Effects of Peracetic Acid and Hydrogen Peroxide Concentration on Kraft Lignin Degradation at Room Temperature

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Degradation characteristics of kraft lignin were investigated during peracetic acid (PAA) treatment at room temperature. PAA was prepared by direct mixing of acetic acid (AA) and hydrogen peroxide (HP) at different ratios. At a ratio of AA to HP of 1:1.5 (v/v), undissolved lignin content was the lowest (34.7%). Lignin-derived compounds that were produced from the initial lignin after PAA treatment were detected in the liquid fraction (EA extracts) in small quantities (< below 0.1% of initial lignin), while their species were different depending on mix ratio. It was found that degradation behavior depends on not only PAA, but also HP concentrations. Meanwhile, the lignin-derived products of EA extracts in liquid fractions showed decreased molecular weight and polydispersity compared with the initial lignin. As reaction severity increased, amounts of low-molecular weight lignin in liquid fractions increased. At room temperature, different lignin degradation behavior can be induced by controlling the mix ratio of AA and HP.

Keywords: Peracetic acid treatment; Lignin degradation; Room temperature solubilization; Molecular weight reduction; Kraft lignin-biorefinery

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INTRODUCTION

Lignin is a promising natural polymer with aromatic functionality, and thus has been introduced as a key source for alternatives to petroleum-based materials and chemicals (Stewart 2008; Naseem *et al.* 2016). However, it is necessary to develop efficient processes to make the lignin value-added products because lignin has drawbacks such as complexity and heterogeneity of structures (Vishtal and Kraslawski, 2011; Beckham *et al.* 2016). For those reasons it is important to find an effective method for making lignin structures more uniform to broaden its use.

Peracetic acid (PAA) is formed by synthesis of acetic acid (AA) and hydrogen peroxide (HP) with acid catalysts, and it has been widely used as a disinfectant and sanitizer in various industries such as food processing, pharmaceutical, medical application, as well as pulp & paper (Tero and Simo 2017). Since PAA is comprised of a peroxy group

(HOO-) acting as a powerful oxidizer, it has been newly applied in the field of biomass for selective removal of lignin from lignocellulosic materials. For example, PAA treatment improves the enzyme accessibility during the bioethanol production process, which can reduce the enzyme loading, and hydrolysis time (Wi *et al.* 2015; Lee *et al.* 2017). In addition, PAA has gained great attention as an alternative agent for chlorine-based chemicals because it has positive features such as antimicrobial activity, inexpensive capital cost, and non-toxicity (Mehmet 2004; Laura *et al.* 2018).

PAA has gained much attention toward bio-refinery lignin since it not only can remove the lignin from complex structure of biomass but also degrade or convert the macromolecular lignin into value-added chemicals as alternatives of petroleum-based chemicals (Ma *et al.* 2014). Previous studies have reported the positive effect of PAA in lignin depolymerization for producing valued-dicarboxylic acids and monomeric aromatic compounds that are derived from various lignin sources (Popova *et al.* 2014; Ma *et al.* 2016). In addition, lignin can be degraded and dissolved during the PAA treatment even at a low reaction temperature (Wi *et al.* 2015; Lee *et al.* 2017). Thus it may have advantages for producing valuable lignin chemicals.

Nevertheless, the commercial PAA used in the recent studies was provided by several manufacturers from various countries, and it shows different solution properties despite reportedly being the same concentration of PAA. Generally, a PAA formulation contains AA, HP, and water with different concentrations. Therefore, it is difficult to grasp which properties of PAA are advantageous for lignin degradation or depolymerization.

For better understanding of lignin degradation by PAA in the present work, the PAA solution was prepared with different concentration by direct mixing AA and HP at different ratios. And, in order to investigate how PAA concentration affect lignin degradation, PAA treatment was conducted at room temperature without heating.

EXPERIMENTAL

Materials

Hardwood kraft lignin (KL; Moorim P&P Co., Ulsan-si, South Korea) was used as the starting material. The chemical composition of the KL is described in Table 1. All chemical reagents were purchased from Sigma Aldrich Co. (South Korea) and used without further purification.

Table 1. Chemical Composition of Kraft Lignin

Chemical composition	KL
Total lignin content (%)	94.1 (± 0.61)
Klason lignin (%)	87.4 (± 0.93)
Acid soluble lignin (%)	6.7 (± 0.32)
Ash (%)	2.9 (± 0.13)
Carbohydrate (%)	1.9 (± 0.07)
M_w (Dalton)	2813
C (wt%)	59.7
H (wt%)	5.3
O[1] (wt%)	31.2
N (wt%)	0.4
S (wt%)	3.3

[1] calculated by difference (O = 100-(C+H+N+S))

Peracetic Acid Treatment

Peracetic acid preparation

Before PAA treatment, AA and HP were used to create a PAA solution to examine the effect of PAA concentration on KL degradation. AA (98%) and HP (30%) were mixed at different ratios (4:1, 1.5:1, 1:1, 1:1.5, and 1:4 (v/v)), and the mixed solvent was stabilized for 1 h. AA and HP (separately) without mixing were used as controls.

