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INFLUENCE OF STEAM PRESSURE ON CHEMICAL CHANGES OF HEAT-TREATED MONGOLIAN PINE WOOD

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Properties of heat-treated wood have been studied extensively in recent years. However, study on wood that has been treated in pressurized steam is limited, as most wood heat treatments are carried out in atmospheric steam. The main purpose of this study was to explore the influence of steam pressure on chemical changes of heat-treated wood. Wet chemical analysis, elemental analysis, and FTIR analysis were performed to investigate the changes of cell wall components of Mongolian pine wood. Samples treated in pressurized steam had lower percentages of polysaccharides and higher percentages of lignin compared to those treated in atmospheric steam, indicating greater chemical changes during the treatment. It was also found that thermal degradation of both samples was modest at the treatment temperature of 205 °C. These results help to explain the better dimensional stability and limited strength deterioration of wood treated in pressurized steam.

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INTRODUCTION

Properties of heat-treated wood, or thermally modified wood have been studied extensively in recent years. As most studies have unveiled, property improvements, especially better dimensional stability and longer biological durability, can be achieved through wood heat treatment (Esteves et al. 2007; Gündüz et al. 2008; Hakkou et al. 2006; Kamdem et al. 2002; Wang et al. 2005). Strength deterioration was also found, but the relative difference in properties, especially the value of modulus of elasticity (MOE), was modest when mild treatment parameters were adopted (Borrega et al. 2008a; Gu et al. 2007; Poncsak et al. 2006).

The main parameters influencing properties of heat-treated wood are treatment temperature and holding time at maximum temperature. In most cases, the heat treatment temperature ranges from 160 °C to 250 °C with hours-long holding time. Another parameter that should be taken into account is the steam pressure of the treatment environment. Steam is adopted by many treatment processes as a shielding gas to avoid excessive oxidation of wood components, such as the Thermowood method in Finland and Le Bois Perdure method in France (Rapp 2001). Most of the heat treatments are performed under atmospheric steam pressure, and relatively little attention has been placed on pressurized environments. Stamm (1956) was among the first who investigated the influence of pressure and concluded that a closed system would yield greater thermal degradation of wood. In the PLATO process, a 2-stage Dutch heat treatment process,

high pressure (6 to 8 bar) is applied in the first stage to maintain the aqueous environment in the treatment chamber. But the subsequent curing stage is still carried out in atmospheric steam condition (Boonstra and Tjeerdsma 2006). Borrega et al. (2008a, b) studied the influence of relative humidity, which was related to steam pressure in the treatment vessel. It was also found in his study that samples treated in pressurized steam exhibited less hygroscopicity than those treated in atmospheric steam, leading to better dimensional stability. Besides, Rosen et al. (1981) suggested that, compared to atmospheric steam, pressurized steam could result in higher equilibrium moisture content (EMC) during the treatment, resulting in faster conditioning. This opinion was supported by the study of Lenth et al. (2003).

Our previous study proved that heat treatment in pressurized steam was superior to that in atmospheric steam in terms of dimensional stability of heat-treated wood, and that mechanical properties of samples treated in both processes were not statistically different (Ding et al. 2011).

In this study, Mongolian Pine (*Pinus sylvestris var. mongolica*) boards were treated alternately in pressurized steam or in atmospheric steam. Wet chemical and instrumental analyses were then made on their milled samples to compare the quantitative and structural changes of cell wall components. The purpose was to explore the underlying reasons for the characteristics of wood treated in pressurized steam.

EXPERIMENTAL

Material and Heat Treatment

Kiln-dried Mongolian pine boards with the dimension of 1250 mm×100 mm×30 mm (L×R×T) were provided by Zhejian Shiyou Timber Co. Ltd. Every board was crosscut into three equal parts, with two of them prepared for heat treatment in atmospheric steam, or in pressurized steam, and the last one was left as a control sample. Property variation caused by sample origin was thus minimized. For each kind of heat treatment, altogether 16 boards were treated. The samples used for various tests were randomly chosen from them. An atmospheric-steam dryer and a pressured-steam dryer were designed for the two heat treatments. Both of them were heated by electric heating units and equipped with a steam generator. During the experiment, steam was conveyed to the dryer to expel the air in it. There was a controllable opening on the top of both dryers to exhaust heated medium. The temperature was first quickly raised to 110 °C. Then, it was raised at a rate of around 10 °C per hour until the temperature reached the maximum value, which was maintained for 1.5 hours before the electric heating units were turned off. In pressurized-steam treatment, the pressure increased along with the temperature and reached 0.35 MPa at the end. The treatment schedules are summarized in Table 1.

