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Changes of major chemical components in larch wood through combined treatment of drying and heat treatment using superheated steam

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Abstract The effects of the combined treatment of drying and heat treatment using superheated steam (SHS) were studied relative to the changes of the major chemical components in larch wood. The green lumber was dried and heat-treated in SHS conditions of 250 °C and 0.5 MPa for 18 h, and the relative percentage contents of sugars, lignin, and extractives were investigated and compared with the relative percentage contents in the lumber heat-treated in hot air conditions of 250 °C and atmospheric pressure for 18 h. After both heat treatment methods, the relative percentage contents of xylan, mannan, galactan, and arabinan were greatly decreased, whereas that of the Klason lignin was increased, additionally that of glucan and extractives remained almost unchanged. Lignin may bind with furan compounds decomposed from hemicellulose following heat treatment, thus contributing to the increase in the apparent relative percentage contents of the Klason lignin. In addition, the condensate collected in the condenser after combined drying and heat treatment using SHS was investigated qualitatively and quantitatively by high-performance liquid chromatography (HPLC). A large amount of furfural and acetic acid decomposed from hemicellulose was detected and some sugar components composed of cellulose and hemicellulose were detected in the liquid condensate.

Keywords Combined treatment · Superheated steam · Wood component · Wood drying · Wood heat treatment

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Introduction

Wood heat treatment is a method of heating to temperatures of 160–260 °C that induces changes in the chemical composition of wood by thermal hydrolysis to improve the physico-mechanical properties and decay resistance of wood [1]. The heat-treated wood has some advantages, such as the improvement of dimensional stability with an increase of hydrophobicity, equalization of surface color, and increase of decay resistance. Because of these advantages, various heat treatment methods have been developed mainly in Europe, and the properties of wood heat-treated by each method have been investigated [2–4].

Wood heat treatment changes the chemical components of wood by degrading cell wall components or extractives. The chemical component changes from heat treatment depend on the time and temperature of the heat treatment, the species, and the type of heat treatment (heat transfer medium) [5–8]. In general, below 150 °C, the wood dries beginning with the loss of free water and finishing with bound water. At 160–260 °C, the main temperature range of

heat treatment, wood undergoes various chemical component changes. The chemical changes of wood at these temperatures are mainly due to auto-catalytic reactions of the cell wall constituents [9]. First, hemicellulose, which is the most sensitive to heat among the wood cell wall components, degrades by deacetylation, followed by depolymerization catalyzed by released acetic acid [10, 11]. Cellulose is less affected by the heat treatment, probably because of its crystalline nature [11]. Heat treatment also causes the cleavage of the β-O-4 linkage of lignin [12]. Extractives such as resin acids were disappeared from the wood at temperatures above 200 °C [13]. In addition, at above 260 °C, wood starts the carbonization with generating pyrolysis products, such as carbon dioxide [11].

Recently, the combined treatment of drying and heat treatment using superheated steam (SHS) for green wood has been studied. SHS, which is steam at a temperature above boiling point, has been used to dry wood, food, and sludge, etc [14]. The combined treatment of drying and heat treatment using SHS, which is called to "combined treatment", for green wood is the method that drying and heat treatment are carried out simultaneously using SHS at a high temperature and high pressure. Park et al. [15] carried out the combined treatment for green pitch pine using SHS at various temperatures and pressures on a lab scale, and determined the proper conditions for the temperature and pressure of SHS without the occurrence of drying checks. Because the combined treatment simultaneously carries out the two processes of drying and heat treatment in one reactor removed oxygen, it can decrease the time and energy required for the drying process and prevent fires.

This study investigated the changes of major chemical components in larch wood treated by combined treatment and compared them with those of wood treated by the conventional hot air heat treatment. In addition, the condensate collected in a condenser after the combined treatment was investigated qualitatively and quantitatively.

Materials and methods

Materials

Green larch (*Larix kaempferi*) lumber which was produced in Kangwon-do, Republic of Korea with a length of 2.2 m (longitudinal), a width of 150 mm (radial), and a thickness of 150 mm was prepared. Segments of 80 mm in length were removed from each end of the lumber to make the initial moisture content along the longitudinal direction uniform; pieces of 20 mm in length were cut from each end of the remaining lumber to evaluate the initial moisture content of the lumber; and the remaining lumber with the

length of 2 m was subjected to heat treatment. A sample with a thickness of 20 mm was used to evaluate the major components of the non-treated wood after evaluating the initial moisture content. The average initial moisture content of 20 pieces of lumber was 40.0% ($\pm$3.7). Ten pieces of lumber were used in each heat treatment method.

