A New Treatment Method of Biomass for Production of Green Resin from Lignin

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1. Introduction

Lignin is one of the main components of biomass. But lignin is just burned for the recovery of energy in biomass conversion processes because of the complex structure. To realize bio-refinery economically for constructing a low-carbon society, it is crucial to produce valuable products from lignin in the high yield. A lignin resin is a powerful candidate as a valuable product because of less sensitivity of complex structure. However, transformation of lignin into resin requires suitable properties of raw lignin materials such as low softening points and high activity for curing reactions. In this study, lignin was extracted from several types of biomass and was hydrothermally depolymerized into small molecules that satisfy the above properties. Finally, the effectiveness of this presented method was examined by comparing the amount of CO_2 emission through production process between the lignin resin and the conventional phenolic resin.

2. Experimental section

(2-1) Extraction of lignin from biomass (1st treatment)

Cedar, rice straw and beech were used as raw biomass samples. Those were ground into particles under 150 μm. 2.0 g of dried powder and 18 g of acetone aqueous solution (50 wt%) were filled into a batch reactor. This completely sealed reactor was soaked in an oil bath at 220 ºC for 1 h. The products were cooled, and then separated into solid residue, water-soluble and acetone-soluble (A.S.) fractions (sample: 1actn_soluble). After that, the ultimate analyses of them were conducted.

(2-2) Hydrothermal depolymerization of lignin (2nd)

The filtrate of the 1st treatment was diluted to a specified concentration and was heated for 8.3 min at 300 ºC in 20 MPa using a flow reactor. The products were separated into A.S. fraction (2actn_soluble) and water-soluble. And their molecular weights and softening points were measured by GPC and TMA, respectively.

(2-3) Preparation of thermosetting resin from lignin

10 phr (per hundred resin) of hexamine was added to the A.S. fractions obtained above. The thermal curing properties of the samples were evaluated with DSC.

(2-4) Estimation of CO_2 emission

CO_2 emissions by the conventional method of producing phenolic resin or the new method of producing lignin resin were calculated by MiLCA (LCA software).

3. Results and discussion

From Table 1, it was found that lignin was extracted as the A.S. fraction by the 1st treatment for all the biomass samples. Next, this extracted lignin (1actn_soluble) was successfully depolymerized into the low molecular weight compounds (2actn_soluble) through the 2nd treatment as shown in Figure 1. The softening points of 2actn_solubles were lower than those of 1actn_soluble samples. Judging from the observation and heat of exothermic resinification reaction in Table 2, depolymerization of lignin brought about the uniform and adequate thermosetting resin.

Table 1 Ultimate analyses of A.S. fractions obtained in this study, compared with lignin and cellulose

Sample	C	H	N	O
Cedar_1actn_soluble	68.0	5.24	0.33	26.5
Rice straw_1actn_soluble	67.6	5.89	0.61	25.9
Beech_1actn_soluble	65.8	5.40	0.18	28.6
Organosolv Lignin	68.0	5.80	0.00	26.2
Cellulose	44.4	6.22	0.00	49.3

Finally, the CO_2 emissions are summarized in Table 3. The lignin resin by the presented method could reduce significantly CO_2 emission as compared with that of the conventional phenolic resin derived from petroleum oil.

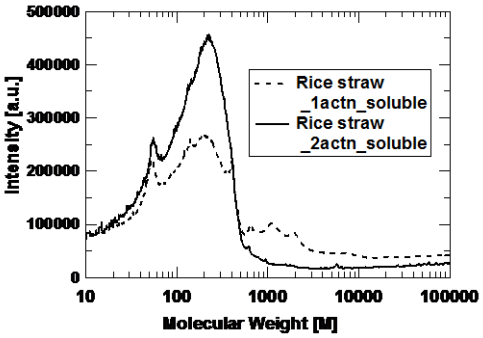

Figure 1 Molecular weight distribution of A.S. samples of rice straw

Table 2 DSC results during resinification

Sample + Hexamine (10 phr)	Peak temp. in DSC curve [ºC]	Calorific value [J·g^{-1}]
Cedar_1actn_soluble	154.6	37.6
Cedar_2actn_soluble	161.9	76.5

Table 3 Calculation results of CO_2 emission

Phenolic resin (conventional method)		All	From mining resources to producing raw materials			Process of producing resin	Combustion
			Hexamine	Phenol	Formaldehyde		
CO_2	(originating from fossil fuel) kg·(kg-Resin)$^{-1}$	**6.672**	0.325	2.050	0.139	0.736	3.422
Lignin resin (new method)		All	From mining resources to producing raw materials			Process of producing resin	Combustion
			Hexamine	Lignin	Formaldehyde		
CO_2	(originating from fossil fuel) kg·(kg-Resin)$^{-1}$	**2.149**	0.345	0.708	0.000	0.736	0.360

4. Conclusions

A new treatment method was developed for production of materials of lignin resin. This process consists of the extraction of lignin and hydrothermal depolymerization (300 ºC, 20 MPa). It was clarified that phenolic resin could be substituted with lignin resin and that this green resin was very effective in reducing CO_2 emission.