After being discharged from the treatment chamber, heat-treated boards, along with the control boards, were conditioned in a climate chamber (Canton Medical Equipment Co. Ltd, LRH-250-S) at 20 °C and 65% relative humidity (RH) until the weight changed by less than 1% a day. For wet chemical and instrumental analysis,

three samples originally from one board were cut into small sticks and then ground in a Wiley mill.

Table 1. Heat Treatment Schedules

Treatment	Max. Temperature (°C)	Holding Time (h)	Stream Pressure* (MPa)
Atmospheric Steam	205	1.5	0
Pressurized Steam	205	1.5	0.35

* steam pressure is expressed in terms of gauge pressure

Wet Chemical Analysis

Extractives, Klason (acid-insoluble) lignin, and holocellulose in different samples were analyzed. Milled samples were sieved by a sieve shaker (Fritsch, A3) for 10 minutes with 2.5 mm amplitude. Wood powders with diameters between 250 and 500 μm were chosen for wet chemical analysis. Each wet chemical analysis was performed twice.

The extractive content was determined according to Chinese national standard GB/T 2677.6-94. Three grams wood powders were Soxhlet extracted for 6 hours with ethanol-benzene solvent (1:2) to measure the waxes, fats, resins, and some other ether-insoluble contents, such as tannins, in the sample.

Klason lignin was determined with the standard 72% sulfuric acid method described in Chinese national standard GB/T 2677.8-94, which is similar to ASTM D1106-96.

Holocellulose content was measured according to Chinese national standard GB/T 2677.10-1995. Two grams extracted sample were placed in a 250 mL flask. Then, 65 mL of distilled water, 0.5 mL glacial acetic acid, and 0.6 g sodium chlorite were added. The mixture was heated at 75 °C for 5 hours. At the end of each hour, another 0.5 mL of glacial acetic acid and of 0.6 g sodium chlorite were added in the flask. The residue was filtered with a sintered glass crucible and washed with distilled water. The remaining material was dried at 105 ± 2 °C.

Elemental Analysis

Elemental analyses were performed to compare the percentage of carbon, hydrogen, oxygen, nitrogen, and sulfur in different samples. An Elementar VARIO EL III elemental analyzer was used with the following process:

CHNS analysis: Oven-dried sample (4 mg) was burned at 1150 °C. The CHNS elements in the sample were oxidized into CO_2, H_2O, NO_x, and SO_2, respectively. The gaseous mixture was then carried into a copper tube, in which NO_x was reduced to N_2 at 850 °C and then detected by the thermo-conductivity detector. Meanwhile, CO_2, H_2O, and SO_2 were collected in 3 adsorption traps. When the detection of N_2 was completed, the 3 adsorption traps were thermally desorbed and the gases inside were detected in sequence in the thermo-conductivity detector.

O analysis: Oxygen in the sample was detected by means of pyrolysis. The sample decomposed in the reaction column at 1150 °C. The oxygen content of the gaseous products was determined by converting O to CO on a carbon black contact. The formed CO was carried by helium gas to the thermo-conductivity detector and detected.

FTIR Analysis

Qualitative Fourier transform infrared spectroscopy (FTIR) analysis was performed by using a Thermo-Nicolet Avatar 360 FTIR spectrometer. Wood powders (d<250μm) and KBr powders (1:60) were well mixed in an agate mortar and then pressed under 200kg/cm^2 to form pellets (D=7mm). The measurements were carried out between wave numbers of 4000 cm^{-1} and 400 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans.

The spectra obtained were analyzed with an EZ OMINIC V7.3 instrument. All spectra obtained were converted to the absorption mode. Then the spectra were smoothed and baseline corrected.

RESULTS AND DISCUSSION

Wet Chemical Analysis

Results of wet chemical analysis and equilibrium moisture content (EMC) from different samples are shown in Table 2. There are 2 values for each result, as all experiments were carried out twice. The mean-value comparison is illustrated by Fig. 1.

After heat treatment, the EMC of samples treated in atmospheric steam and pressurized steam decreased significantly. Pressurized-steam treatment made samples more hydrophobic than atmospheric-steam treatment. Since hygroscopicity of wood is strongly connected with the amount of free hydroxyl groups in amorphous polysaccharides, lower moisture content indicates that heat treatment in pressurized steam resulted in a greater reduction in hydrophilic groups in the wood. This is supported by values of holocellulose content. The percentage of holocellulose in samples treated in atmospheric steam and pressurized steam decreased, with a greater effect observed in the case of pressurized steam. Holocellulose is composed of cellulose and hemicelluloses, the polysaccharides in the wood. It is widely accepted that thermal stability of crystalline cellulose is much higher than that of amorphous hemicelluloses. So, the percentage decrease of holocellulose is mainly due to the degradation of hemicelluloses, where most free hydroxyl groups are located.