Heat treatment equipment

Hot air heat treatment for kiln-dried lumber and combined treatment for green lumber were carried out with the heat treatment equipment (Hanwoul Engineering Co., Gunpo-si, Republic of Korea) as shown in Fig. 1. The equipment was composed of a reactor, a condenser, a vacuum pump, and a water feed-tank. The cylindrical reactor with a diameter of 640 mm, a length of 640 mm, and a volume capacity of 0.7 m^3 has a ceramic heater at the inner surface to heat the air or steam in the reactor. The outer surface of the reactor is insulated with grass wool to minimize the loss of heat in the reactor. Three fixed temperature sensors (K-type thermocouple, Fluke, WA, USA) to measure the temperature of the air or steam in the reactor, three flexible temperature sensors to measure the temperature in the wood or on the wood surface, and one pressure sensor (PA21SR, Keller, NC, USA) to measure the pressure of the air or steam in the reactor are installed in the reactor. The measured values of the temperature and pressure are monitored in real time and recorded on the connected computer. In addition, three regulators are installed on the top of the reactor. Because all pipes connect the reactor to the condenser, all chemicals decomposed and water removed from the lumber are collected in the condenser. The vacuum pump is used to remove the air in the reactor before the beginning of the combined treatment, and the water feed-tank is used to inject distilled water into the reactor for generating SHS in the combined treatment.

Combined drying and heat treatment by SHS

In the combined treatment, SHS is generated in the reactor by boiling the injected distilled water [15]. The procedures for the combined treatment are as follows: after the reactor, with 10 pieces of stacked lumber, is made airtight, some distilled water is injected into the reactor. The amount of distilled water depends on a specific volume of SHS at the target temperature and target pressure and the volume capacity of the reactor. In this study, the target temperature of the SHS was set to 250 °C, the temperature of the lumber reached 220 °C at this SHS temperature, and the target pressure of the SHS was set to 0.5 MPa (absolute pressure). In this condition, the specific volume of SHS is 474 L/kg and the volume capacity of the reactor is 700 L. Therefore, the amount of distilled water to be injected into the reactor is
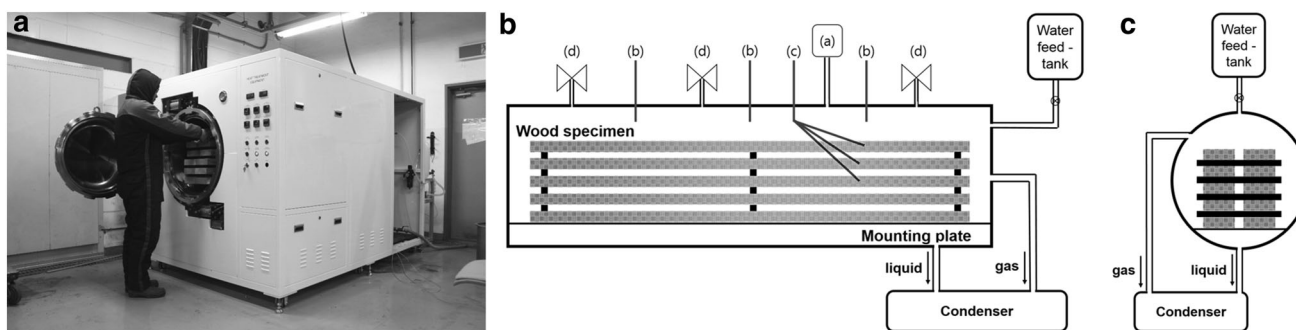
Fig. 1 Wood heat treatment equipment [19]. **A** Overall view of the equipment. **B** Side view of the reactor. *a* Pressure sensor for measuring steam pressure. *b* Temperature sensors for measuring steam temperature. *c* Temperature sensors for measuring wood temperature. *d* Pressure regulators. **C** Front view of the reactor

calculated as 1.5 kg. Nevertheless, to fill up the reactor with steam quickly at the beginning of the process, a larger amount was necessary. After injecting 3 kg of distilled water, the air in the reactor was removed. When the absolute pressure was dropped to below 0.01 MPa, the heater was operated to boil the water in the reactor. By evaporating the water in the reactor, the pressure in the reactor and the temperature of the steam were increased, and the reactor was then filled with SHS. The temperature of the SHS was maintained by the On/Off system of the heater, which was shut off when the temperature of the SHS reached the target temperature, and was the system re-operated when the temperature of the SHS dropped to below the target temperature. In addition, the pressure of the SHS was maintained while drawing off excess steam through regulators when the steam pressure reached the target pressure. The operation time of the heater was 18 h. The total oven dry weight of the lumber used in the combined treatment was estimated to be 81.0 kg.