Titration of peracetic acid solution

The concentration of PAA and HP in prepared solutions was measured by titration with modification (Hach 2014; Solvay Chemicals 2014; Domínguez-Henao *et al*. 2018). First, 0.5 g of mixed solvent with AA and HP was weighed in a 250 mL Erlenmeyer flask, and 50 mL of 1 N ice-cold sulfuric acid was added to the flask with stirring. In addition, two drops of ferroin indicator were added to the solution. The solution was titrated with 0.1 N ceric sulfate ($Ce(SO_4)_2$) until the salmon color disappeared and a light blue color appeared. Next, 10 mL of 2.5 N potassium iodide (KI) was added, and this was titrated with 0.1 N sodium thiosulfate ($Na_2(SO_2)O_3$) until a light brown-yellow color appeared. The concentration of PAA and HP in the mixed solvent was calculated with Eqs. 1 through 6,

$$H_2O_2\ (\%) = \frac{V_1 \times N_1 \times meq\ H_2O_2 \times F \times 100}{m} \quad (1)$$

where V_1 is the volume of $Ce(SO_4)_2$ solution consumed for the H_2O_2 titration (mL), N_1 is the normality of $Ce(SO_4)_2$, and meq H_2O_2 is the milliequivalents of H_2O_2 divided by the number of electrons exchanged in the oxidation-reduction reaction divided by 1,000.

$$\frac{34\text{g/mol}}{2e^-(1000)} = 0.017\text{g}\ H_2O_2/\text{milliequivalent} \quad (2)$$

In addition, F is the dilution factor (= 1 for undiluted samples), and m is the amount of sample (g). If N_1 = 0.1 and F = 1, then

$$\%\mathbf{H_2O_2} = \frac{0.17 \times V_1}{m} \quad (3)$$

$$\%\text{PAA} = \frac{\boldsymbol{V_2 \times N_2 \times meqPAA \times F \times 100}}{\boldsymbol{m}} \quad (4)$$

where V_2 is the volume of $Na_2(SO_2)O_3$ solution consumed for the PAA titration (mL), N_2 is the normality of $Na_2(SO_2)O_3$, and *meq* PAA is the milliequivalents of PAA divided by

the number of electrons exchanged in the oxidation-reduction reaction divided by 1,000.

$$\frac{76\text{g/mol}}{2e^{-}(1000)} = 0.038\text{g PAA/milliequivalent} \quad (5)$$

Again, F is the dilution factor (= 1 for undiluted samples), and m is the amount of sample (g). If N_2 = 0.1 and F = 1,

$$\%\mathbf{PAA} = \frac{0.38 \times V_2}{m} \quad (6)$$

Peracetic acid treatment

For PAA treatment, KL (0.1 g) was placed in a glass bomb with 3 mL PAA solution (prepared in advance). The reaction was conducted in a dry block (MG-2200, EYELA, Tokyo, Japan) at room temperature (25 ± 1°C) for 1, 4, and 8 h. The solid samples were partially degraded after the reaction finished. The solid and liquid phases were separated by first diluting the PAA-treated samples with 10 times the amount of distilled water to adjust the pH of the solution for further experiments. Solid and liquid fractions were divided by centrifugation. Solid lignin was washed again using distilled water to completely remove the solvent. Dried-solid samples were obtained by lyophilization, and liquid samples were stored in a vial at 4 °C.

Analysis of Solid Fractions

Nitrobenzene oxidation (NBO)

NBO was performed to identify the oxidation products by cleavage of *β-O-4* linkages in solid fractions, as described by Iiyama and Wallis (1990). A total of 40 mg of each solid sample was placed in a 10 mL glass bomb with 4 mL of 2 M aqueous sodium hydroxide and 250 μL of nitrobenzene at 170 °C for 2 h. After the reaction, 20 μL of 3-ethoxy-4-hydroxybenzaldehyde (0.5 g dissolved in 10 mL of methanol) was added as an internal standard. The oxidized samples were extracted twice using 20 mL of dichloromethane (DCM), and 4 M HCl was added to the solution until the pH value fell below 2. The acidified sample was extracted twice again by diethyl ether, and then the filtrate was evaporated. For identifying the degradation products, extracted samples were silylated using 100 μL pyridine and 100 μL *N,O*-bis (trimethylsilyl) trifluoroacetamide (BSTFA) at 105 °C for 2 h. The silylated sample was analyzed using a gas chromatograph (Agilent 7890B) and mass selective detector (Agilent 5975A). Product separation was set at a split ratio of 1:20 using a DB-5 capillary column (60 m × 0.25 mm × 0.25 μm film thickness). Helium (99.9% purity) was used as a carrier gas. The injector and detector temperature were set at 200 °C and 250 °C, respectively. The oven temperature program consisted of 120 °C for 10 min, followed by heating at a rate of 10 °C/min to 280 °C, where the final temperature was maintained for 20 min.

Phosphorus-31 nuclear magnetic resonance (^{31}P-NMR)

The hydroxyl group contents in solid sample generated after PAA treatment was determined by conducting ^{31}P-NMR analysis in accordance with established methods (Argyropoulos 1994; Pu *et al.* 2011). A solvent solution of 1.6:1 (v/v) of pyridine to chloroform-d_3 was prepared. The solvent solution (1 mL) was used to prepare a mixture solution containing 4 mg of cyclohexanol (internal standard) and 3.6 mg of chromium acetylacetonate (relaxation regent). An accurately known amount (20 to 25 mg) of a dried solid lignin obtained after PAA treatment was introduced into a 4 mL vial with a magnetic

spin bar. The sample was dissolved in 400 μL of the solvent solution, and 150 μL of the mixture solution and was mixed for a few minutes (completely dissolved in mixture solution). Lastly, 70 μL of phosphorylating reagent (2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane) was added and transferred into a 5 mm NMR tube for subsequent NMR acquisition. ^{31}P-NMR spectra of the prepared samples was obtained using a NMR spectrometer (JEOL JNM-LA400 with LFG, JEOL, Tokyo, Japan).

