

Development of effective utilization method of lignin from rice straw

Akihiro Kurosumi, Chizuru Sasaki, Yuya Yamashita, Yoshitoshi Nakamura*

Department of Life System, Institute of Technology and Science, The University of Tokushima, 2-1
Minamijosanjima-cho, Tokushima 770-8506, Japan
Fax: 81-88-656-9071, e-mail: ynakamu@bio.tokushima-u.ac.jp

A novel extraction method of low molecular weight lignin suitable as a raw material for epoxy resin production was investigated using rice straw. The physical properties of the lignin extracted from rice straw treated by steam explosion, sulfuric acid and dry milling were evaluated. It was observed that, the extraction method using steam explosion and methanol was effective for extracting low molecular weight lignin. Low molecular weight lignin extracted from the steam-exploded rice straw had 0.67 mmol/g-sample of phenolic hydroxyl group. This value is about 1/13 of the quantity of phenolic hydroxyl group in bisphenol A. The extracted lignin can be used as a raw material for production of epoxy resin.

Key words: rice straw, lignin, steam explosion, epoxy resin, biomaterial

1. INTRODUCTION

The production of useful materials from underutilized plant biomass has drawn a lot of interest in recent decades. Agricultural waste is cheap renewable resource available in large quantities. Rice straw is one of the most abundant agricultural waste materials in the world. Annually, about 731 million tons of rice straw are produced in which Asia, America, Africa, Europe, America and Oceania account for 667.6, 37.2, 20.9, 3.9, and 1.7 million tons, respectively. [1]. However, rice straws has traditionally been incinerated or used as animal fodder, both methods being ineffective.

Lignin is a natural amorphous polymer which, together with cellulose and hemicellulose, is one of the main constituents of agricultural waste such as rice straw, bagasse and corncob. Lignin composition is different not only between the plants of different genetic origin, but also between different tissues of an individual plant. In softwood lignin, the structural elements are predominantly derived, for more than 95 %, from coniferyl alcohol. In hardwoods (and dicotyl crops like flax and hemp), various ratios of coniferyl/sinapyl have been observed, whereas in lignin derived from cereals straws and grasses the presence of coumaryl alcohol is typical [2]. Lignin utilization has drawn attention for more than a century. However, only small portion of lignin and its derivatives has found applications [3,4]. In recent decades, lignin based polymer has been more and more considered as potential way to use lignin reasonably in large scale [5-7]. Some researchers have also studied lignin based epoxy resin [8-13]. Epoxy resins are recognized as one of the important thermoset polymers, since they are used in various materials such as adhesives, matrix of composites and elastomers.

The pretreatment of agricultural waste is very important because the separation of components in agricultural waste such as lignin, cellulose and hemicellulose is indispensable for utilization of agricultural waste. Steam explosion is a technology useful for the treatment of plant biomass [14-16]. In

steam explosion, saturated vapor at high pressure is used to rapidly heat the biomass in a digester. The biomass is maintained at the desired temperature for a short time. During this period, hemicellulose is hydrolyzed and dissolved. At the end of this period, the pressure rapidly decreases to atmospheric one in order to stop the chemical reaction. The explosive decompression gives rise to loss of water from the cells and the cleavage of cellular structures. Meanwhile, sulfuric acid treatment is widely investigated for the hydrolysis of cellulose and hemicellulose in plant biomass [17-20]. However, the extraction method of lignin suitable as a raw material for epoxy resin production has not been fully investigated.

In this work, the pretreatment methods for extracting the low molecular weight lignin suitable for epoxy resin synthesis from rice straw was examined. The physical properties of the lignin extracted from rice straw treated by various methods (i.e. steam explosion, sulfuric acid and dry mill treatment) were evaluated, and the suitable pretreatment for the raw materials was determined by evaluating the thermodynamic characteristics of epoxy resin.

2. MATERIALS AND METHODS

2.1 Rice straw

Rice straw used in this experiment was obtained from a field in Tokushima, Japan. It was air-dried to a constant weight and chopped into about 4 cm in length.

