Effect of Vacuum Heat Treatment on the Chemical Composition of Larch Wood

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The effects of vacuum heat treatment were studied relative to the chemical composition of larch wood. The samples were heat-treated in vacuum at 160 °C, 200 °C, and 240 °C for 4 h, and the chemical changes were investigated by wet chemical analysis, elemental analysis, calorific value determination, and pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS). The relative percentage contents of lignin and extractives increased after heat treatment. Additionally, the relative percentage contents of holocellulose, cellulose, and hemicelluloses decreased as a result of the thermo-vacuum treatment. Elemental analysis showed a slight reduction in the contents of hydrogen and oxygen. Vacuum heat treatment also increased the calorific value compared with untreated samples.

Keywords: Larch wood; Thermo-vacuum treatment; Chemical modifications

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INTRODUCTION

Wood is a biopolymer that can be utilized in many fields; however, its utilization is limited by its intrinsic properties, such as hygroscopicity and poor durability. Many modification processes have been developed to improve the quality of wood, one of which is heat treatment. Heat treatment avoids the use of toxic chemicals and therefore does not have the same deleterious effects on the environment as chemical treatments. However, the major disadvantage of heat treatment is that the resultant decrease in bending strength causes an increased likelihood of breakage (Esteves *et al*. 2011). In recent years, several industrial heat treatment processes have been used: stream treatment in Finland (Viitanen *et al*. 1994), a combination of steam and heated air treatment in the Netherlands (Tjeerdsma *et al*. 1998), and oil treatment in Germany (Rapp 2001).

Heat treatment induces changes in the chemical composition of wood, which are mainly due to autocatalytic reactions of the cell wall constituents (Tjeerdsma and Militz 2005). First, hemicelluloses degrade by deacetylation because they are most sensitive to heat, followed by depolymerization catalysed by the released acetic acid (Boonstra and Tjeerdsma 2006; Esteves and Pereira 2009). Cellulose is more stable than hemicelluloses in heat, but during heat treatment the degradation of amorphous hemicellulose results in increased cellulose crystallinity (Bhuiyan and Hirai 2000). Thermal modification also causes the cleavage of β–O–4 linkages in lignin (Wikberg and Maunu 2004). According to Esteves *et al.* (2008), the extractive content of heat-treated *Eucalyptus globulus* wood increases at the beginning of the treatment and decreases afterwards. Almost all of the original extractives disappear, and new compounds are formed after heat treatment.

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Thermo-vacuum treatment is a novel thermal wood modification technology in which the concentration of oxygen inside a furnace is reduced by applying vacuum. Damage to the mechanical properties of wood is less pronounced during thermo-vacuum treatment compared with other heat treatment technologies because the volatile compounds that contribute to the degradation of the polysaccharides in the wood cell wall are removed by applying vacuum (Allegretti *et al*. 2012; Ferrari *et al*. 2013). The changes in chemical composition of vacuum heat-treated wood have been studied by some recent works (Candelier *et al*. 2013; Sandak *et al*. 2015; Yang *et al*. 2015).

Larch wood is an important plantation tree that is extensively planted in northeast China (Li 2006). However, the effects and mechanisms of thermo-vacuum treatment are not well understood with regard to changes in the chemical composition of larch wood. The aim of this study was to investigate the effects of thermo-vacuum treatment on the wood chemical composition. For this purpose, the chemical groups and composition of larch wood were analyzed before and after thermo-vacuum treatment by wet chemical analysis, elemental analysis, calorific value determination, and Py-GC-MS analysis.

EXPERIMENTAL

Materials

Raw larch (*Larix kaempferi*) wood obtained from Qingyuan in Liaoning Province, China, was sawn and processed with a planer in order to obtain specimens with a length of 400 mm (longitudinal), a width of 40 mm (radial), and a thickness of 40 mm (tangential). The air-dried density of wood was 0.693 g cm^{-3}. The specimens were free of macroscopic defects such as knots and splits. There were 15 samples treated in each group.

Methods

Prior to the heat treatment, all specimens were oven-dried at 103 ± 2 °C to 0% moisture content and then placed in a vacuum pressure furnace. A heating cord in the processing box helped to achieve a high-temperature environment. There were two layers of walls in the processing box with the heating cords located between the two layers. Therefore, when the cords were heating, wood in the vacuum processing box was also being heated. Heat treatment was conducted at temperatures of 160 °C, 200 °C, and 240 °C for 4 h (time for temperature increasing and decreasing not included) under vacuum conditions (-0.05 to -0.09 MPa). At the end of each heat treatment, the furnace was turned off, and the wood was kept inside until the temperature reached 40 °C. The wood was then removed and stored. The change rate of temperature was 3 °C min^{-1} during the warm up and cooling down. The untreated specimens were used as reference.

Chemical analyses were performed on untreated and heat-treated milled samples (40- to 60-mesh). The contents of ethanol-benzene extractives (GB/T 10741 2008), hollocelulose (GB/T 2677.10 1995), cellulose (GB/T 744 2004), and Klason lignin (GB/T 747 2003) were measured. The hemicelluloses content was calculated by subtracting the cellulose content from the holocellulose content.