Table 2. Results of Wet Chemical Analysis and EMC Presented as Weight Percentage (%)

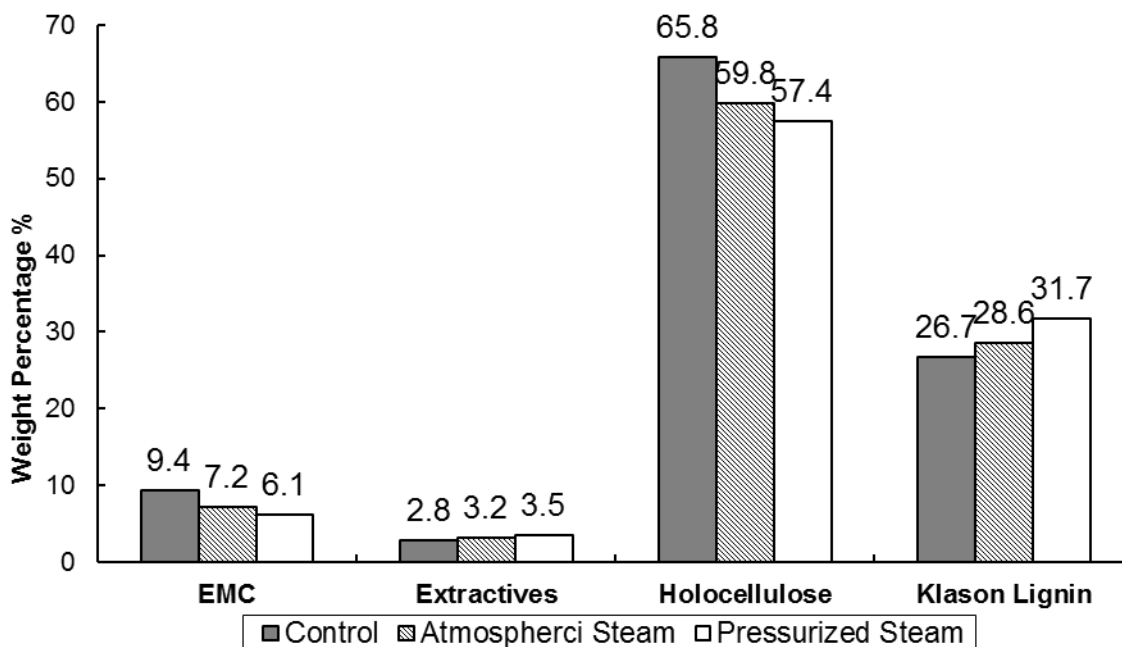|	Control	Atmospheric Steam	Pressurized Steam
EMC	9.36	6.97	6.32
	9.42	7.35	5.96
Extractives	2.83	3.31	3.54
	2.78	3.15	3.35
Holocellulose	65.64	59.53	57.49
	65.88	59.97	57.39
Klason Lignin	26.68	28.62	31.97
	26.79	28.52	31.35

Extractives in wood increased after heat treatment, rising from 2.8% in the control sample to 3.2% and 3.5% in the samples treated atmospheric steam and pressurized steam. Wood extractives consist of both low-molecular-weight volatile compounds and

high-molecular-weight polymers. During heat treatment, the volatile parts are emitted from the wood. Therefore, the increase of extractives in heat-treated wood indicates the formation of new extractable compounds during heat treatment. Boonstra et al. (2006) attributed this to the degradation of cell wall components. According to this opinion, the sample with the highest extractive content, i.e., the one treated in pressurized steam, underwent more thermal degradation.

What also rose after heat treatment was lignin content. Several factors may contribute to the rise:

Among the 3 main cell wall components, thermal stability of lignin is higher than that of cellulose and hemicelluloses. Milled wood lignin begins to degrade at around 200°C, but with a rate much slower than that of the carbohydrates. A substantial amount of lignin will still remain after the other two components have degraded completely (Rowell 2005). As a result, the decrease of holocellulose in heat-treated samples will lead to the relative increase of lignin content.

Another contributor is the possible condensation reactions occurring during heat treatment. Cross-linked structures are formed as a result, in which aromatic rings are linked by methylene bonds (Windeisen et al. 2007, 2008). However, such reactions were questioned by some researchers (Kamdem et al. 2002, Inari et al. 2007), and may not occur under all treatment circumstances.

