Acidic Solvolysis of Softwood in Recycled Polyethylene Glycol System

Eri Takata,[a] Thi Thi Nge,[a] Shiho Takahashi,[a] Yasunori Ohashi,[b] and
Tatsuhiko Yamada [a],*

The acidic solvolysis of lignocellulose using a glycol solvent such as polyethylene glycol (PEG) is a promising process for separating its components and producing a valuable lignin product that can be used as thermoplastic and fusible materials. To decrease operational costs, a glycol solvent that is used as a solvolysis reagent must be recovered and reused. In the present study, PEG was recovered by the removal of water by evaporation from the supernatant after glycol lignin production by acidic solvolysis of Japanese cedar using PEG with an average molecular weight of 200 (PEG200). The recovered PEG200 worked as a solvolysis reagent and produced glycol lignin with appropriate yield. The thermomechanical analysis of glycol lignin from the fresh and recovered PEG200 systems exhibited two inflection points, which were assigned to a glass transition point (T_g) and a thermal softening point (T_s). The T_s of the glycol lignin from the recovered PEG200 system was higher than that from the fresh PEG200 system. These results suggest that the glycol lignin from the recovered PEG200 system had high thermostability as well as high thermal fusibility.

Keywords: Acidic solvolysis; Lignin; Polyethylene glycol (PEG); Solvent recovery; Softwood

*Contact information: a: Forestry and Forest Products Research Institute, 1 Matsunosato, Tsukuba, Ibaraki 305-8687, Japan; b: Harima Chemicals, Inc., 6-18-1 Inari, Soka, Saitama 340-0003, Japan;
* Corresponding author: yamadat@affrc.go.jp*

INTRODUCTION

Solvolysis of lignocellulose using an organic solvent has been investigated as a pulping process (Sarkanen 1980; Johansson *et al*. 1987). A wide variety of organic solvents have been applied as delignification solvents, with or without acidic catalysts (Sarkanen 1980; Johansson *et al*. 1987; Muurinen 2000). The solvents used include ethanol (Kleinert 1974; Lora and Aziz 1985), methanol (Aronovsky and Gortner 1936; Nakano *et al*. 1976), ethylene glycol (Nelson 1977; Gast and Puls 1985; Thring *et al*. 1989), acetic acid (Pan *et al.* 1999), and phenol (Funaoka and Abe 1989).

Kleinert (1974) reported that an aqueous mixture of 45 wt.% ethanol was a strong delignification agent for hardwood and softwood pulping. The pulps produced by aqueous ethanol pulping gave about 4 to 4.5% higher yields than the conventional kraft pulps of the same lignin content. Gast and Puls (1985) investigated an ethylene glycol-water (1:1 v/v) system with respect to the component separation of hardwoods. A sufficient quantity of delignified pulp was obtained from the system, and the lignins produced showed promising results as extenders in phenolic resin adhesives. High-boiling solvent (HBS) pulping using aqueous high-boiling solvents such as 1,4-butanediol, 1,3-butanediol, and tetrahydrofurfuryl alcohol has been suggested (Kajimoto *et al*. 2000; Kishimoto and Sano 2003). HBS pulping has an apparent advantage because of the lower pressure attained during solvolysis than pulping using low-boiling solvents such as ethanol. The solvolysis of wheat straw using aqueous 1,4-butanediol under atmospheric pressure was reported by Li *et al.* (2015).

Sarkanen (1980) stated in a review that the separation of lignocellulose into its components by solvolysis represents one of the simplest options for the integrated utilization of lignocellulose. Cellulosic fibers obtained by solvolysis are suitable for papermaking (Kleinert 1974; Nelson *et al.* 1977) or conversion to glucose by enzymatic hydrolysis (Zhang *et al.* 2013; Sun and Cheng 2002). Lignins isolated by solvolysis are usable as fuel and adhesives (Gast and Puls 1985), resin (Lora and Aziz 1985), and starting materials for several application (Espinoza-Acosta *et al.* 2014; Moghaddam *et al.* 2014). Thring *et al.* (1989) isolated lignin from the spent black liquor produced during the solvolysis of poplar using ethylene glycol, with the aim of using the lignin fraction as chemical feedstocks for conversion into monomeric chemicals.

Recent studies (Kubo *et al.* 2007; Lin *et al.* 2012) revealed that lignin isolated from softwood by acidic solvolysis using a glycol solvent such as ethylene glycol or polyethylene glycol (PEG) exhibited thermal fusibility. In the current report, the lignin used is defined as “glycol lignin.” Thermal fusibility is an important property for utilization as an industrial material in terms of moldability. Kraft lignin and acetic acid lignin isolated from softwood do not show thermal fusibility (Uraki *et al.* 1995; Kubo *et al.* 1997), which is one of the reasons their material utilization is limited. Glycol lignin was converted into fibers by melt spinning without additional chemical modification (Lin *et al.* 2012). These findings indicated that solvolysis using a glycol solvent such as PEG is a promising process for isolating cellulose and lignin for use as industrial materials. To decrease the operational costs, it is necessary to recover and reuse the solvolysis solvent. Few papers concerning solvent recovery have been published (Kajimoto *et al*. 2000; Muurinen 2000). Distillation is preferable for recovering the solvent from solvolysis pulping in a low-boiling solvent system (Muurinen 2000). In the case of high-boiling solvents such as ethylene glycol, PEG, and 1,4-butanediol, distillation of the solvents involves high separation energy consumption and investment costs. Kajimoto *et al*. (2000) reported that the recovery of the high-boiling solvent 1,4-butanediol was prepared by the evaporation of water from the spent liquor and the recovered solvent was reused as a solvolysis solvent for HBS pulping.

