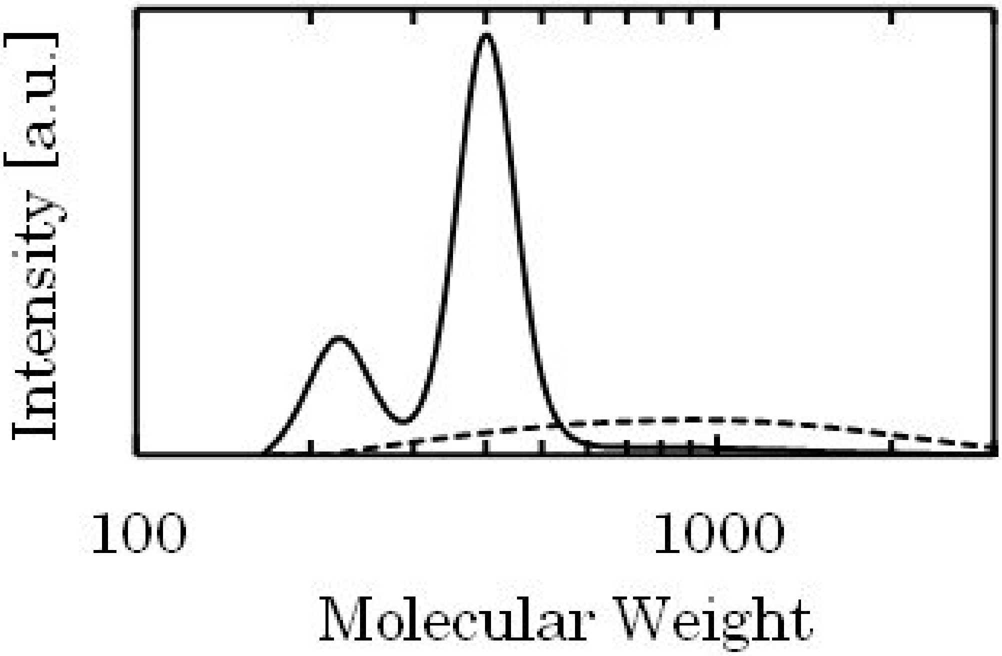

1.2
1
0.8
0.6
0.4
0.2
0
Yield [g/g-lignin]
30
40
50
Acetone Conc. [wt%]

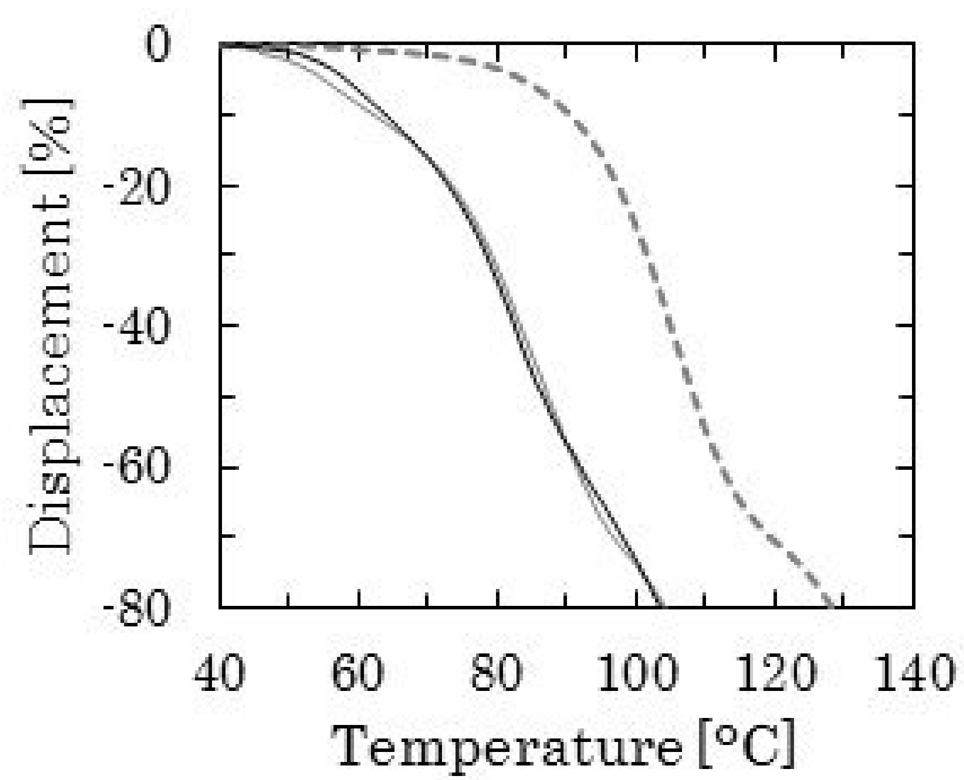

100
80
60
40
20
0
Composition [wt%]
30
40
50
Lig.
Cell.
Acetone [wt%]
H
O
C


Exothermic energy [μV/mg]
25
20
15
10
5
0
30
40
50
Acetone Conc. [wt%]