Fig. 1. Chemical component and EMC comparison of control sample and samples treated in atmospheric steam and pressurized steam

Elemental Analysis

Wood is primarily composed of carbon, oxygen, and hydrogen, which account for 50.1%, 46.6%, and 6.5% of the dry weight of the control sample of Mongolian pine, respectively (Table 3). This result is very close to the average values of wood, i.e., 50%,

43%, and 6% (Fenger and Wegener 1984). There are also trace amounts of nitrogen and sulphur in the wood. The former comes from protein content in the wood and the latter may from inorganic ash content. It can be noticed that the sum of the element percentages is a little more than 100%. This is most probably caused by 2 factors. First, minor element content differences may exist between the two samples used to complete a measurement of the five elements. Besides, uncontrollable factors influencing the instrument and the experiment process may also contribute to it.

According to Table 3, the percentage of both H and O dropped after heat treatment, which was accompanied by the percentage rise of C. Such modifications have been proved by many studies (Alen et al. 2002; Boonstra et al. 2006; Bourgois et al. 1989; Inari et al. 2006; Prins et al. 2006) and are due to thermal degradation of carbohydrates. The O/C ratios in cellulose and hemicelluloses are around 0.83 and 0.8 respectively. In lignin, the ratio is around 0.33 (Inari et al. 2006, 2009). Therefore, the opposite change of carbohydrates and lignin must lead to higher percentage of C and lower percentage of O in heat-treated wood. What's more, the remaining carbohydrates contain more C because both the dehydration and decarboxylation reactions occurring during heat treatment result in lower O and H content (Boonstra et al. 2006; Inari et al. 2006).

Table 3. Elemental Composition of Control and Heat-treated Samples (%)

| Samples	O	C	H	N	S
Control	46.6	50.1	6.5	0.1	0.1
Atmospheric-steam treated	44.9	52.5	6.4	0.1	0.1
Pressurized-steam treated	44.0	52.9	6.2	0.1	0.2

In agreement with the findings of wet chemical analysis, it can be found that pressurized steam has greater influence on wood samples than atmospheric steam. However, the change of element content induced by both heat treatments is rather limited. For the elements O, C, and H, the variation is 5.6%, 5.6%, and 4.6% at most, respectively. That means that only a small part of wood polymers degrade to low-molecular-weight volatile compounds, and the degradation degree of wood is modest.

FTIR Analysis

Spectra of control and heat-treated samples are shown in Fig. 2. The relationship between absorption peaks and functional groups in wood was determined according to Kuo et al. (1988) and Pandey (1998). Spectra of different samples look similar to each other. However, some features of the spectra show changes in intensity of absorption peaks. The 1605 cm^{-1} peak in the spectrum of the control sample looks broad and presents a double-peak feature. This feature is weakened in the spectrum of sample treated in atmospheric steam, which exhibits a steeper one-peak feature. The 1605 cm^{-1} peak is caused by aromatic skeletal vibration breathing with C=O stretching. The change of its shape indicates a structural change of aromatic polymers in the wood after heat treatments.

The intensity of the 1510 cm^{-1} peak, purely due to aromatic skeletal vibration of lignin, remained almost unchanged after treatment. This finding is supported by the study of Akgul et al. (2007). However, various research results have been obtained related to this peak. Weiland et al. (2003) suggested that the relative height of the 1510 cm^{-1} peak increased after heat treatment. Windeisen et al. (2007), after studying the spectra of heat-treated spruce and beech, suggested that hardwood and softwood behaved differently here, with a rising up of softwood and no obvious change of hardwood. These variations may indicate that both wood species and treatment procedure influence the behavior of this peak.