The purpose of this study was to investigate acidic solvolysis of softwood using recovered PEG with an average molecular weight of 200 (PEG200). PEG200 was used for solvolysis, and a small amount of sulfuric acid was added as a catalyst. Solvolysis was performed as described in a previous report (Lin *et al*. 2012), with some modifications.

EXPERIMENTAL

Materials

Japanese cedar (*Cryptomeria japonica*), which is the most popular species in conifer plantations in Japan, was used as a lignocellulosic material. The bark-free wood was air-dried, milled, and sieved. The air-dried wood meal (smaller than 1 mm in size) contained about 10 to 13 wt.% water. It was dried in an oven at 80 °C for 18 h and kept in a desiccator at room temperature until the use. The water content of the wood meal was 2.6 wt.%. The Klason lignin content of the wood meal was 34.1 wt.%.

PEG200 was purchased from the Lion Corporation (Tokyo, Japan). All other extra-pure grade chemicals were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and Junsei Chemical Co., Ltd. (Tokyo, Japan).

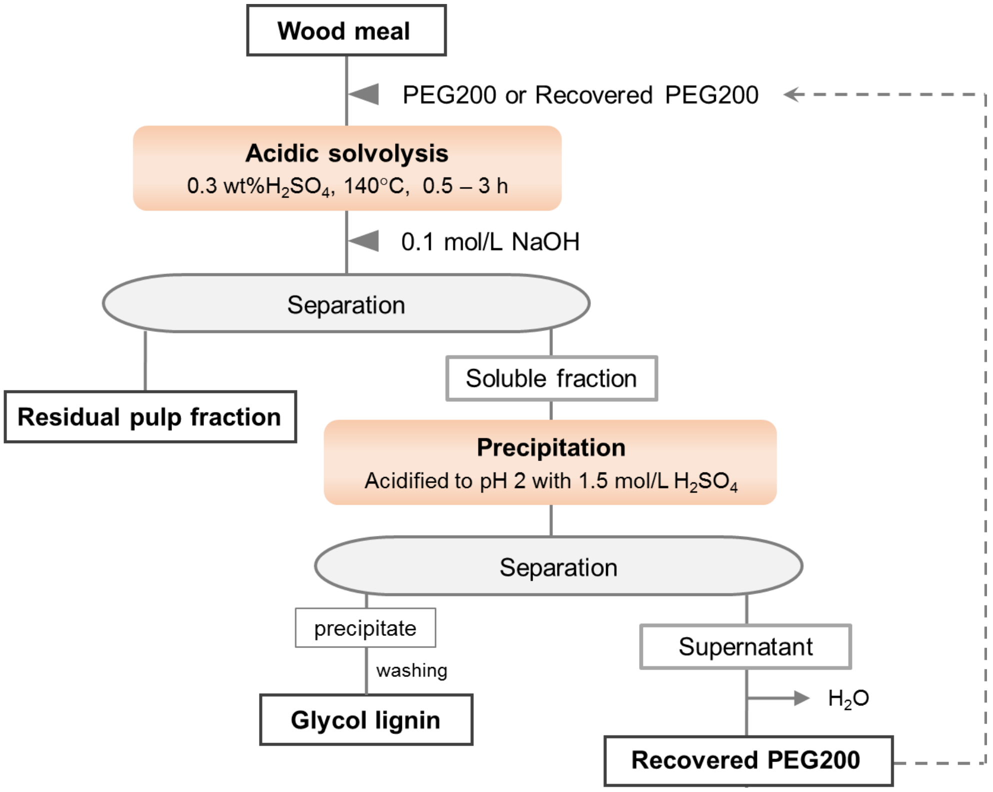

Fig. 1. Acidic solvolysis with fresh and recovered PEG200

Acidic Solvolysis

Figure 1 shows the process for acidic solvolysis, as described previously (Lin *et al*. 2012). Solvolysis was performed in a 20-mL glass flask equipped with a mechanical stirrer. PEG200 and 0.3 wt.% sulfuric acid were mixed well, and the mixture was used as a solvolysis reagent. Wood meal (1.0 g) and the solvolysis reagent (5.0 g) were mixed in a flask, and the flask was immersed in an oil bath preheated to 140 °C to start the solvolysis reaction. The reaction was carried out with stirring (150 rpm) under atmospheric pressure. After prescribed reaction times (0.5 to 3.0 h), the flask was quenched in a water bath to stop the reaction.