Heat treatment by hot air after the conventional kiln drying

Because when green lumber was heat-treated by hot air at atmospheric pressure, some severe drying checks occurred in the wood, the lumber dried to approximately 12% of the moisture content was used in the conventional hot air heat treatment [15]. Therefore, 10 green larch lumber pieces were kiln-dried to 12% of the moisture content according to the FPL conventional kiln drying schedule and heat-treated by hot air of 250 °C with the equipment used in the combined treatment (Fig. 1). Unlike the combined treatment, the reactor was not made airtight. It was possible to exhaust the air in the reactor and the vapor removed from the lumber. The operation time of heater was 18 h. The total oven dry weight of the lumber used in the conventional hot air heat treatment was estimated to be 86.8 kg.

Analysis of major chemical components in larch lumber

The chemical composition of the lumber before both heat treatments was supposed to be same as that of the pieces of 20 mm in length to evaluate the initial moisture content of the lumber. The chemical composition of the lumber after both heat treatments was also supposed to be the same as that of the pieces of 20 mm in length cut from the center of the lumber along the longitudinal direction after the heat treatment. All pieces were milled to below 0.5 mm and used to estimate the changes of major chemical components before and after both heat treatment methods. When the milled samples were extracted with alcohol–benzene (1:2, v/v) solution, the amount of chemicals extracted from the solution was considered to be the amount of extractives of the larch lumber. The analytical procedure for estimating amount of Klason lignin, acid soluble lignin (ASL), and sugars was performed with reference to the previous studies [16–18]. The samples of alcohol–benzene-extracted solid residue (0.3 g) were swelled in 3 mL of 72% sulfuric acid at 30 °C for 1 h and later added to 84 mL distilled water for dilution (4% sulfuric acid). These samples were reacted in an autoclave at 121 °C for 1 h and were filtered using distilled water through glass filters (1G4, Iwaki, Japan). The residue on the filters was oven-dried and weighed for measuring Klason lignin [16]. To analyze chemical components of the residue after Klason lignin method, pyrolysis gas chromatography/spectrograph (pyrolysis-GC/MS) analysis was carried out. For pyrolysis-GC/MS analysis, 2 mg of sample was put into a quartz tube with a 2.6 µg of an internal standard (fluoranthene). Then, it was pyrolyzed using CDS Pyroprobe 5000 (CDS Analytical Inc., Oxford, PA, USA) at 600 °C for 20 s with a heating rate of 10 °C/ms in helium gas, which is a representative inert atmosphere. Released volatile products were analyzed by gas

chromatography (Agilent Technologies 7890A) with a mass selective detector (Agilent Technologies 5975A). ASL was analyzed by the absorbance of the filtrate which was determined using a UV–visible spectrophotometer (UV-1601 PC, Shimadzu, Japan). The filtrates were diluted with distilled water (1:14, v/v), and the absorbance was measured at 205 nm with a quartz cuvette [17]. The amount of sugars (glucan, xylan, mannan, galactan, and arabinan) in the filtrate after Klason lignin method was determined by a bio-liquid chromatograph (ICS-2500, Thermo Dionex, Palo Alto, CA, USA) outfitted with a CarboPac PA-1 column (250 × 4 mm, Dionex, Palo Alto, CA, USA) and a pulsed amperometry detector (HP 1100, Hewlett Packard, USA) [18]. The evaluation of the major chemical components in lumber was carried out along the procedures in Fig. 2.