Gel permeation chromatography (GPC)

GPC was performed to analyze the molecular weights (M_w) and polydispersity index (PDI, M_w/M_n) of KL-derived products in the solid fractions using a 1260 Infinity II refracting index detector (Agilent, Santa Clara, CA, USA). A portion of the solid products (2 to 3 mg) were dissolved in 2 mL of tetrahydrofuran (THF) as mobile phase (completely dissolved in THF). The THF solutes were introduced into GPC instrument equipped with a PLgel5 μm MIXED-C column (300 × 7.5 mm^2, Agilent). The rate of mobile phase (THF) flow was set at 1 mL/min. Several polystyrene standards were used to calibrate the molecular weight, and the range was from 266 to 60,000 Daltons. The injection volume was 20 μL.

Analysis of Liquid Fractions

Solvent extraction

Solvent extraction was performed using ethyl acetate (EA) as an organic solvent. Each liquid fraction (30 mL and 60 mL) of EA were poured into a 250 mL funnel, and the solution was mixed using a shaking extractor. The extraction step was repeated twice to sufficiently dissolve the lignin-derived compounds.

Gas chromatography-mass spectrometry (GC-MS)

Monomeric degradation products generated by PAA treatment were identified using the same instruments described in the NBO experiment. For analysis of the degradation products, the solutes dissolved in EA (after dryness) were silylated using 100 μL pyridine and 100 μL *N,O*-bis (trimethylsilyl) trifluoroacetamide (BSTFA) at 105 °C for 2 h. The product separation for degradation product analysis was at a split ratio of 1:15 using a DB-5 capillary column, and helium (99.9% purity) was used as a carrier gas. Inlet injector and flame ionization detector (FID) temperatures were set at 220 °C and 300 °C, respectively. The oven temperature program was consisted of 50 °C for 5 min, followed by heating at a rate of 3 °C/min to 300 °C, and the final temperature was maintained for 10 min. Mass data of degradation products were identified by NIST MS Search software (NIST/EPA/NIH Mass Spectral Database (NIST11)).

Ultraviolet (UV)-visible spectroscopy

Relative phenolic hydroxyl group contents of EA-soluble products was determined by UV-visible spectrophotometer (UV-1601PC, Shimadzu, Kyoto, Japan). This method is based on the difference in absorption at 200 to 300 nm between phenolic units of the solutes in EA. 100 μL of aliquot (dissolved in 10 mL of EA) of each sample were added to 2900 μL of EA in a quartz cell. Detection wavelength ranges were set from 200 to 500 nm. EA was used as reference in order to obtain the baseline.

Gel permeation chromatography (GPC)

The molecular weights and polydispersity index (PDI) of the lignin-derived

compounds extracted by EA were determined by GPC using a 1260 Infinity II refracting index detector (Agilent). The solutes (2 to 3 mg) were purged by nitrogen gas to remove the solvent and were dissolved in THF as mobile phase. The sample was introduced into GPC instrument equipped with a PLgel5 μm MIXED-C column (300 × 7.5 mm^2, VARIAN). The rate of mobile phase (THF) flow was set at 1 mL/min. Several polystyrene standards were used to calibrate the molecular weight, and the range was from 266 to 60,000 Daltons. The injection volume was 20 μL.

RESULTS AND DISCUSSION

Concentration of PAA Solution Depending on the Mix Ratio

Commercial PAA is generally comprised of AA, HP, PAA, and water. In addition, catalysts such as sulfuric acid are commonly added to the solution to facilitate reaching equilibrium (Zhao *et al*. 2008). In this study, AA and HP were separately used to understand how the degradation behavior of lignin depends on the concentration of PAA solutions without a catalyst.

AA and HP were mixed according to various solvent mix ratios (4:1, 1.5:1, 1:1, 1:1.5, and 1:4, v/v), which were used to degrade KL at room temperature. The concentrations of PAA and HP were determined by titration method. Table 2 shows how the concentration depends on the mix ratio. The concentration of HP in the solution increased with increasing HP input amount; however, the PAA concentration showed a lower increase rate than the HP concentration. The highest concentration of PAA was 3.0% at 1:4 (v/v), while that of the HP was 20.1%.

Table 2. PAA and HP Concentrations depending on the Solvent Mix Ratio

Mix ratio (v/v)	Concentration (%)	
AA:HP[1]	PAA	HP
AA	-	-
4:1	1.5	5.8
1.5:1	1.5	12.6
1:1	1.5	15.0
1:1.5	2.3	15.6
1:4	3.0	20.1
HP	-	30

[1] mix ratio (v/v) of acetic acid and hydrogen peroxide

Generally, the concentrations of commercial PAA provided by global corporations are 20 to 40%. Added acids such as sulfuric and formic acid can provide higher concentration of PAA. However, the PAA solutions used in this study were prepared without any catalyst and so the concentration was lower than those of PAA solutions described in other studies (Sun *et al.* 2000; Barros *et al.* 2010; Ma *et al.* 2016).