The reaction products were diluted with 12 mL of 0.1 M NaOH and stirred with a magnetic stirrer for 15 min at room temperature. The diluted products were separated into a pulp fraction and a soluble fraction by centrifugation at 2300 × *g* for 20 min. The pulp fraction was washed with water (30 mL) and centrifuged again. The washing step was carried out twice, and the rinsing water was combined with the soluble fraction. The pulp fraction was oven-dried at 105 °C for 18 h and then weighed to calculate the yield.

The soluble fraction was adjusted to pH 2 with 1.5 M sulfuric acid to produce a precipitate, which was centrifuged at 2300 × *g* for 20 min to separate the supernatant, which contained a high amount of unreacted PEG200. The precipitate was subsequently washed with dilute sulfuric acid (pH 2.5) to remove unreacted PEG200 and recovered by centrifugation. The washing step was performed twice, and the rinsing solution was combined with the supernatant. The glycol lignin precipitate was collected as the target product, dried at room temperature in a vacuum oven, and weighed to measure the yield.

The supernatant separated from the glycol lignin precipitate (2-h reaction using fresh PEG200) was transferred into a flask equipped with a distillation apparatus and then heated to its boiling point under nitrogen gas bubbling to remove water. When almost all the water was removed, the internal temperature increased to over 100 °C. The evaporation was stopped when the internal temperature reached 120 °C. The remaining liquid in the flask was collected and used as recovered PEG200. Acidic solvolysis of Japanese cedar with the recovered PEG200 and the subsequent separation were carried out as described above.

Analyses

The glycol lignin was washed thoroughly with water to remove residual sulfuric acid. Subsequently, it was recovered by centrifugation, dried at room temperature in a vacuum oven, and used as an analytical-grade sample for chemical and thermal analyses.

Measurement of lignin content and phenolic hydroxyl group content

The Klason lignin content of the glycol lignin was estimated from the absorption coefficient of a UV method (Lin and Dence 1992; Takahashi *et al*. 2015). The dried glycol lignin was weighed in a volumetric flask and dissolved completely in dioxane/0.2 M NaOH (v/v = 1:1). Each sample solution was adjusted to pH 5.0 with acetic acid, and the absorbance at 280 nm was measured. The absorption coefficient was determined as previously described (Takahashi *et al*. 2014). The Klason lignin content of the glycol lignin produced by the solvolysis of Japanese cedar (using PEG200 containing 0.3 wt.% sulfuric acid, 140 °C, 2 h) was measured using the Klason method (Lin and Dence 1992). The absorption coefficient of glycol lignin was determined on the basis of the relationship between the concentration and the UV absorbance at 280 nm of the glycol lignin, which was 25.2 L/g·cm.

The lignin content in the recovered PEG200 fraction was determined using a modified UV method as follows. The recovered PEG200 fraction was diluted by dioxane/0.2 M NaOH (v/v = 1:1) and reduced by $NaBH_4$ for one week to eliminate UV-absorbing furans (Chi *et al*. 2009). The reduced sample was adjusted to pH 5.0 with acetic acid, and the absorbance at 280 nm was measured as described above.

The phenolic hydroxyl group content of glycol lignin was estimated *via* the ionization difference method (Lin and Dence 1992; Takahashi *et al*. 2014). Glycol lignin dissolved in dioxane/0.2 M NaOH (v/v = 1:1) was reduced by $NaBH_4$ for two weeks. The difference between the UV absorbance at 300 nm of the glycol lignin solution in alkaline conditions and that in acidic conditions was measured to calculate the phenolic hydroxyl group content on the basis of a molar extinction coefficient of 4100 L/mol·cm.

Size exclusion chromatography analysis

Size exclusion chromatography (SEC) was performed to determine the molecular weight and molecular weight distribution of the glycol lignin and the recovered PEG fraction. A Shimadzu Prominence GPC system (Kyoto, Japan) equipped with a UV detector and a RI detector on a two-column sequence of Shodex KD-802 and KD-806M was used to analyze the samples. N,N-dimethylformamide (DMF) containing 10 mM LiBr was used as an eluent with a flow rate of 1.0 mL/min. The samples were prepared in the eluent and filtered through a 0.45-µm syringe filter. The molecular weight of the samples was calculated based on the polyethylene glycol standard (ReadyCal Set Mp 102-40000 and ReadyCal Set Mp 200-1200000, Sigma-Aldrich, St. Louis, MO, USA).

Thermomechanical analysis

Thermomechanical analysis (TMA) of the glycol lignin was performed on a TA Instruments Q400 thermomechanical analyzer (New Castle, DE, USA; Lin *et al*. 2012). The dried glycol lignin powder (5 mg) was placed in a platinum pan (6 mm inner diameter × 2.5 mm depth) with a lid. The sample was heated from room temperature to 450 °C at a rate of 5 °C/min with a force of 0.050 N under a N_2 stream at 100 mL/min.