Analysis of condensate collected in condenser after combined treatment using SHS

In the combined treatment, unlike the conventional hot air heat treatment, the chemicals decomposed from lumber by heat treatment can be recovered in the condenser. The condensate recovered in the condenser was classified as the gas condensate with excess steam drawn off through regulators during the combined treatment and the liquid condensate condensed in the reactor and recovered in the condenser through a discharge pipe after combined treatment. Because various effective components were included in the chemicals decomposed by heat treatment according to the previous studies, two types of condensates were analyzed qualitatively and quantitatively by high-performance liquid chromatography (HPLC). Dionex Ultimate 3000 (USA) was used in the HPLC analysis. RI (ERC, RefractoMAX520, Japan) was used as a detector, and an Aminex 87H column was used. The chemicals were analyzed in the HPLC oven, which was set to 40 °C with the rate of 0.5 ml/min for 90 min.
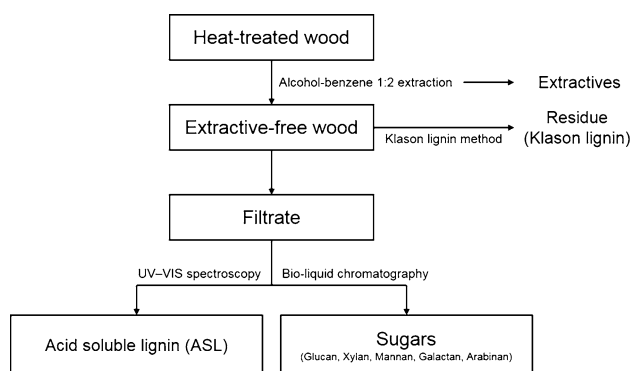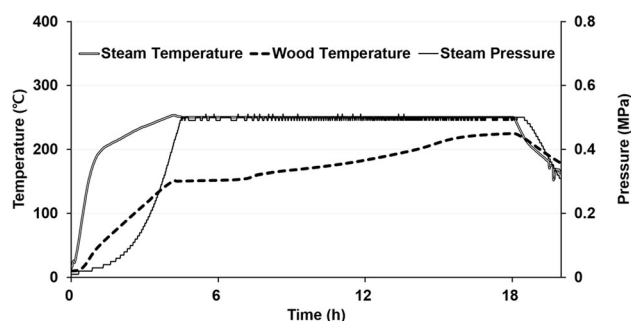
Results and discussion

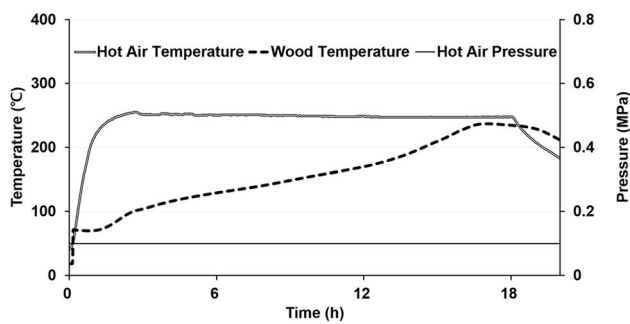### Combined drying and heat treatment by SHS (combined treatment)

Figure 3 shows changes of the temperature and pressure of SHS in the reactor and temperature of the lumber during the combined treatment for green larch lumber. At the beginning of the combined treatment, the temperature and pressure of the SHS and temperature of the lumber increased rapidly. When the temperature and pressure of the SHS reached the target temperature (250 °C) and the target pressure (0.5 MPa), the temperature of the lumber reached the saturation temperature (151.8 °C) of steam at 0.5 MPa and was maintained for 3 h. Park et al. [19] reported that the wood specimen was oven-dried when the temperature of the wood specimen was maintained constantly and re-increased. In other words, the water in the wood was completely removed for the duration of the constant temperature, and the temperature of the wood was re-increased by the heat energy which had been used to remove the water in the wood was used to heat the wood. The temperature of the lumber reached 220 °C at the end of the combined treatment. Considering that the temperature range inducing changes of the chemical components of wood by heat treatment is 160–260 °C, the lumber was heat-treated for 10 h. The final moisture content of the lumber after the combined treatment was almost 0%. The total oven dry weight of the treated lumber was 73.9 kg, and 7.1 kg of the mass was lost.

Heat treatment by hot air

Figure 4 shows the changes of the temperature and pressure of hot air in the reactor and temperature of the lumber during the hot air heat treatment for kiln-dried larch lumber. At the beginning of the hot air heat treatment, the temperature of the air and lumber was increased rapidly; however, the pressure of the air maintained and

Fig. 2 Procedures for analyzing major components in larch lumber

Fig. 3 Changes of temperature and pressure of SHS in the reactor and temperature in the lumber during combined treatment (target conditions of steam: 0.5 MPa and 250 °C)

Fig. 4 Changes of temperature and pressure of steam in the reactor and temperature in the wood specimen during the hot air heat treatment (target conditions of the hot air: atmospheric pressure and 250 °C)

atmospheric pressure. The temperature of the lumber almost increased to the maximum temperature (220 °C) without the duration of constant temperature in the hot air heat treatment, unlike the combined treatment. This is why the heat energy to remove water in the lumber in the hot air heat treatment for kiln-dried lumber was much smaller than that of the combined treatment for green lumber. The duration that the lumber was heat-treated, in which the temperature of the lumber was maintained above 160 °C, was 10 h. After the hot air heat treatment, the final moisture content of the lumber was 0%. The total oven dry weight of the treated lumber was 71.5 kg, and 15.3 kg of the mass was lost.