2.2 Steam explosion

The steam explosion apparatus (Japan Chemical Engineering and Machinery Co., Ltd, Osaka, Japan) consisted of a pressurized reactor, a steam generator, a receiver, and a condenser with a silencing action [15,16]. The reactor was maintained at a constant temperature. The capacity of the reactor was 1.2 dm³ and the highest temperature was 275°C (5.5 MPa). Fifty gram of rice straw was put into the reactor and then steam-heated at a steam temperature of

243°C (3.5 MPa) for a steaming time of 5 min. A ball valve at the bottom of the reactor was then suddenly opened to bring the reactor rapidly to the atmospheric pressure. The product containing solid and liquid materials was recovered in the receiver.

2.3 Sulfuric treatment

The rice straw was mixed with dilute sulfuric acid (0.1-2 % (v/v)) and autoclaved at 121°C with a residence time of 2 h. The strong sulfuric acid (80 % (v/v)) treatment of rice straw was performed at room temperature for 2 h. The liquid fraction was separated by filtration and the unhydrolysed solid residue was washed with warm water at 60°C.

2.4 Dry mill treatment

Rice straw was dry-milled by commercial mill (TML 20, TESCOM & Co., Ltd, Tokyo) and reduced to 2 mm in length.

2.5 Extraction method

Extraction method for obtaining a low molecular weight lignin from rice straw shown in Fig. 1. The rice straw pretreated by various methods (steam explosion, sulfuric treatment, dry mill treatment, and untreated) were used. Water extraction was used to remove water soluble materials from steam exploded and dry milled rice straw. Five gram of the dry samples were extracted in a 300 ml Erlenmeyer flask with the 100 ml distilled water at 60°C for 2 h. Then, the low molecular weight lignin was extracted from this dry residue by methanol. Dry residue was extracted in a 300 ml Erlenmeyer flask with 100 ml methanol at 25°C for 3 h. Sulfuric acid soluble materials were removed from sulfuric treated rice straw by filtration and washing. Low molecular weight lignin, i.e. methanol soluble lignin (MSL), was extracted from this dry residue.

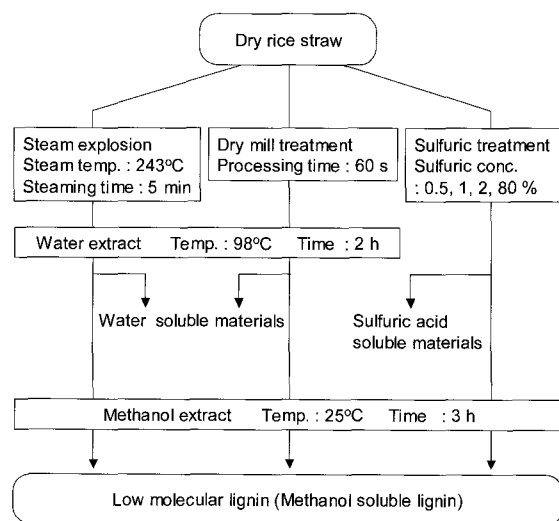


Fig. 1 Extraction method for obtaining the low molecular weight lignin from rice straw.

2.6 Epoxy resin synthesis

MSL was used as a sample for resinification. Two grams of the sample was dissolved in 15 ml of 10 % NaOH aqueous solution. The epoxy reaction was conducted at 90°C for 30 min after adding 100 ml of

epichlorohydrin (ECH) to sample solution. In order to remove the NaCl produced by the epoxy reaction, the washing by distilled water and the evaporation of the solvent were carried out. In this way, the epoxidized lignin, i.e. lignin epoxy resin, was obtained. Dimethyltri-amine was used as a curing reagent of epoxidized lignin. The epoxy equivalent was measured by hydrochloric acid - pyridine method [21,22].

2.7 Analytical method

The amount of phenolic hydroxyl group in MSL was measured by *ε*Di method [23,24].