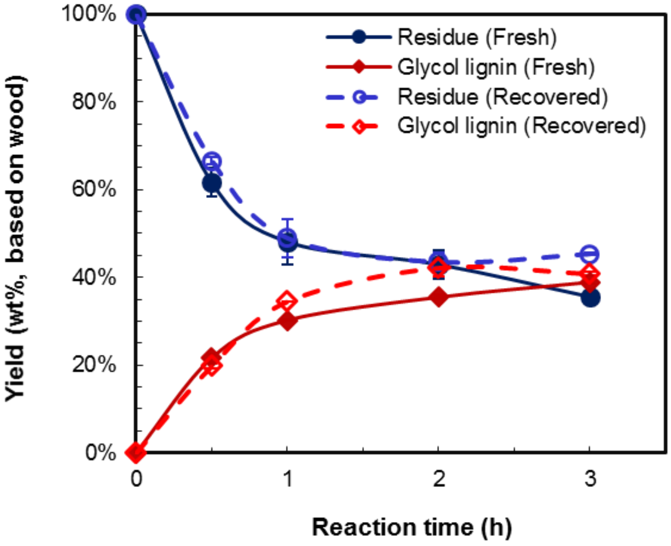

Fig. 2. Yield of solvolysis residue and glycol lignin with fresh and recovered PEG200. Error bars show the variation from the average (n = 2).

RESULTS AND DISCUSSION

Acidic Solvolysis Reaction of Softwood with Fresh PEG200

The acidic solvolysis of softwood with fresh PEG200 was carried out with 0.3 wt.% sulfuric acid at 140 °C for 0.5 to 3 h (Fig. 1). The solid lines in Fig. 2 show the yields of the solvolysis residue and glycol lignin. The yield of the residue gradually decreased to 48.1 wt.% after 1 h and then slightly decreased after a longer reaction time. However, the yield of glycol lignin increased with reaction time. The yield of glycol lignin was 38.9 wt.% after 3 h.

Acidic Solvolysis of Softwood with Recovered PEG200

SEC analysis of the recovered PEG200

The recovered PEG200 was prepared by removing water by evaporation from the supernatant after glycol lignin preparation. The weight recovery of the recovered PEG200 was about 83%, and the water content was very low (0.2 wt.%). Figure 3 shows RI chromatograms of fresh and recovered PEG200 from SEC analysis. Table 1 shows the ratio of each peak area to the total peak area in the RI chromatogram and the weight-average molecular weight (Mw) of each peak. The retention time of peak 3 in the recovered PEG200 was almost the same as that of fresh PEG200, and the ratio of peak area 3 to the total peak area was 75%. Two other peaks in the chromatogram of the recovered PEG200 had molecular weights of approximately 910 and 470. The recovered PEG200 was expected to include soluble lignin, soluble lignin derivatives, sugars, and sugar derivatives derived from the wood. The two additional peaks may have indicated the presence of these soluble compounds.

Table 1. The Ratio of Each Peak Area and the Weight-average Molecular Weight (Mw) in the Chromatogram of Fresh and Recovered PEG200

Type of PEG200	Value	Peak Area in the Chromatogram		
		Area 1	Area 2	Area 3
Fresh	%Area [a]	0%	5.1%	94.9%
	Mw	-	451	260
Recovered	%Area [a]	7.5%	17.5%	75.0%
	Mw	908	474	251

[a] The %area was calculated from the ratio of each peak area to total peak area in the RI chromatogram shown in Fig. 3.

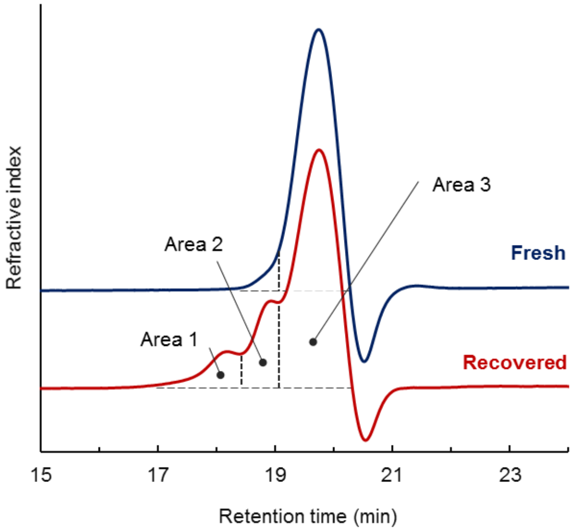

Fig. 3. RI chromatograms of fresh and recovered PEG200 by SEC analysis

Acidic solvolysis with the recovered PEG200

Acidic solvolysis of softwood with the recovered PEG200 was performed with 0.3 wt.% sulfuric acid at 140 °C for 0.5 to 3 h. The dashed lines in Fig. 2 show the yield of solvolysis residue and glycol lignin. The yield of residue in the recovered PEG200 gradually decreased after 1 h and then slightly decreased after 2 h. Thus, the recovered PEG200 worked as a solvolysis reagent of softwood.

In the reactions with recovered PEG200, the yield of glycol lignin increased sequentially (Fig. 2). The 2-h reaction gave the highest yield of glycol lignin, which was 42.2 wt.%. The yield of glycol lignin produced from recovered PEG200 were approximately 2 to 7 wt.% higher than the glycol lignin produced using fresh PEG200. Because the recovered PEG200 contained soluble compounds, such as soluble lignin, the yield of glycol lignin might have been increased by reactions with soluble compounds. The UV method indicated that the amount of soluble lignin in the recovered PEG200 was 0.57 wt.% of the solution. This study revealed for the first time that recovered PEG200 worked as a solvolysis medium and produced glycol lignin.