Analysis of major chemical components in larch lumber

Table 1 shows the relative percentage contents of the major chemical components in larch lumber before and after the combined treatment and hot air heat treatment. Although different heat transfer mediums were used in the two different heat treatment methods, the changes of the relative percentage contents of the major chemical components in

larch lumber before and after heat treatment were very similar. In both cases, after heat treatment, the relative percentage contents of the glucan and extractives were almost unchanged or slightly decreased. However, there was a large decrease in the relative percentage contents of the xylan, mannan, galactan, and arabinan, which are known for component of the hemicellulose and a large increase in the relative percentage contents of the Klason lignin compared with before heat treatment.

Hemicellulose is known as the most sensitive among the wood cell wall components. According to the previous studies, the degradation starts with deacetylation, and the released acetic acid acts as a depolymerization catalyst that further increases polysaccharide decomposition [10, 11]. Acid-catalyzed degradation leads to the formation of formaldehyde, furfural, and other aldehydes [20]. At the same time, hemicellulose undergoes dehydration reactions with the decrease of hydroxyl groups [21].

The relative percentage contents of Klason lignin were increased. However, the lignin determined by the Klason lignin method, which is a standard method to measure the amount of lignin, is probably not native lignin. According to the previous studies, polycondensation reactions with other cell wall components, resulting in further cross-linking, contribute to the increase in the apparent relative percentage contents of lignin [3, 9, 10, 22]. Based on the oven dry weight (81.0 kg) of the lumbers before the combined treatment and the relative percentage content of the Klason lignin (28.8%), the calculated weight of the Klason lignin of the lumbers before the combined treatment was 23.3 kg. On the other hand, the calculated weight of the Klason lignin of the lumbers after the combined treatment was 41.1 kg. Considering that the absolute amount of lignin would not increase following heat treatment, the increase in the amount of the Klason lignin may result from the increase in the amount of the residue, which was not dissolved by H_2SO_4 after the Klason lignin method due to cross-linking with lignin and some other chemicals

Table 1 Relative percentage contents of the major chemical components in larch lumber before and after combined treatment and hot air heat treatment

Major chemical components in larch lumber	Combined treatment		Hot air heat treatment	
	Before treatment (%)	After treatment (%)	Before treatment (%)	After treatment (%)
Glucan	37.5	34.9	33.8	34.3
Arabinan	2.1	0.0	2.7	0.2
Galactan	10.9	0.3	17.0	2.3
Xylan	3.6	1.2	3.5	1.2
Mannan	11.8	3.9	9.9	4.3
Klason lignin	28.8	55.6	28.4	54.1
Acid soluble lignin	0.4	0.3	0.3	0.4
Extractives	4.9	3.8	4.4	3.2

(possibly chemicals decomposed from hemicellulose). Figure 5 shows the chromatographs of pyrolysis/GC/MS for the Klason lignin before and after the combined treatment. Unlike the Klason lignin of non-treated larch lumber, some furan compounds such as 2-methylfuran, 2,5-dimethylfuran, 2-ethyl-5-methylfuran, and 5-methyl-2-furancarboxaldehyde were detected within 15 min of reaction time. These furan compounds seemed to be decomposed from hemicellulose following heat treatment and bound to lignin. The furan–lignin compounds were not dissolved by H_2SO_4 during the Klason lignin method and remained as a Klason lignin residue. Therefore, the presence of these furan–lignin compounds may be a reason why the amount of the Klason lignin appeared to be increased by heat treatment.

Cellulose was less affected by the heat treatment, probably because of its crystalline nature [11]. For this reason, there is almost no change in the relative percentage contents of glucan before and after the heat treatment.

There is also little change in the relative percentage of the extractives. However, because native extractives in the non-treated wood are very sensitive to heat, they were volatilized, degraded, and disappeared, and new compounds that can be extracted from wood appeared, resulting from the degradation of cell wall structural components [3, 13, 23].