Fourier Transform Infrared Spectroscopy (FTIR) analysis was performed by FT/IR 420 (JASCO Corporation) using KBr pellet technique. Each spectrum was recorded over 32 scans, in the range from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} . Background spectra were collected before every sampling. KBr was previously dried with silica gel to avoid interferences due to the presence of water.

The molecular weights were determined by gel permeation chromatography (GPC) using HPLC (Shimadzu LC-9A, Shimadzu Co. Ltd., Kyoto, Japan) with suitable columns (TSK-GEL G2000HXL and TSK-GEL G3000HXL; Tosoh Co., Ltd., Tokyo). Polystyrene (TSK standard PORYSTYRENE; Tosoh Co., Ltd., Tokyo), bisphenol A and phenol was used as a standard to determine the molecular weights. Tetrahydrofuran (THF) was used as an eluent at the flow rate of 1.0 ml/min. Molecular weight distribution was determined by an elution curve at 280 nm.

The thermogravimetric curve was measured by a thermogravimetric analyzer (TG/DTA 6300, Seiko Instruments Inc., Chiba, Japan) under the atmosphere of nitrogen (heating rate of 10°C/min). α -Alumina was used as a primary standard substance.

3. RESULTS AND DISCUSSION

3.1 Extraction of MSL

Table 1 shows the effects of various pretreatments methods on yield (MSL and residue) and phenolic hydroxyl group. Yield of MSL extracted from the steam-exploded rice straw reached 21 %. Part of lignin and the hemicellulose were degraded into water-soluble materials by steam explosion, and the yield of residue was 70 %. The residue consists mainly of cellulose and lignin. In addition, high molecular weight lignin was degraded into a low molecular weight lignin by hydrolysis reaction and fragmentation effect. It is thought that steam explosion had an influence on the increase of the yield of MSL.

A part of hemicellulose and cellulose was hydrolyzed into water-soluble materials by dilute sulfuric acid treatment, but the yield of MSL was very low. The reason why the yield of MSL was very low could be due to the fact that lignin was not degraded.

Most cellulose and hemicellulose were hydrolyzed into water soluble materials such as glucose and xylose by concentrated sulfuric acid treatment. However, MSL was not extracted from the residue because lignin underwent the condensation polymerization by strong sulfuric acid.

Phenolic hydroxyl group is a high-reactive functional group in lignin. The epoxy group is added to lignin after

the phenolic hydroxyl group reacts with ECH. MSL extracted from the rice straw pretreated by the sulfuric acid and the dry mill had little phenolic hydroxyl groups. However, MSL extracted from the steam-exploded rice straw had 0.67 m mol/g-sample of phenolic hydroxyl group. This value corresponded to about 1/13 of the quantity of phenolic hydroxyl group of bisphenol A. It is thought that lignin containing the phenolic hydroxyl group was extracted because β -O-4 and/or α -O-4 combination in lignin was dipolymerized by the steam explosion treatment [25].

A parallel study using bamboo (a monocotyledonous species like rice straw), at the steam-explosion steam temperature of 243°C, steaming time of 5 min was carried out. Lignin was extracted from this steam-exploded bamboo by various organic solvents (methanol, ethanol, acetone, ethyl acetate and 1,4-dioxan). Extraction yield to dry steam-exploded bamboo and amount of phenolic hydroxyl group in the extracted lignin were evaluated. When methanol and ethanol were used as a solvent, the yields were 34 and 31 %, respectively. The amounts of phenolic hydroxyl group in the extracted lignin were 2.94 and 2.66 m mol/g-sample, respectively. When ethyl acetate was used as a solvent, the yield and amount of phenolic hydroxyl group were 36 % and 2.52 m mol/g-sample, respectively. When acetone and 1,4-dioxan were used as a solvent, the yields from both solvents were 49 %. However, the amounts of phenolic hydroxyl group were 1.83 and 1.17 m mol/g-sample, respectively. It is thought that the comparatively less amount of phenolic hydroxyl group obtained could be due to the fact that either high molecular weight lignin or part of the sugar contents was extracted. Therefore, methanol or ethanol is suitable solvent for the extraction of high reactivity lignin. In this work, methanol was preferred because it has a lower boiling point.