Solid Content after PAA Treatment

PAA is known as a powerful oxidizing agent, and it has been applied to degrade and depolymerize lignin macromolecules under various treatment conditions. Particularly, PAA can degrade and depolymerize lignin at a relatively low temperature, compared to most thermal oxidation techniques.

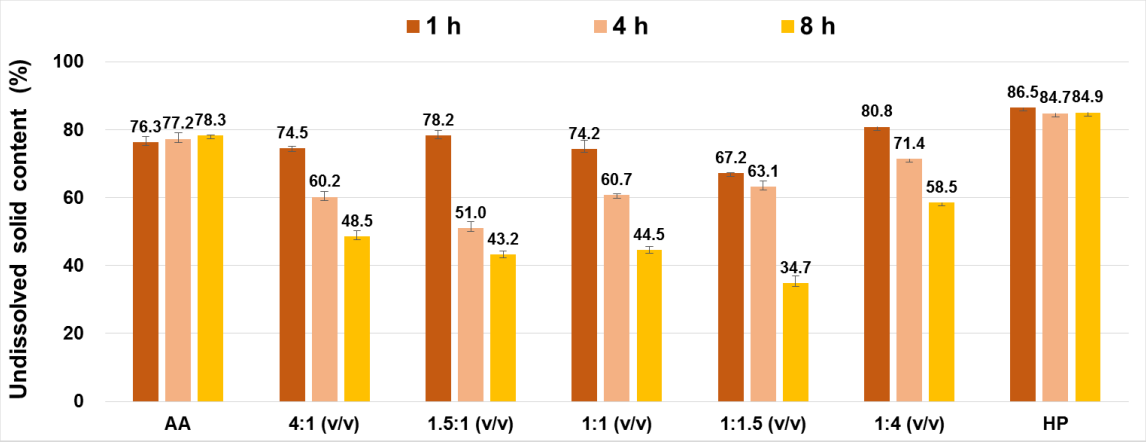

Fig. 1. Undissolved solid content (%) after the PAA treatment of KL

This study used kraft lignin as starting material to understand the degradation behavior by PAA, depending on the concentration of PAA at room temperature. Even at a low reaction temperature (25 °C), KL was partially dissolved in PAA. As shown in Fig. 1, undissolved solid content (%) of the KL by PAA decreased as the reaction time increased except for at 1:4 (v/v) mix ratio of AA to HP. Among solvent mix ratios, the 1:1.5 (v/v) showed the strongest dissolving power and the content was 34.7%. In addition, more than half of the initial lignin content was reduced in the 8 h reaction using PAA except for 1:4 (v/v). Based on the result of PAA solution concentrations, all solutions of AA and HP formed PAA, and concentrations of PAA and HP were the highest at 1:4 (v/v). However, the lowest solid content was observed at 1:1.5 (v/v). These results demonstrated that not only PAA concentration affects for lignin degradation at room temperature; in other words, both PAA and HP concentrations can be involved in KL degradation.

Additional experiments were conducted to compare degradation behavior when using AA or HP as controls, respectively. AA and HP also partially dissolved KL at room temperature. However, the undissolved solid content did not show a large difference as the reaction time increased, which means that the formation of PAA is a crucial factor in lignin degradation. Furthermore, acidity of the solution also can affect the lignin degradation. The HP solution had lower acidity than other solutions, resulting in the highest undissolved solids content.

Analysis of Solid Fractions

Nitrobenzene oxidation products

PAA can degrade KL into low molecular weight products. These degraded compounds are dissolved in liquid fractions. However, a large amount of solids remained until after 8 h of reaction. To compare the degradation degree of *β*-O-4 linkage of KL after PAA treatment, NBO were conducted.

The total amounts of NBO products from KL were determined to 572.0 μmol/g, as shown in the control of Fig. 2. The total amounts of S and G units from KL were 336.5 and 235.5 μmol/g respectively, and the S/G ratio was 1.43. Small quantities of H (p-hydroxylphenyl) units were also present in that lignin, and their amounts were contained in the total amounts of NBO products.

The total contents of NBO products in solid fractions after PAA treatment

decreased as the reaction time increased in all solutions with AA and HP. In particular, the lowest contents of NBO products were observed for the 1:1.5 (v/v) condition. This means that the mix ratio was most effective for lignin degradation in this study.

Meanwhile, AA and HP solutions were used to demonstrate the effect of PAA for lignin degradation. In the case of AA and HP without mixing, their total content did not show any large difference as the reaction time increased. In particular, HP without mixing showed the highest content of NBO products among all conditions. It was found that HP had no effect on lignin degradation at room temperature compared to other conditions even then the reaction continued for 8 h. Therefore, the total amount of NBO products was similar to the initial KL.

Hydroxyl group contents

The concentrations of different hydroxyl groups were calculated in relation to the peak area of the derivative hydroxyl groups of the internal standard. The hydroxyl group contents of each solid fraction after PAA treatment are shown in Fig. 3. PAA oxidized the lignin and induced degradation, which was attributed to changes in functional groups.

The contents of aliphatic, phenolic, and carboxylic groups changed during PAA treatment. Phenolic-OH groups mostly tended to decrease as reaction time increased in most conditions. This was because formation of PAA accelerated the lignin oxidation by ring-cleavage as reaction time increased. PAA has a powerful ability to attack aromatic nuclei, thus consequently, resulting in ring-opened carboxylic compounds with different molecular weight (Sakai and Kondo 1972). Accordingly, KL showed a proportional increase of carboxylic-OH groups when the mixed solutions were used.