Lignin Content and Phenolic Hydroxyl Group Content in the Glycol Lignin

The lignin content of glycol lignin was determined using the UV method (Table 2). In the fresh PEG200 series, lignin content in the glycol lignin increased with reaction time. The lignin content was 81.8% after 2 h and increased to 94.5% after 3 h. When the reactions were performed with recovered PEG200, the lignin contents in the glycol lignin increased with reaction times up to 2 h. The lignin contents of the glycol lignin after reaction times of 2 h and 3 h were almost the same (approximately 86%).

The phenolic hydroxyl group content of the glycol lignin was determined by the ionization difference method and was calculated on the basis of 100 C9 units (M_w 180) (Table 2). In both the fresh and the recovered PEG200 series, the phenolic hydroxyl group contents showed almost the same values. The phenolic hydroxyl group contents of the glycol lignin were calculated as 28 to 29 per 100 C9 units after 2 h of solvolysis with fresh and recovered PEG200, which was higher than the values for typical milled wood lignin and soda-anthraquinone lignin prepared from Japanese cedar (16.9 and 19.1, respectively (Ikeda and Magara 2015)).

Table 2. Lignin Content and Phenolic Hydroxyl Group Content in Glycol Lignin from Solvolysis with Fresh and Recovered PEG200

Type of PEG200	Value	Reaction Time			
		0.5 h	1 h	2 h	3 h
Fresh	Lignin content (%) [a]	69.9 ±0.91*	74.6 ±0.49	81.8 ±0.86	94.5 ±1.37
	Phenolic OH content [b] (based on 100 C9 units)	27.2 ±2.01	29.8 ±1.45	29.2 ±0.48	26.1 ±1.17
Recovered	Lignin content (%) [a]	n.d.	77.2 ±0.43	85.4 ±2.54	86.0 ±0.04
	Phenolic OH content [b] (based on 100 C9 units)	n.d.	30.0 ±0.99	28.3 ±0.30	27.9 ±1.26

[a] Lignin content is shown as a %yield of the glycol lignin.

[b] Phenolic hydroxyl group content is shown as a number based on 100 C9 units (Mw 180).

* The plus-minus sign (±) shows the variation from the average (n = 2).

n.d., the values could not be measured because of poor solubility in the analytical solvent (dioxane/0.2 N NaOH (v/v = 1:1)).

Molecular Weight of the Glycol Lignin

Figure 4 shows SEC-UV chromatograms of glycol lignin from solvolysis reactions with fresh and recovered PEG200 from 0.5 to 3 h. Table 3 shows the weight-average molecular weights and the molecular weight distributions calculated from these chromatograms. In the fresh PEG200 series, the molecular weights of the glycol lignin gradually decreased with reaction time. The molecular weight was approximately 9800 after 0.5 h and approximately 4400 after 2 h (Table 3).

During the initial stages of the reaction in the recovered PEG200 system (0.5 and 1 h), the glycol lignin showed quite high molecular weights (37000 and 14100, respectively). The chromatograms had broad peaks in the high-molecular-weight region after reaction times of 0.5 and 1.0 h (Fig. 4). However, the broad peaks disappeared when the reaction time was prolonged. The molecular weight of the glycol lignin after 2.0 h of reaction was approximately 4500, which was almost the same as for the corresponding reaction using fresh PEG200 (Table 3).

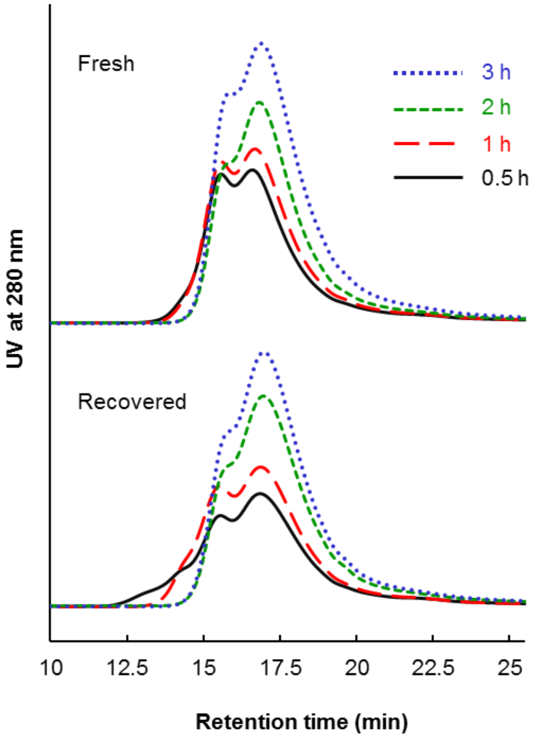

Fig. 4. SEC-UV chromatograms of glycol lignin from solvolysis with fresh and recovered PEG200

Table 3. Molecular Weights (M_w) and Molecular Weight Distributions (M_w/M_n) of Glycol Lignin from Solvolysis with Fresh and Recovered PEG200

Type of PEG200	Value	Reaction Time			
		0.5 h	1 h	2 h	3 h
Fresh	M_w	9781 ± 511*	6848 ± 701	4442 ± 5	4072 ± 240
	M_w/M_n	7.6	5.9	4.4	4.4
Recovered	M_w	36717 ± 389	14096 ± 3116	4524 ± 398	4149 ± 37
	M_w/M_n	32.7	13.2	4.9	4.6

* The plus-minus sign (±) shows the variation from the average (n = 2).