Table 1 Effect of various pretreatment methods on yield (MSL and residue) and phenolic hydroxyl group.

Pretreatment	Yield (%)		Phenolic hydroxyl group (m mol/g-sample)
	Residue ¹⁾	MSL (%)	
Steam explosion	70	21	0.67
Sulfuric acid			
0.5 %	89	2	> 0.01
1 %	89	5	> 0.01
2 %	84	7	> 0.01
80 %	24	> 1	> 0.01
Dry mill	90	> 1	> 0.01
Untreated	98	> 1	> 0.01

¹⁾ Residue after water extract followed by pretreatment

Fig. 2 shows the effects of pretreatments on IR spectrum of MSL extracted from rice straw. MSL peaks at 1512 cm⁻¹ is due to aromatic rings. The peaks at 2842 and 3412 cm⁻¹ are due to C-H stretch and -OH (hydroxyl group), respectively. The characteristic absorption band (C-H stretch and aromatic rings) which is a characteristic of the lignin was confirmed in MSL extracted from

the steam-exploded rice straw. However, MSL extracted from the rice straw treated by sulfuric acid had no characteristic absorption band of lignin. This observation seems to be due to the fact that sugars and lignin derivatives were present in these MSL.

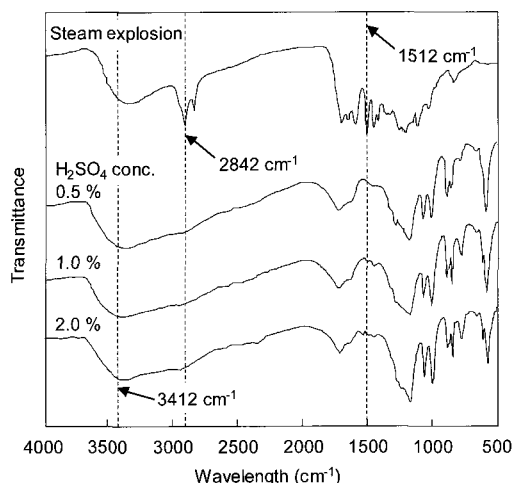


Fig. 2 Effects of pretreatments on IR spectrum of MSL extracted from rice straw.

Fig. 3 shows the elution curve of MSL extracted from the steam-exploded rice straw and the calibration curve. Polystyrene, bisphenol A and phenol were used as standard materials.

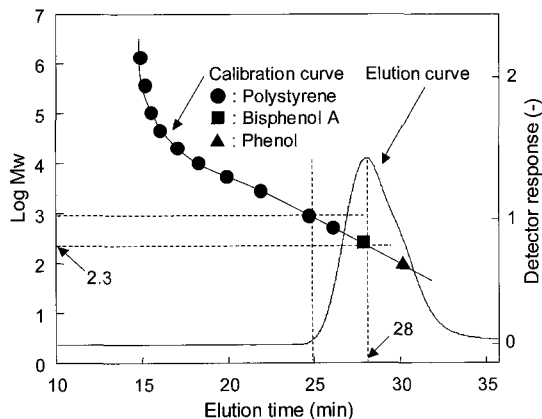


Fig. 3 Elution curve of MSL extracted from steam-exploded rice straw and calibration curve.

These results indicated that the molecular weights of MSL extracted from the steam-exploded rice straw was below 1000 and the weight average was about 200. Colombini *et al.* investigated molecular weight of lignin extracted from archaeological waterlogged wood with acetone-water (9:1). They reported that molecular weight of the lignin was 29,000-39,600 [26]. Sun *et al.* investigated the molecular weight of HCl insoluble lignin isolated from wheat straw and reported it to be 4,500-6,500 [27]. Xiao *et al.* reported that the molecular weight of the lignin and hemicellulose preparations, isolated with 1 M NaOH from maize stems, rye straw, and rice

straw was 3,680-21,760 [28]. The epoxy resin composed of high molecular weight raw materials is fragile. Therefore, the extraction and separation method of the low molecular weight lignin is important. In this study, steam explosion pretreatment and methanol extraction was effective in obtaining a low molecular weight lignin. However, low molecular weight lignin derivatives degraded by steam explosion were included in the MSL. Therefore, the separation and identification of these derivatives will be the focus of our future research.