CHNO elemental analyses were performed on both untreated and thermally treated larch wood. Before analyses, the samples were powdered and screened through a 200-mesh sieve. The powders were oven-dried at 103 °C. The contents of C, H, and N were determined using a Vario EL multi-element analyzer (Elementar, Hanau, Germany). The oxygen content was calculated by difference ($100\% - C\% - H\% - N\%$).

The calorific value was also determined in untreated and thermally treated larch wood. The samples were powdered and screened through a 200-mesh sieve, and the moisture content (MC) was measured according to GB/T 2677.2 (1993). The higher heat value (HHV) was determined by a 1281 adiabatic bomb calorimeter (Parr Instrument Inc., Moline, IL, USA). Samples weighing from 0.5 to 0.6 g were incinerated in a pure oxygen environment. According to Todaro *et al.* (2015), the lower heat value (LHV) was calculated as:

$$LHV = HHV \times [1 - (0.01 \times MC)]$$ (1)

The pyrolysis system consisted of a fast pyrolysis analyzer (CDS5200) and a GC-MS instrument (Clarus 680GC-SQ8MS, PerkinElmer, Santa Clara, CA, USA). For Py-GC-MS analysis, the untreated and treated wood samples were milled into fine powders (200-mesh). Pyrolysis of each sample (0.5 mg) was carried out at 600 °C. Helium was used as the carrier gas at a flow rate of 1 mL/min in split mode, and the split ratio was 50:1. The pyrolysis products were separated in an HP-5 (Agilent Technologies, Santa Clara, CA, USA) capillary column (30 m × 0.25 mm × 0.25 μm). The GC oven was kept at 50 °C for 5 min and programmed to increase to 300 °C in increments of 5 °C/min. The interface temperature between GC and MS was 280 °C, and the ion source temperature was 200 °C. The mass spectrometer was operated in EI mode using 70 eV of electron energy. The mass range m/z 30 to 600 was scanned. The pyrolysis compounds were identified by comparison with characterized GC-MS spectra, with reference to information in the NIST database (http://www.nist.gov/srd/nist1a.htm.).

RESULTS AND DISCUSSION

Chemical Composition Analysis

Table 1 shows the changes in chemical composition of larch wood during thermo-vacuum treatment. There was an increase in the relative percentage contents of lignin and extractives, but a decrease in the relative percentage contents of holocellulose, cellulose, and hemicelluloses compared with the untreated samples. A higher proportion of hemicellulose degradation was observed compared with other constituents in this study.

In the treated samples, the relative percentage contents of hemicellulose decreased by 15.04% (160 °C), 35.48% (200 °C), and 59.17% (240 °C) compared with untreated samples. At temperatures above 200 °C, more extensive degradation of hemicelluloses was observed. The degradation of hemicelluloses begins with deacetylation, followed by depolymerization catalysed by the released acetic acid, according to previous studies (Boonstra and Tjeerdsma 2006; Esteves and Pereira 2009).

The relative percentage contents of cellulose were 46.45% (untreated), 46.14% (160 °C), 44.96% (200 °C), and 43.89% (240 °C). Cellulose is more stable than hemicellulose due to its crystalline nature and is therefore affected less by heat treatment (Yildiz *et al*. 2006). After treatment, the relative percentage contents of lignin increased from 22.40% (untreated) to 23.85% (160 °C), 24.94% (200 °C), and 31.40% (240 °C). Similar results were obtained by Boonstra and Tjeerdsma (2006), who observed that the lignin content of some softwoods increased because of hemicellulose degradation.

The relative percentage contents of extractives increased at low treatment temperatures, reaching a maximum value of 4.62% at 160 °C, after which the relative percentage contents of extractives decreased. Similar results have been reported by

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previous studies (Esteves *et al*. 2008, 2011). This trend could be due to the appearance of new extractable compounds resulting from polysaccharide degradation at 160 °C. When the treatment temperature is increased further, new compounds degrade to volatiles that leave the wood, resulting in a decrease in the extractives content.

Table 1. Chemical Composition of Untreated and Treated Wood

Sample	Lignin (%)	Holocellulose (%)	Cellulose (%)	Hemicelluloses (%)	Extractives (%)
Untreated	22.40	69.79	46.45	23.34	2.83
160	23.85	65.97	46.14	19.83	4.62
200	24.94	60.02	44.96	15.06	3.40
240	31.40	52.42	43.89	9.53	3.32

CHNO Elemental Analysis

There was a slight reduction in the contents of hydrogen and oxygen, whereas the carbon content increased slightly. The ratios of H/C and O/C decreased with increasing treatment temperature, which might have resulted from the elimination of water caused by dehydration of the carbohydrates, yielding aldehydes (Bobleter and Binder 1980; Tjeerdsma *et al*. 1998) and resulting in a reduction of hydrogen and oxygen. Moreover, the reduction of oxygen content may be a result of decarboxylation (cleavage of acetic acid from hemicelluloses).

Condensation reactions could also contribute to a further decrease of hydrogen and oxygen content.