Consequently, cleaved compounds became dissolved in the liquid fraction, while undegraded lignin remained in solid form even after PAA treatment.

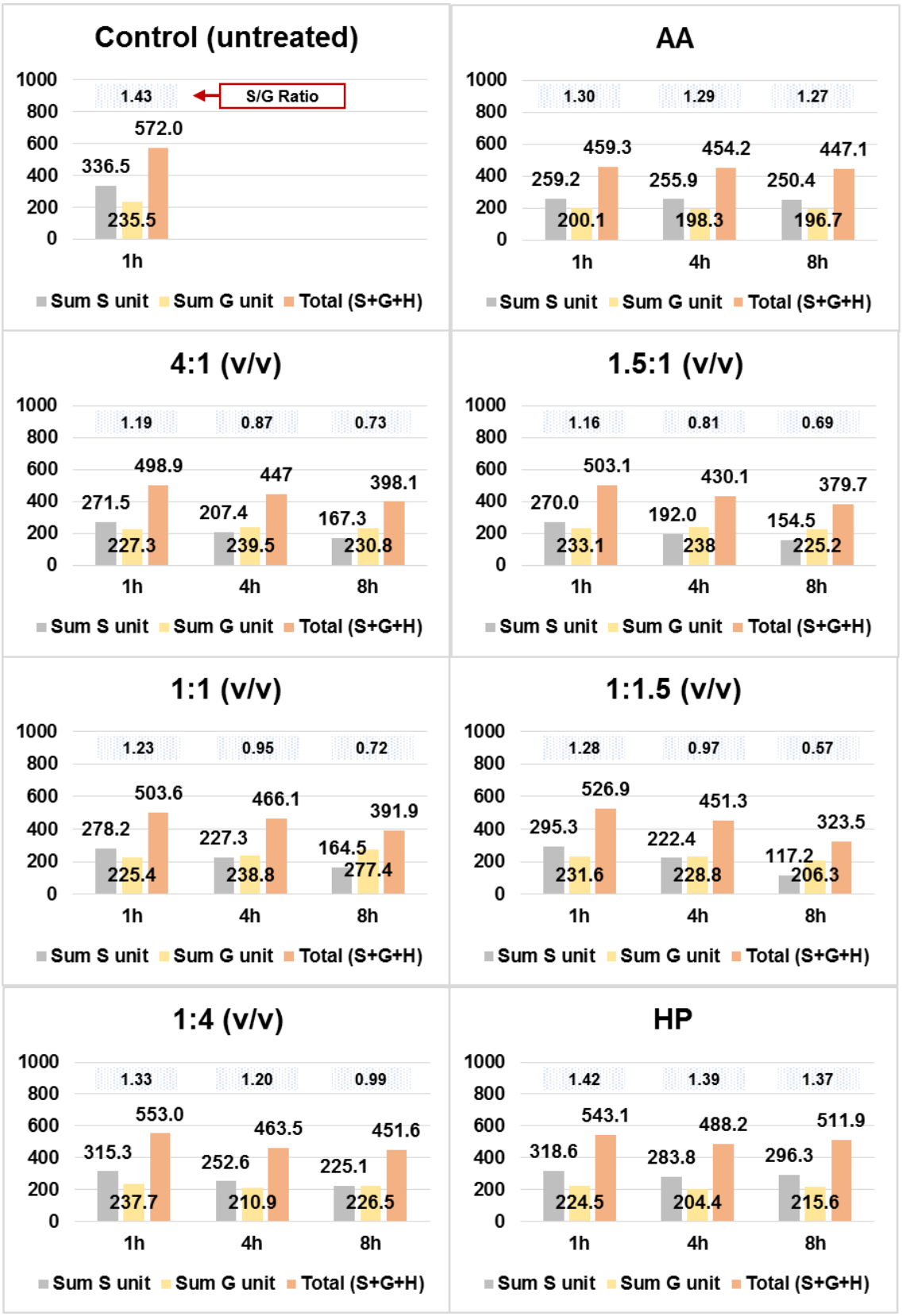

Fig. 2. Nitrobenzene oxidation products (μmol/g) in the solid fraction from KL with PAA treatment