3.2 Epoxy resin synthesis

Fig. 4 shows the IR spectrum of ECH insoluble material, ECH soluble material and MSL. The peaks at 850 and 923 cm^{-1} are based on the epoxy group. After the epoxy reaction, ECH insoluble materials and ECH soluble materials were produced, and more than 90 % were ECH insoluble materials. FTIR of these materials were measured after the removal of ECH. The spectra shift around 850 and 923 cm^{-1} were observed, probably due to induction by the epoxy group. However, the difference of IR spectrum between ECH soluble material and MSL was not confirmed. Therefore, it is thought that ECH soluble materials could be the lignin with no epoxy groups. In addition, the spectra shift around 850 and 923 cm^{-1} were confirmed to be ECH insoluble materials. Therefore, a low molecular weight lignin was successfully extracted and separated using steam explosion and methanol, and then converted into lignin epoxy resin.

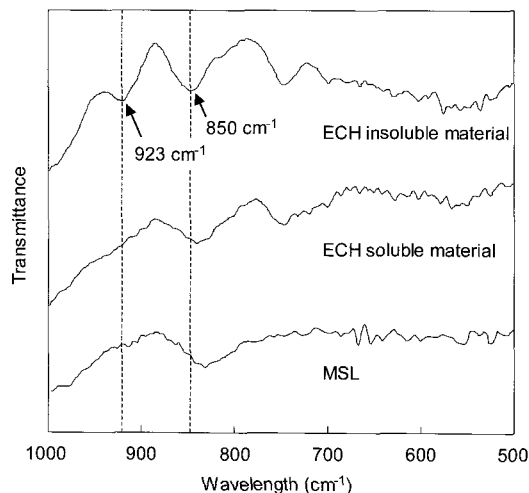


Fig. 4 IR spectra of ECH insoluble material, ECH soluble material and MSL.

Fig. 5 shows thermogravimetric (TG) curve of lignin epoxy resin (ECH insoluble material). The thermal decomposition of organic polymers is commonly determined by thermogravimetric analysis under helium or nitrogen atmosphere. Below 100°C, the weight of lignin epoxy resin decreased due to the presence of the remaining hardening agent residue. After heating to 700°C

20–30 wt% of lignin epoxy resin still remains unvolatilized due to the formation of highly condensed aromatic structures.

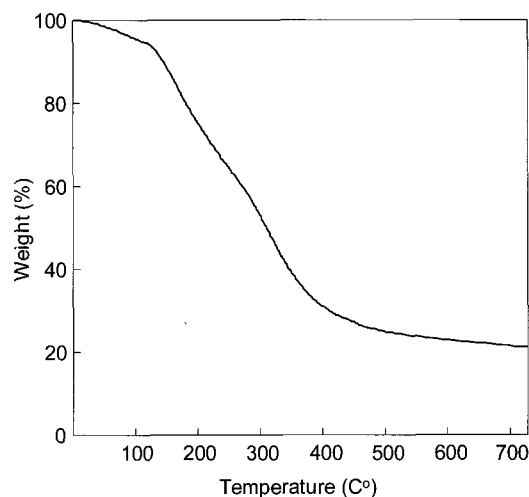


Fig. 5 TG curve of lignin epoxy resin (ECH insoluble material).

4. CONCLUSIONS

The extraction method using steam explosion and methanol was very effective in extracting a low molecular weight lignin. MSL extracted by this method had 0.67 m mol/g-sample of phenolic hydroxyl group (about 1/13 quantity of phenolic hydroxyl group of bisphenol A). The study elucidated a novel synthesis method of epoxy resin using lignin contained in the rice straw.