Thermomechanical Analysis of the Glycol Lignin

The thermophysical properties of glycol lignin were studied using TMA, where changes in the volume of lignin with rising temperature were detected by changes in the position of a probe. Two clear phase-transition points on the TMA curve were assigned to the glass transition point (T_g) and the thermal softening point (T_s) (Kubo *et al*. 1996).

Figure 5 shows TMA curves for glycol lignin in the fresh PEG200 series (0.5 to 3 h). The TMA curve for glycol lignin produced after 0.5 h showed that a remarkable decrease in volume began at 116.1 °C, followed by a slight increase at 142.5 °C. The decrease in volume was attributable to the glass transition, and a final increase in the volume was attributed to swelling and foaming solids (Kubo *et al*. 1996). The TMA curves of glycol lignin produced after 1 and 3 h also exhibited only one phase transition, *i.e.*, T_g, at 122.3 °C and 149.2 °C, respectively. In contrast, the glycol lignin produced after 2 h of reaction showed two points of inflection when the volume decreased. The first of these was assigned to the T_g, which was 132.6 °C. The second was assigned to the thermal softening point (T_s), which was 181.2 °C.

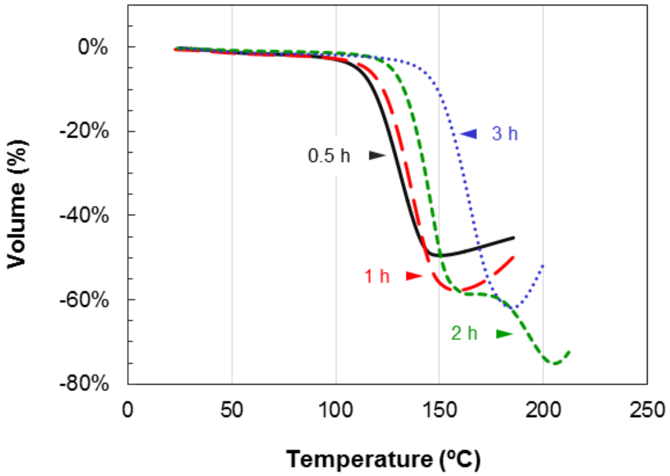

Fig. 5. TMA curves of glycol lignin from solvolysis with fresh PEG200

In the fresh PEG200 series, only the glycol lignin produced after 2 h exhibited a T_s in the TMA curve. The thermal fusibility of glycol lignin has been attributed to the PEG moiety being substituted for the hydroxyl group of lignin side chains (Kubo *et al*. 2007; Lin *et al*. 2012). It is thought that when glycol lignin is substituted by a greater amount of PEG, it exhibits better thermal fusibility. The lignin content of the glycol lignin indicates the content of components other than lignin in the glycol lignin, such as PEG. The lignin content of the glycol lignin was 81.8% after 2 h (Table 2). The glycol lignin produced after 2 h appeared to be substituted with enough of the PEG moiety to give it thermal fusibility. After 0.5 and 1.0 h, the solvolysis of softwood was still in its initial stages, thus the amount of introduced PEG moiety might have been insufficient to confer thermal fusibility. Although the lignin contents of the glycol lignin produced after 0.5 and 1 h of reaction were lower (69.9% and 74.6%, respectively) than that produced after 2 h, in the initial stages, the glycol lignin contained components other than the introduced PEG moiety. Decomposition products derived from hemicelluloses might be candidate substances. However, the lignin content of the glycol lignin was very high (94.5%) after 3 h. This data suggested that the content of introduced PEG moiety was very low in the glycol lignin produced after 3 h. It appears that when the reaction time was prolonged to 3 h, the introduced PEG moiety was partially cleaved, and the thermal properties of the resultant glycol lignin were thus changed.

Figure 6 shows TMA curves of glycol lignin in the recovered PEG200 series (0.5 to 3 h of reaction). Surprisingly, all of the TMA curves displayed two inflection points. The first transition points (T_g) were 122.1, 129.0, 134.2, and 133.7 °C after 0.5, 1, 2, and 3 h, respectively. The T_g of the glycol lignin produced after 2 h was almost the same as that of the glycol lignin produced after 2 h with fresh PEG200 (132.6 °C). The second transition points ranged from 333.1 °C to 342.3 °C, which were much higher than the glycol lignin produced after 2 h with fresh PEG200 (181.2 °C). These results suggested that glycol lignin from the recovered PEG200 system had a higher thermostability.

All glycol lignin samples in the recovered PEG200 series had two transition points, although they had different lignin contents and molecular weights. It was considered that the thermophysical properties of the glycol lignin were influenced by the compounds in the recovered PEG200, such as soluble lignin, soluble lignin derivatives, sugars, and sugar derivatives derived from the wood. The effect of each component will be determined in a future investigation.