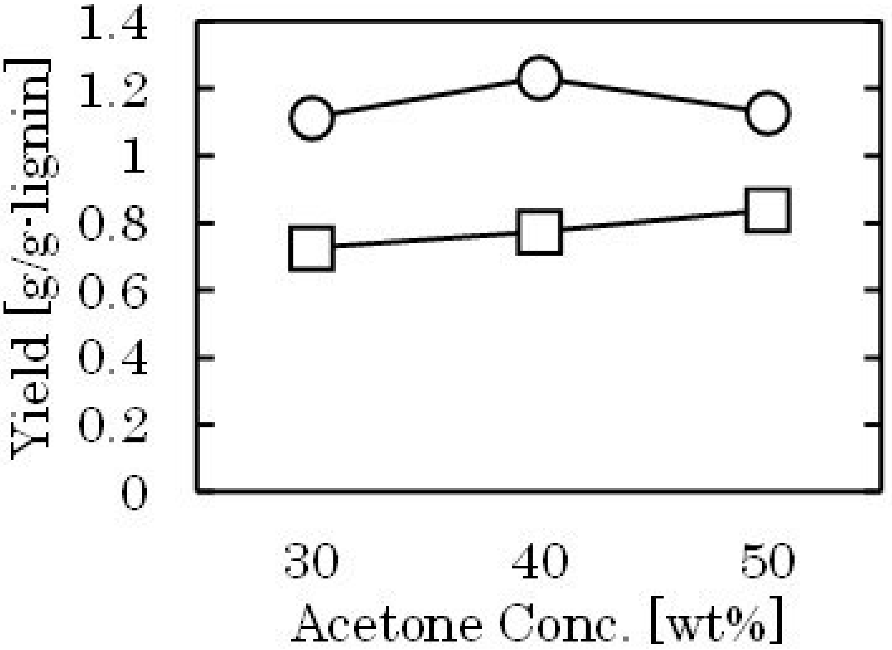

Intensity [a.u.]
Acetone conc.
[wt%]
50
40
30
100
1000
Molecular Weight


Before
15 s
1 min


Intensity [a.u.]
100
1000
Molecular Weight



0
-20
-40
-60
-80
Displacement [%]
40
60
80
100
120
140
Temperature [°C]



1.4
1.2
1
0.8
0.6
0.4
0.2
0
Yield [g/g-lignin]
30
40
50
Acetone Conc. [wt%]

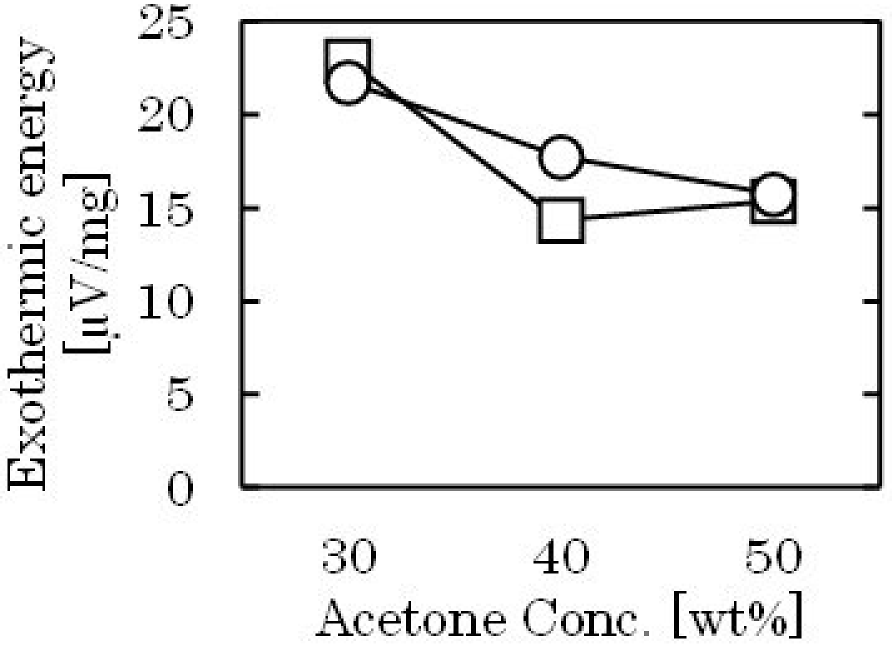

Exothermic energy [μV/mg]
25
20
15
10
5
0
30
40
50
Acetone Conc. [wt%]

Table 1. Contents of biomass samples

	Cellulose	Hemicellulose [wt% (dry ash free)]	Lignin
Japanese cedar	52.7	13.8	33.5
Eucalyptus	44.9	28.9	26.2

- Two-step production of lignin-based resin from lignocellulosic biomass was examined.
- Useful lignin-based resin was successfully produced from lignocellulosic biomass.
- Some components which decrease the performance of products were clarified.
- Product was indicated to be compatible with conventional phenolic resin.
- The proposed method was effective on some types of lignocellulosic biomass.