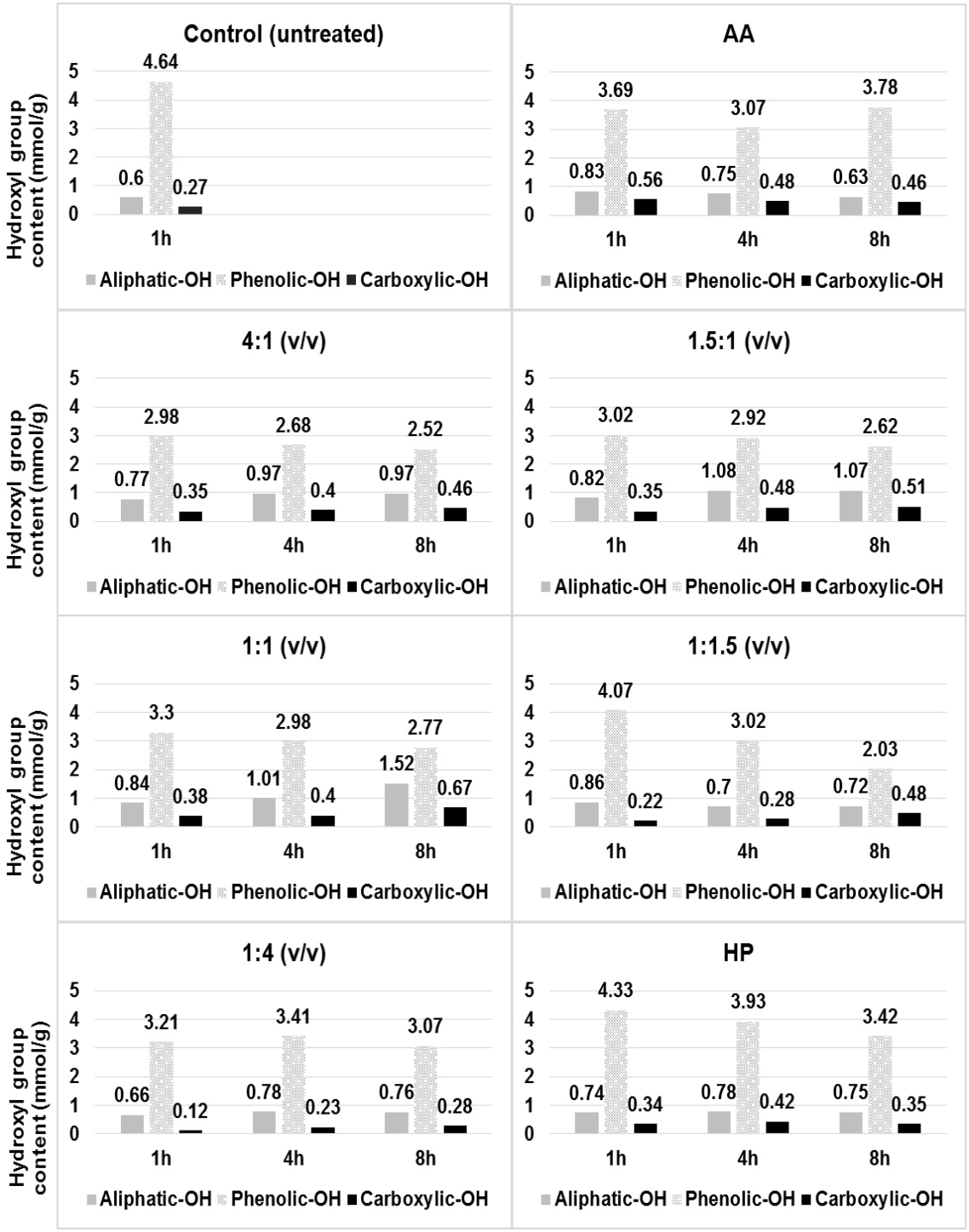

Fig. 3. Hydroxyl group contents (mmol/g) in solid fractions of PAA-treated KL

Molecular weight distribution

The molecular weight distributions of solid fractions after PAA treatment varied according to the experimental conditions, as shown in Table 3. The initial KL showed an M_w of 2,813, and M_n of 970 Da. The polydispersity indexes (PDI) of KL were 2.90.

As listed in Table 3, the molecular weights of solid samples obtained after PAA treatment increased as the reaction time increased; the PDI of most samples also increased. After PAA treatment, the high molecular weight lignin remained in a solid state, while low molecular lignin fragments were generated and dissolved in the liquid fraction. In other words, the molecular weight of the remaining solid lignin increased as the oxidized low-molecular weight lignin were isolated. Meanwhile, the molecular weight of AA or HP-treated lignin did not show consistent tendency.

Table 3. Molecular Weights (Dalton) of the Lignin Products in the Solid Fractions from PAA-treated-Lignin

AA:HP ratio (v/v)	Reaction time								
	1 h			4 h			8 h		
	M_w	M_n	PDI	M_w	M_n	PDI	M_w	M_n	PDI
AA	3397	1243	2.73	3612	1273	2.84	3294	1217	2.71
4:1	2803	1148	2.44	3048	1167	2.61	3186	1200	2.66
1.5:1	2783	1106	2.52	2998	1103	2.72	3120	1147	2.72
1:1	2654	1128	2.35	2958	1121	2.64	3093	1112	2.78
1:1.5	2736	1092	2.51	2878	1022	2.82	3053	1055	2.89
1:4	2659	1063	2.50	2851	1123	2.54	3147	1214	2.59
HP	2695	1042	2.59	2751	1125	2.45	2721	1146	2.37
Control[2]	2813	970	2.90						

[1] mix ratio of acetic acid (AA) and hydrogen peroxide (HP)
[2] initial kraft lignin

Analysis of Liquid Fractions

Lignin-derived compounds distribution

PAA converted lignin into small fragments, which were dissolved in the liquid fraction. Generally, low molecular compounds are worthwhile value-added chemicals (such as vanillin and phenol derivatives) for further applications. Therefore, GC-MS was conducted to investigate the possibility of producing degraded compounds and comparing the compound distribution depending on the mix ratio.