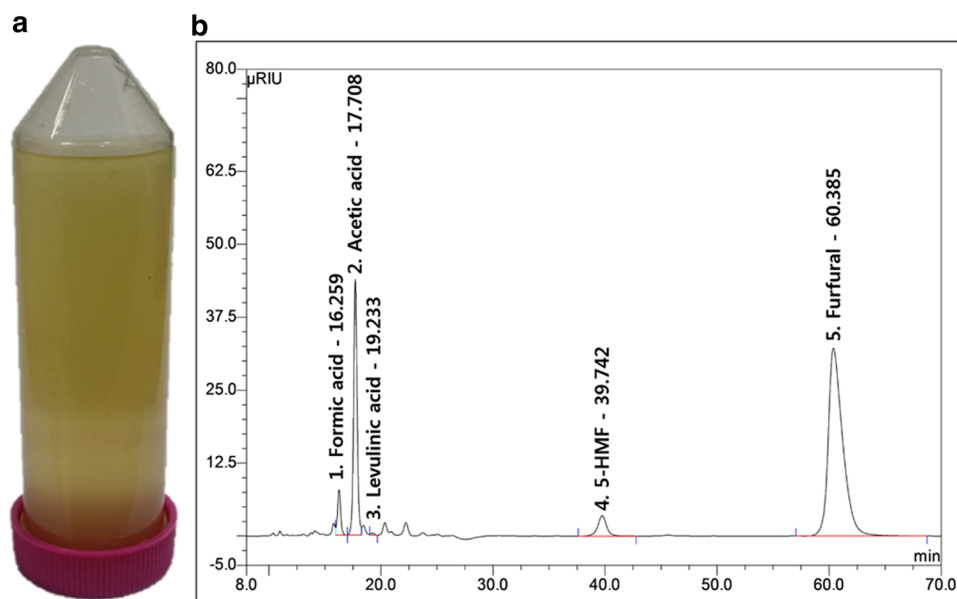## Analysis of condensates collected in condenser after combined treatment using SHS

Figure 6a shows the picture of the gas condensate, and Fig. 7a shows the picture of the liquid condensate collected in the condenser after the combined treatment using SHS. A total of 20.5 kg of yellow gas condensate and 4.9 kg of brown liquid condensate were collected in the condenser.

Figure 6b shows the results of the HPLC analysis for gas condensate. There are five peaks, which represent formic acid, acetic acid, levulinic acid, 5-hydroxymethylfurfural, and furfural in order from the left, respectively (Table 2). The amount of furfural was the highest in the liquid condensate, and a large amount of acetic acid degraded from hemicellulose was also included.

Fig. 5 Pyrolysis GC/MS chromatographs for Klason lignin. a Klason lignin of larch lumber before combined treatment. b Klason lignin of larch lumber after combined treatment
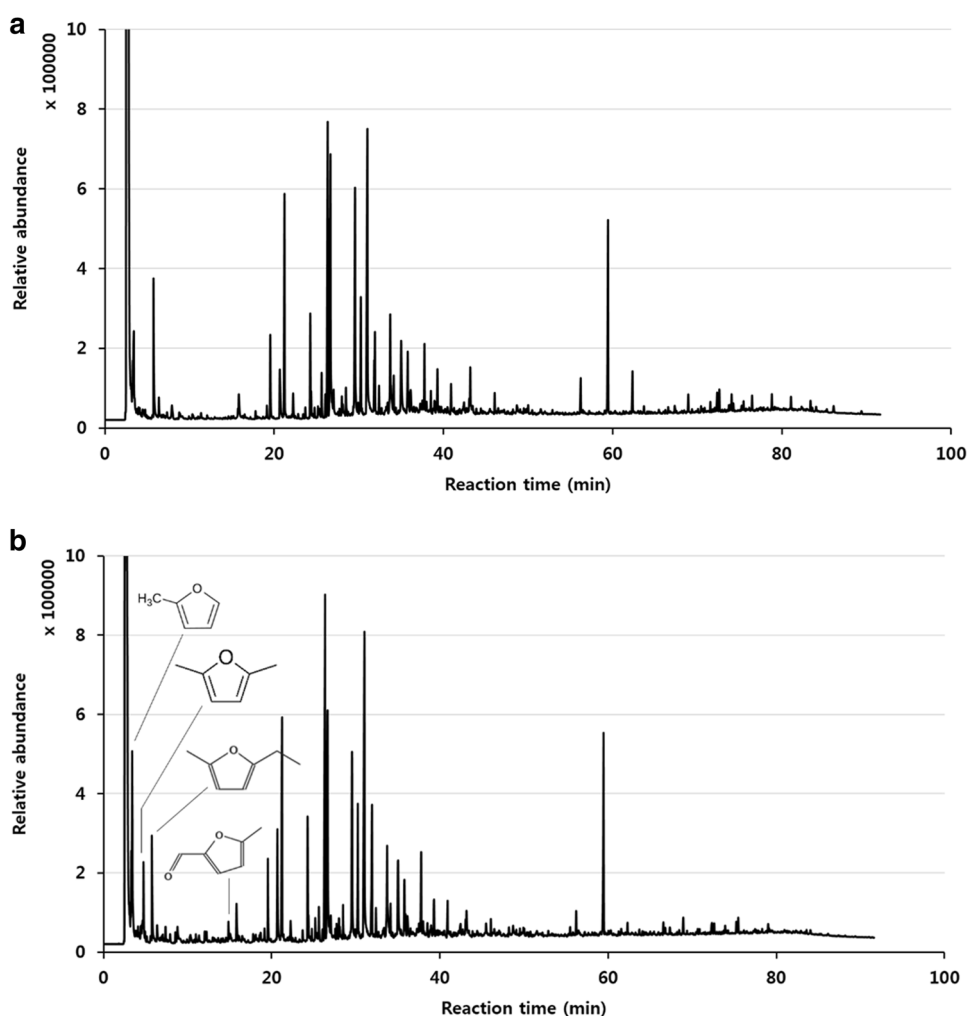
Fig. 6 Gas condensate collected in the condenser during the combined treatment. **a** Gas condensate. **b** HPLC analysis for gas condensate