REFERENCES

- [1] K. Karimi, G. Emtiazi and M.J. Taherzadeh, *Enzyme Microb. Technol.*, **40**, 138-44 (2006).
- [2] C. Bonini, M. D'Auria, P. Di Maggio and R. Ferri, *Industrial crops and products*, **27**, 182-88 (2008).
- [3] G. Sun, H. Sun, Y. Liu, B. Zhao, N. Zhu and K. Hu, *Polymer*, **48**, 330-37 (2007).
- [4] C.I. Simionescu, V. Rusan, M.M. Macoveanu, G. Cazacu, R. Lipsa, C. Vasile and A. Stoleriu and A. Ioanid, *Compos. Sci. Technol.*, **48**, 317 (1993).
- [5] B. Zhao, G. Chen, Y. Liu, K. Hu and R. Wu, *J. Mater. Sci. Lett.*, **20**, 859-62 (2001).
- [6] S.Y. Lin, "Progress in Biomass Conversion", Vol. 4 edited by A. David, Tillman and Edwin C. Hahn, 31 (1983) pp. 31.
- [7] H.H. Nimz, "Wood Adhesives, Chemistry and Technology" edited by Pizzi A. (1983) pp. 247.
- [8] D. Feldman, D. Banu, A. Natansohn and J. Wang, *J. of Appl. Polym. Sci.*, **42**, 1537 (1991).
- [9] J. Wang, D. Banu and D. Feldman, *J. Adhes. Sci. Technol.*, **6**, 587 (1992).
- [10] D. Feldman, D. Banu, C. Luchian and J. Wang, *J. of Appl. Polym. Sci.* **42** 1307 (1991).
- [11] CR.I. Simionescu, G. Cazacu and M.M. Macouveau, *Cellul. Chem. Technol.*, **21**, 525 (1987).
- [12] D'alelio, US Patent no. 3,984,363, October 5 (1976).
- [13] K. Hofmann and W.G. Glasser, *J. Wood Chem. Technol.*, **13**, 73 (1993).

- [14] A. Kurosumi, F. Kobayashi, G. Mtui, Y. Nakamura, *Biochem. Eng. J.*, **30**, 109-13 (2006).
- [15] T. Sawada, Y. Nakamura, *J. Chem. Technol. Biotechnol.*, **76**, 139-46 (2001).
- [16] C. Asada, Y. Nakamura, F. Kobayashi, *J. Chem. Eng. Jpn.*, **38**, 158-61 (2005).
- [17] B.C. Saha, L.B. Iten, M.A. Cotta, Y.V. Wu, *Proce. Biochem.*, **40**, 3693-700 (2005).
- [18] Y. Sun, J.J. Cheng, *Bioresource Technology*, **96**, 1599-606 (2005).
- [19] C. Cara, E. Ruiz, J.M. Oliva, F. Sa'ez, E. Castro, *Bioresource Technology*, **99**, 1869-76 (2008).
- [20] S.H.A. Rahman, J.P. Choudhury, A.L. Ahmad, *Biochem. Eng. J.* **30**, 97-103 (2006).
- [21] J.L. Jungnickel, "Organic Analysis 1", edited by J. Michell, Inter-Science, Now York, (1953) pp. 127.
- [22] Y. Nakamura, T. Sawada, Y. Nakamoto, *Network Polymer*, **19**, 26-33 (1998).
- [23] O. Goldschmid, *Anal. Chem.*, **26**, 1421 (1954).
- [24] E. Alder, S. Hernestam, *Acta Chem. Scand.* **9**, 319 (1955).
- [25] E. Minami, H. Kawamoto, S. Saka, *J. Wood Sci.*, **49**, 158-165 (2003).
- [26] M.P. Colombini, M. Orlandi, F. Modugno, E.L. Tolppa, M. Sardelli, L. Zoia, C. Crestini, *Microchem. J.*, **85**, 164-73 (2007).
- [27] R.C. Sun, J. Tomkinson, Y. Ye, *Polymer Degradation and Stability*, **79**, 241-51 (2003).
- [28] B. Xiao, X.F. Sun, R.C. Sunb, *Polymer Degradation and Stability*, **74**, 307-19 (2001).

(Received June 6, 2008 ; Accepted September 5, 2008)