As shown in Table 4, nine species of monomeric compounds were produced from PAA-treated KL. In this study, acetic acid was omitted from the table list because it is difficult to distinguish, as a reaction products form that as a co-solvent owing to the surplus existence of the liquid fractions. Meanwhile, lignin derived-compounds were divided into two groups: dicarboxylic acids (DCA) and aromatics (Ar). The aromatic compounds were mainly comprised of vanillic acid, syringic acid, and 1,4-dihydroxy-2,6-dimethoxybenzene. In addition, various types of DCAs were produced by the ring-opening of aromatic structures in lignin. Glycolic, maleic, and succinic acid were mainly generated as DCAs (Farrand and Johnson 1971; Linger *et al.* 2014; Ma *et al.* 2014). Interestingly, many kinds of DCAs were only produced at 1:1.5 (v/v). These results demonstrated that certain mix ratio of AA and HP induces the accelerated production of DCA compounds. Even though the concentration of PAA was highest at 1:4 (v/v), it was not clear whether the cleavage of aromatic rings had or had not occurred.

Table 4. Monomeric Compounds in EA Extracts of PAA-treated-KL detected by GC/MS

No.	RT[1]	Product	Group	Mix ratio (v/v)						
				AA	4:1	1.5:1	1:1	1:1.5	1:4	HP
1	16.08	glycolic acid	DCA		v	v	v	v	v	
2	22.78	maleic acid	DCA					v		
3	22.93	succinic acid	DCA					v		
4	23.29	methylsuccinic acid	DCA					v		
5	23.50	glyceric acid	DCA					v		
6	23.82	fumaric acid	DCA					v		
7	30.49	1,4-dihydroxy-2,6-dimethoxybenzene	Ar		v	v	v	v	v	
8	33.40	vanillic acid	Ar	v	v	v	v	v	v	
9	38.04	syringic acid	Ar	v	v	v	v	v	v	

[1] retention time
[2] dicarboxylic acid
[3] aromatic compound
[4] detected in GC-MS

The total contents of the lignin-derived compounds were calculated based on the contents of the internal standard. However, the highest contents as of lignin-derived compounds were below 0.08% of the initial KL. These results indicated that the degradation compounds from KL were mainly present as larger molecules rather than monomers in the liquid fractions and demonstrated that PAA oxidation had less of an effect on the production of monomeric compounds at room temperature (although lignin degradation occurred). Other previous studies reported that PAA can produce a much larger amounts of monomeric lignin compounds from corn-stove lignin treated with diluted acid. The highest yield of monomeric phenols from lignin was 22% after 60 min of PAA treatment at 60 °C. However, when the reaction was conducted at 30 °C, the monomeric phenol yield decreased to about 5% (Ma *et al.* 2016). This meant that the reaction temperature during PAA treatment was an important factor when producing lignin-derived monomeric compounds.

Phenolic hydroxyl group

Lignin is linked in a complicated manner to the C-O, C-H, and O-H bonds of hydroxyl and methyl groups. In particular, the hydroxyl group is an important functional group involved in lignin functionality. Therefore, the UV absorbance difference was observed to compare the relative content of the hydroxyl group in EA-soluble products.

Distinct regions in the UV spectra can be divided into two parts. First, absorbance peaks were observed at 270 to 280 nm, which is assigned to $n \rightarrow \pi^*$ electronic transitions. The symbol "n" refers to non-bonding electrons, which correspond to the lone electron pairs of the ether (-O-) bond and the hydroxyl (-OH) bond.