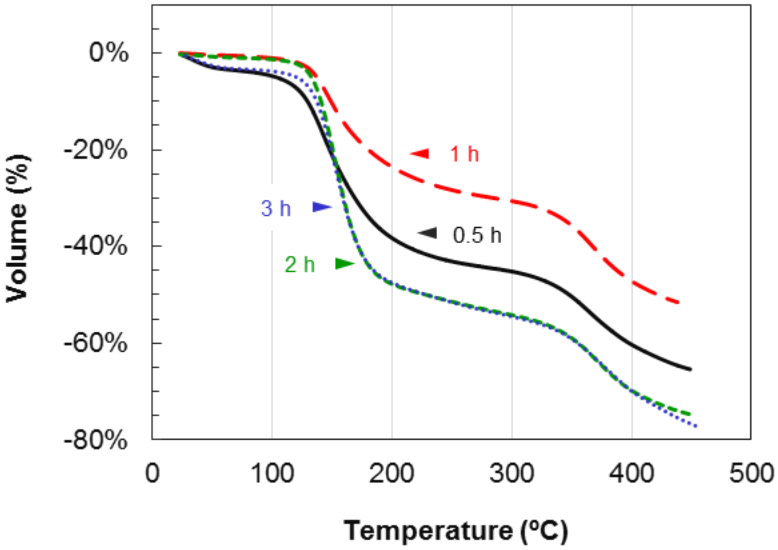

Fig. 6. TMA curves of glycol lignin from solvolysis with recovered PEG200

CONCLUSIONS

1. This study revealed for the first time that recovered PEG worked in the acidic solvolysis of softwood, producing an appropriate amount of glycol lignin (the highest yield; 42.2 wt.%). PEG200 was recovered by removing water by evaporation from the supernatant after glycol lignin production.
2. The thermal properties of the glycol lignin from the recovered PEG200 system were largely different from those of the glycol lignin from the fresh PEG200 system. TMA results indicated that glycol lignin from the recovered PEG200 system had a higher thermostability than that from the fresh PEG200 system.

ACKNOWLEDGMENTS

This work was supported by the following projects: the Rural Biofuel Research Project through a grant from the Ministry of Agriculture, Forestry and Fisheries of Japan, the SIP-Lignin project, Technologies for creating next-generation agriculture forestry and fisheries Cross-ministerial Strategic Innovation Promotion Program (SIP), and the Council for Science Technology and Innovation (CSTI).

REFERENCES CITED

Aronovsky, S. I., and Gortner, R. A. (1936). "The cooking process, IX, pulping wood with alcohols and other organic reagents," *Ind. Eng. Chem.* 28(11), 1270-1276. DOI: 10.1021/ie50323a009

Chi, C., Zhang, Z., Chang, H.-m., and Jameel, H. (2009). "Determination of furfural and hydroxymethylfurfural formed from biomass under acidic conditions," *J. Wood Chem. Technol*. 29(4), 265-276. DOI: 10.1080/02773810903096025

Espinoza-Acosta, J. L., Torres-Chávez, P. I., Carvajal-Millán, E., Ramírez-Wong, B., Bello-Pérez, L. A., Montaño-Leyva, B. (2014). "Ionic liquids and organic solvents for recovering lignin from lignocellulosic biomass," *BioResources* 9(2), 3660-3687. DOI: 10.15376/biores.9.2.3660-3687

Funaoka, M., and Abe, I. (1989). "Rapid separation of wood into carbohydrate and lignin with concentrated acid-phenol system," *TAPPI J*. 72(8), 145-149.

Gast, D., and Puls, J. (1985). "Improvement of the ethylene glycol water system for the component separation of lignocelluloses," in: *Energy from Biomass*, Palz, W. (ed.), Elsevier, London, UK, pp. 949-951.

Ikeda, T., and Magara, K. (2015). "Chemical properties of softwood soda-anthraquinone lignin," *J. Wood Chem. Technol*. 35(3), 167-177. DOI: 10.1080/02773813.2014.905605

Johansson, A., Aaltonen, O., and Ylinen, P. (1987). "Organosolv pulping—Methods and pulp properties," *Biomass* 13(1), 45-65. DOI: 10.1016/0144-4565(87)90071-0

Kajimoto, J., Sano, Y., Widodo, W. E., Kishimoto, T., and Uraki, Y. (2000). "HBS pulping (1)—Pulping of softwood," *Japan TAPPI* 54(9), 1252-1259. DOI: 10.2524/jtappij.54.1252

Kishimoto, T., and Sano, Y. (2003). "Delignification mechanism during high-boiling solvent pulping. IV. Effect of a reducing sugar on the degradation of guaiacylglycerol-beta-guaiacyl ether," *J. Wood Chem. Technol*. 23(3–4), 233-248. DOI: 10.1081/WCT-120026931

Kleinert, T. N. (1974). "Organosolv pulping with aqueous alcohol," *TAPPI* 57(8), 99-102.