Fig. 7 Liquid condensate collected in the condenser after the combined treatment. **a** Liquid condensate. **b** HPLC analysis for liquid condensate
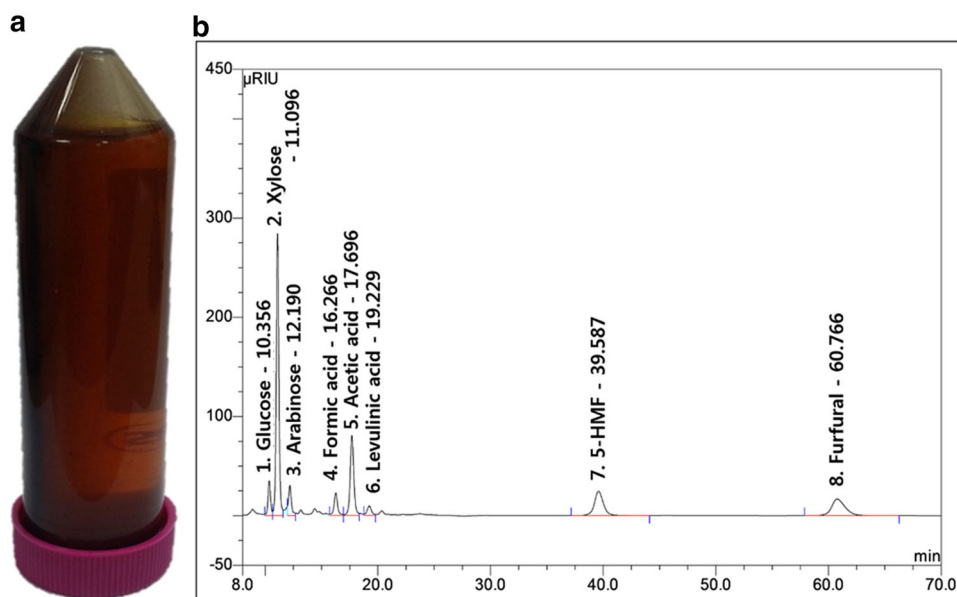
Table 2 Chemical name and content in gas condensate by HPLC analysis

No.	Retention time (min)	Chemical name	Chemical content (mg/L)
1	16.26	Formic acid	2508.2
2	17.71	Acetic acid	11,818.5
3	19.23	Levulinic acid	59.5
4	39.74	5-Hydroxymethylfurfural	881.0
5	60.39	Furfural	15,750.6

Chemical content means weight (mg) of chemical per 1 L of condensate

HPLC high-performance liquid chromatography

Figure 7b shows the results of the HPLC analysis for liquid condensate; there are eight peaks, which represent glucan, XMG (xylan + mannan + galactan), arabinan, formic acid, acetic acid, levulinic acid, 5-hydroxymethylfurfural, and furfural in order from the left, respectively (Table 3). The amount of XMG, which did not exist in the

Table 3 Chemical name and content in liquid condensate by HPLC analysis

No.	Retention time (min)	Chemical name	Chemical content (mg/L)
1	10.36	Glucan	3166.9
2	11.10	XMG	27,764.9
3	12.19	Arabinan	3235.2
4	16.27	Formic acid	8092.4
5	17.70	Acetic acid	22,595.7
6	19.23	Levulinic acid	2047.2
7	39.59	5-Hydroxymethylfurfural	6254.9
8	60.77	Furfural	7690.5

Chemical content means weight (mg) of chemical per 1 L of condensate

HPLC high-performance liquid chromatography, *XMG* xylan + mannan + galactan

Table 4 Mass balance of chemical composition before and after combined treatment by superheated steam and hot air heat treatment