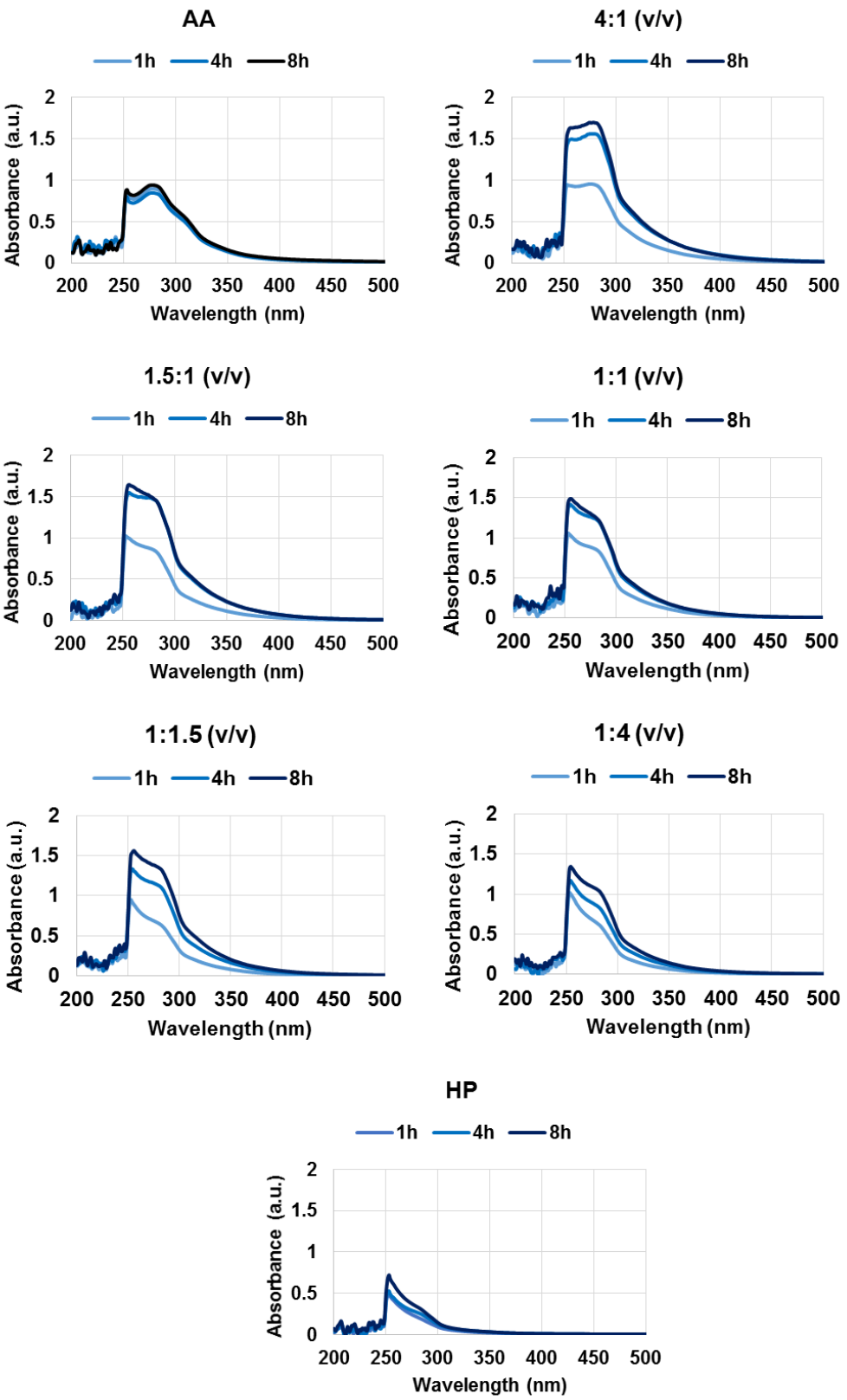

Fig. 4. UV Absorbance Differences between the EA Extracts depending on the AA and HP mix ratios (KL)

In addition, the strong peak at 270 nm was assigned to the π → π* electronic transition of aromatics (Yáñez *et al.* 2014; Song *et al.* 2015). These absorbance peaks were attributed to degraded products from the initial solid AL and KL. Meanwhile, those below 200 nm were regarded as noise peaks because these are irrelevant peaks in lignin structures. In the UV spectra of EA-soluble products generated after PAA treatment depending on the solvent mix ratio, the absorbance peaks at 270 to 280 nm show increasing tendencies as the reaction time increased as shown in Fig 4.

The absorbance differences were attributed to the relative content of the lignin-derived compounds dissolved in EA extracts of liquid fraction. Among the solvent mix conditions, the highest absorbance at 270 to 280 nm was observed at 4:1 (v/v). More aromatic compounds related to ether and hydroxyl bonds in lignin were found at 4:1 (v/v). Based on GC-MS results, aromatic lignin compounds were mostly detected as lignin-derived products at 4:1 (v/v) with KL, while dicarboxylic acids were produced at high HP concentrations. Dicarboxylic acids can be generated by the ring-opening of lignin compounds, and thus the absorbance peaks attributed to lignin structures were decreased.

Molecular weight distribution

The molecular weight distributions of EA extracts in liquid fractions from KL were observed after PAA treatment, and the results were described in Table 5.

In all conditions, the molecular weights of KL-derived compounds in the EA extracts decreased after PAA treatment, while the PDI of most samples also decreased. The M_w values of KL-derived compounds in the EA extracts were 829 to 1,204 Da. This means that PAA treatment is possible to generate lower molecular compounds than the initial lignin even at room temperature. According to the results of GC-MS, monomeric compounds were detected in very small amounts. However, low-molecular compounds in the liquid fractions showed narrower molecular distributions than the initial lignin, which may have improved lignin complexity and heterogeneity.

Table 5. Molecular Weights (Dalton) of the Lignin Products in the EA Extracts from PAA-treated-KL

	Reaction time								
AA:HP ratio (v/v)[1]	1 h			4 h			8 h		
	M_w	M_n	PDI	M_w	M_n	PDI	M_w	M_n	PDI
AA	898	586	1.53	867	560	1.55	896	585	1.53
4:1	1067	641	1.66	1204	708	1.70	1090	638	1.71
1.5:1	901	558	1.61	1028	618	1.66	1013	615	1.65
1:1	924	580	1.59	894	538	1.66	949	582	1.63
1:1.5	829	531	1.56	907	560	1.62	969	595	1.63
1:4	950	597	1.59	981	606	1.62	1006	633	1.60
HP	-[4]	-	-	-	-	-	-	-	-
Control[3]	2813	970	2.90						

[1] mixed ratio of acetic acid (AA) and hydrogen peroxide (HP)
[2] initial alkali lignin
[3] initial kraft lignin
[4] not detected

CONCLUSIONS

1. Kraft lignin (KL) was partially dissolved at room temperature using peracetic acid (PAA) solutions with different mix ratios. Although the PAA concentration was lower than that of commercial PAA, lignin degradation was even possible at room temperature.
2. KL showed the highest respective dissolution rates at 1:1.5 (v/v) condition. The solid lignin dissolution tended to increase as the hydrogen peroxide (HP) concentration was increased. However, at 1:4 (v/v), the dissolution rate decreased even though the PAA concentration was highest in that solution. Therefore, it was concluded that the concentrations of both PAA and HP (present in the PAA solutions) may simultaneously affect lignin degradation.
3. The molecular weight and polydispersity in the EA extracts of liquid fractions showed lower values than the initial KL, which meant that low-molecular weight products were produced from initial solid lignin, suggesting that it is possible to produce lignin that has a more uniform structure.

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