Kubo, S., Uraki, Y., and Sano, Y. (1996). "Thermomechanical analysis of isolated lignins," *Holzforschung* 50(2), 144-150. DOI: 10.1515/hfsg.1996.50.2.144

Kubo, S., Ishikawa, N., Uraki, Y., and Sano, Y. (1997). "Preparation of lignin fibers from softwood acetic acid lignin: Relationship between fusibility and the chemical structure of lignin," *Mokuzai Gakkaishi* 43(8), 655-662.

Kubo, S., Yamada, T., Hashida, K., and Ono, H. (2007). "Grafting of ethylene glycol chains in lignin during the solvolysis for biomass conversion using ethylene carbonate/ethylene glycol system," *Chem. Lett.* 36(4), 502-503. DOI: 10.1246/cl.2007.502

Li, Y. Z., Jia, H. Z., Ruxianguli, R., Yin, H. Q., and Zhang, Q. S. (2015). "Extraction of lignin from wheat straw by catalysts in 1,4-butanediol medium under atmospheric pressure," *BioResources* 10(1), 1085-1098. DOI: 10.15376/biores.10.1.1085-1098

Lin, J., Kubo, S., Yamada, T., Koda, K., and Uraki, Y. (2012). "Chemical thermostabilization for the preparation of carbon fibers from softwood lignin," *BioResources* 7(4), 5634-5646. DOI: 10.15376/biores.7.4.5634-5646

Lin, S. Y., and Dence, C. W. (1992). *Methods in Lignin Chemistry*, Springer-Verlag, New York, NY, USA.

Lora, J. H., and Aziz, S. (1985). "Organosolv pulping: A versatile approach to wood refining," *TAPPI J.* 68(8), 94-97.

Moghaddam, L., Zhang, Z., Wellard, R. M., Bartley, J. P., O'Hara, I. M., Doherty, W. O. S. (2014). "Characterisation of lignins isolated from sugarcane bagasse pretreated with acidified ethylene glycol and ionic liquids," *Biomass and Bioenergy*, 70, 498-512. DOI: 10.1016/j.biombioe.2014.07.030.

Muurinen, E. (2000). *Organosolv Pulping: A Review and Distribution Study Related to Peroxyacid Pulping*, Ph.D. Dissertation, University of Oulu, Oulu, Finland.

Nakano, J., Takatsuka, C., and Daima, H. (1976). "Studies on alkali-methanol cooking. (1). Behavior of dissolution of lignin and carbohydrate," *Japan TAPPI* 30(12), 650-655. DOI: 10.2524/jtappij.30.12_650

Nelson, P. J. (1977). "Pulping of wood with glycol solutions of salicylic acid derivatives," *Appita* 31(1), 29-32.

Pan, X. J., Sano, Y., and Ito, T. (1999). "Atmospheric acetic acid pulping of rice straw - II: Behavior of ash and silica in rice straw during atmospheric acetic acid pulping and bleaching," *Holzforschung* 53(1), 511-518. DOI: 10.1515/HF.1999.009

Sarkanen, K. V. (1980). "Acid-catalyzed delignification of lignocellulosics in organic solvents," in: *Progress in Biomass Conversion (Vol. 2)*, K. V. Sarkanen and D. A. Tillman (eds.), Academic Press, Cambridge, MA, USA, pp. 127-144.

Sun, Y., and Cheng, J. (2002). "Hydrolysis of lignocellulosic materials for ethanol production: A review," *Bioresour. Technol.* 83(1), 1-11. DOI: 10.1016/S0960-8524(01)00212-7

Takahashi, S., Hattori, M., Morimoto, M., Uraki, Y., and Yamada, T. (2014). "Performance of softwood soda-anthraquinone lignin as water-reducing chemical admixture in concrete," *J. Wood Chem. Technol.* 34(1), 31-38. DOI: 10.1080/02773813.2013.820322

Takahashi, S., Hosoya, S., Hattori, M., Morimoto, M., Uraki, Y., and Yamada, T. (2015). "Performance of softwood soda-anthraquinone lignin–polyethylene glycol derivatives as water-reducing admixture for concrete," *J. Wood Chem. Technol.* 35(5), 348-354. DOI: 10.1080/02773813.2014.968739

Thring, R. W., Chornet, E., Overend, R. P., and Heitz, M. (1989). "Production and hydrolytic depolymerization of ethylene glycol lignin," in: *Lignin Properties and Materials*, W. G. Glasser and S. Sarkanen, (eds.), American Chemical Society, Washington, DC, pp. 228-244.

Uraki, Y., Kubo, S., Nigo, N., Sano, Y., and Sasaya, T. (1995). “Preparation of carbon fibers from organosolv lignin obtained by aqueous acetic acid pulping,” *Holzforschung* 49(4), 343-350. DOI: 10.1515/hfsg.1995.49.4.343

Zhang, Z., O'Hara, I. M., and Doherty, W. O. S. (2013). “Pretreatment of sugarcane bagasse by acidified aqueous polyol solutions,” *Cellulose* 20, 3179-3190. DOI: 10. 1007/s10570-013-0068-3.

Article submitted: December 25, 2015; Peer review completed: February 27, 2016; Revised version received: March 9, 2016; Accepted: March 19, 2016; Published: March 31, 2016.
DOI: 10.15376/biores.11.2.4446-4458