Major component of wood	Combined treatment by SHS				Hot air heat treatment			
	Before treatment		After treatment		Before treatment		After treatment	
Glucan	30.4 kg	(37.5%)	25.8 kg	(31.8%)	29.3 kg	(33.8%)	24.5 kg	(28.3%)
Arabinan	1.7 kg	(2.1%)	0.0 kg	(0.0%)	2.3 kg	(2.7%)	0.2 kg	(0.2%)
Galactan	8.8 kg	(10.9%)	0.2 kg	(0.3%)	14.8 kg	(17.0%)	1.6 kg	(1.9%)
Xylan	2.9 kg	(3.6%)	0.9 kg	(1.1%)	3.1 kg	(3.5%)	0.9 kg	(1.0%)
Mannan	9.6 kg	(11.8%)	2.9 kg	(3.6%)	8.6 kg	(9.9%)	3.1 kg	(3.5%)
Klason lignin	23.3 kg	(28.8%)	41.1 kg	(50.8%)	24.6 kg	(28.4%)	38.7 kg	(44.6%)
Acid soluble lignin	0.3 kg	(0.4%)	0.2 kg	(0.2%)	0.3 kg	(0.3%)	0.3 kg	(0.3%)
Extractives	4.0 kg	(4.9%)	2.8 kg	(3.4%)	3.8 kg	(4.4%)	2.3 kg	(2.6%)
Gas condensate	–	–	0.6 kg	(0.8%)	–	–	–	–
Liquid condensate	–	–	0.4 kg	(0.5%)	–	–	–	–
Mass loss	–	–	6.1 kg	(7.5%)	–	–	15.2 kg	(17.6%)
Total	81.0 kg	(100.0%)	81.0 kg	(100.0%)	86.8 kg	(100.0%)	86.8 kg	(100.0%)

SHS superheated steam

gas condensate, was the highest in the liquid condensate. It seems that these sugars degraded by heat treatment ran out in the liquid state from the lumber and were collected in the condenser. This is the evidence that hemicellulose is the most degraded component by heat treatment among the wood cell wall components.

Mass balance of heat-treated wood

Because some wood cell wall components are degraded by heat treatment, the oven dry weight of wood after heat treatment is smaller than the expected oven dry weight of wood before heat treatment. In the case of the conventional hot air heat treatment, volatile chemicals cannot recover, because they are volatilized and disappear into the surrounding air. Some liquid chemicals were used to recover; however, most of the chemicals burned out at the bottom of the reactor. On the other hand, in the case of the combined treatment, most of the volatile and liquid chemicals are

dissolved in the SHS and can be recovered in the condenser. Therefore, when these chemicals are separated, refined, and re-used, the amount of mass loss by heat treatment can decrease. To quantitatively evaluate the amount of chemicals recovered in the combined treatment compared with that in the hot air heat treatment, the mass balances of chemicals on the basis of expected oven dry weight before heat treatment have to be compared with each other in the case of two heat treatment methods.

Table 4 shows the mass balance of each component on the basis of the expected oven dry weight of lumber before heat treatment, including oven dry weight and mass loss after the heat treatment. In the combined treatment, there were 7.1 kg of mass loss on the oven dry weight before and after heat treatment. If 0.8 kg of chemicals in the 20.5 kg of gas condensates and 0.4 kg of chemicals in the 4.9 kg of liquid condensates were separated, refined, and re-used, 1.2 kg of chemicals degraded from wood could be re-used and the mass loss could be decreased to 5.9 kg. In the case

of the hot air heat treatment, 15.3 kg of mass was lost. This is why wood cell wall components were oxidized due to oxygen in the hot air, which was used as the heat transfer media in the hot air heat treatment. This mass loss is difficult to decrease. Consequently, the combined treatment has advantages in that the amount of degraded wood cell components was lower and the mass loss by heat treatment could be decreased by recovery compared with the hot air heat treatment.

Conclusions

The relative percentage content of xylan, mannan, galactan, and arabinan was decreased, whereas that of the Klason lignin was increased, additionally, that of glucan and extractives remained almost unchanged. Lignin may bind with furan compounds decomposed from hemicellulose following heat treatment, thus contributing to the increase in the apparent relative percentage contents of the Klason lignin. In the gas and liquid condensate collected in the condenser after the combined treatment, large amounts of chemicals degraded from hemicellulose were detected. In particular, significant amounts of sugars degraded from cellulose and hemicellulose were detected in the liquid condensate.

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