The 1110 cm^{-1} peak is caused by glucose ring stretch. Heat treatment in pressurized steam intensified this peak. This effect is most probably attributable to the following two factors: percentage increase of crystalline cellulose due to the cleavage and dehydration of amorphous carbohydrates, and crystallization of the quasicrystalline region of cellulose (Bhuiyan et al. 2000).
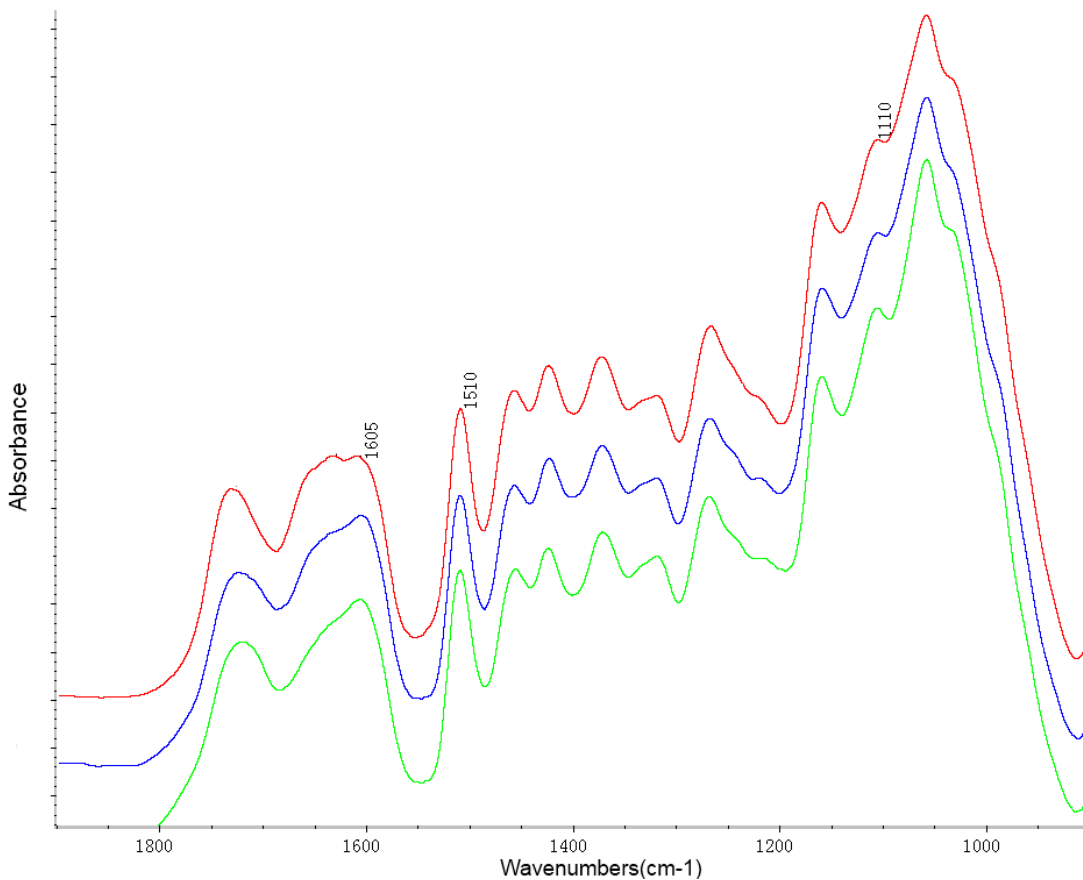
Fig. 2. Comparison of FTIR spectra of control and heat-treated samples;
From top to bottom: control, atmospheric-steam treated, pressurized-steam treated

All the three analyses showed that heat treatment in pressurized steam exerted more influence on wood components than the treatment in atmospheric steam. Wood

treated in pressurized steam was found to have less holocellulose content, more crystalline cellulose, and more lignin content than that treated in atmospheric steam.

What also can be drawn from analyses above is that the influence of heat treatment on wood components is limited at the temperature of 205 °C. Elemental analysis revealed a rather limited change, and the spectra of the three samples also look similar to each other.

According to this study, we can conclude that the lower strengths of wood treated in pressurized steam are attributable to greater degradation of its chemical components. However, at the treatment temperature around 200 °C, thermal degradation of wood cell wall components is rather limited. What's more, lower hygroscopicity and higher crystallinity of wood treated in pressurized steam play a positive role in wood mechanical performance. These factors combined together make mechanical properties of wood treated in pressurized steam statistically the same as that of wood treated in atmospheric steam.

Dimensional stability is mainly determined by the number of free hydroxyl groups in amorphous polysaccharides, the most thermally susceptible component in wood. Pressurized steam accelerates the degradation of amorphous polysaccharides, as proven by data shown above. Therefore, wood treated in pressurized steam exhibits lower hygroscopicity and better dimensional stability than wood treated in atmospheric steam.

CONCLUSIONS

1. Pressurized steam has a greater influence on chemical changes of cell wall components than atmospheric steam, which is supported by the results of all the 3 analyses. More percentage decrease of polysaccharides was found in the sample treated in pressurized steam, which was accompanied by more percentage increase of lignin in the same sample. FTIR analysis suggested more crystallinity of samples treated in pressurized steam.
2. There were only limited effects of heat treatment on wood chemistry, regardless of whether the treatment was in pressurized steam or in atmospheric steam, as long as the temperature was around 200 °C.
3. These factors described in the first two conclusions explain the better dimensional stability and limited strength deterioration of wood treated in pressurized steam.

ACKNOWLEDGMENTS

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