Table 2. Elemental Compositions of Untreated and Treated Wood

Sample	N (%)	C (%)	H (%)	O (%)
Untreated	0.12	46.92	6.73	46.23
160	0.11	47.08	6.72	46.09
200	0.12	47.48	6.62	45.78
240	0.14	47.75	6.45	45.66

Calorific Value

The calorific values of untreated and heat-treated wood are shown in Table 4. Heat treatment of larch wood resulted in a high HHV and LHV. Compared with the HHV of untreated samples, the HHV of treated samples increased by 0.2% (160 °C), 3.6% (200 °C), and 8.6% (240 °C). However, the LHV of treated samples increased by 0.7% (160 °C), 4.9% (200 °C), and 11.3% (240 °C).

Some previous studies have indicated that lignin and extractive contents have a considerable effect on the calorific value (White 1987; Günther *et al*. 2012). The LHV of cellulose, hemicelluloses, and lignin are 17.3 MJ/kg, 16.2 MJ/kg, and 27.0 MJ/kg (Todaro *et al*. 2015), respectively. Fuwape (1989) indicated that the HHVs of cellulose, lignin, and extractives isolated from Gmelina are 19.7 MJ/kg, 25.4 MJ/kg, and 25.1 MJ/kg, respectively.

Accordingly, the higher calorific value of larch wood after heat treatment could be primarily due to higher contents of lignin in the treated samples (see Table 1). In terms of the calorific value, Kim *et al*. (2012) reported that there was more energy in C–C bonds than C–H and C–O bonds. Therefore, the higher C content after heat treatment (Table 3) could result in a higher calorific value.

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Table 3. The HHV, LHV, and Moisture Content of Untreated and Treated Wood

Sample	HHV (MJ/Kg)	LHV (MJ/Kg)	Moisture Content (%)
Untreated	17.30	16.09	7.0
160	17.34	16.20	6.6
200	17.92	16.88	5.8
240	18.78	17.90	4.7

Py-GC-MS Analysis

Py-GC-MS is a promising method for analyzing chemical modifications that occur during heat treatment and has been used by other researchers (Grinins *et al*. 2013). The identities of the main compounds during pyrolysis and their relative contents are listed in Table 4. The pyrolysis products in the treated samples were similar to those found in untreated samples; the main differences that arose between the two were the contents of the products.

Table 4. The Identities and Relative Contents of the Main Compounds during Pyrolysis

Peak	Compound	RT	Relative Content (%)			
			NT	160	200	240
1	4-Methyl-2-pentanol	1.57	5.31	3.84	4.21	3.62
2	2-Methoxy-1-Propene	1.69	7.29	6.04	7.11	5.62
3	Hydroxy-acetaldehyde	1.87	5.48	4.45	5.34	4.35
4	3-Amino-1,2-propanediol	1.89	4.26	3.96	3.54	2.97
5	Methyl vinyl ketone	1.94	4.18	3.56	3.81	-
6	2-Methyl-furan	1.99	3.15	3.03	3.68	-
7	Acetic acid, methyl ester	2.06	3.76	2.95	2.46	1.96
8	Acetic acid	2.51	8.67	7.26	5.34	3.46
9	1,2-Ethanediol, monoacetate	3.69	2.71	1.57	-	-
10	2(5H)-Furanone	4.33	-	1.53	-	-
11	Furfural	5.31	3.03	2.78	3.58	-
12	2-Hydroxy-2-cyclopenten-1-one	8.55	1.77	2.74	-	-
13	Butanedioic acid, cyclic hydrazide	9.90	2.66	3.29	2.29	2.66
14	2,2-Diethyl-3-methyl-oxazolidine	11.21	2.33	3.00	1.22	2.79
15	P-Cresol	13.85	-	-	-	2.00
16	2-Methoxy-phenol(Guaicol)	14.08	3.33	4.56	4.19	5.11
17	Creosol(4-methylguaiacol)	17.35	8.49	9.65	9.68	12.79
18	6-Hydroxyhexahydrocyclopenta[b]furan-2-one	17.46	-	-	1.31	-
19	Catechol	17.79	-	-	-	1.36
20	5-Hydroxymethylfurfural(HMF)	18.57	1.35	1.12	1.43	2.74
21	4-Ethyl-2-methoxy-phenol	19.77	-	1.92	-	2.50
22	4-Methyl-1,2-benzenediol	20.65	-	-	0.92	1.93
23	2-Methoxy-4-vinylphenol	20.82	8.85	9.70	11.68	12.50
24	Butanoic acid, 2,3-dimethyl-4-nitro-, 1,1-Dimethylethyl ester	20.96	-	-	-	2.45
25	Eugenol	21.93	4.09	2.96	3.67	2.90
26	4-Ethylcatechol	22.81	-	-	-	0.55
27	Vanillin	23.14	2.27	2.62	1.48	3.75
28	Trans-iso-eugenol	24.40	10.99	9.52	9.85	10.71
29	1-(3-hydroxy-4-methoxyphenyl)-Ethanone	25.25	-	-	-	1.56

NT: untreated samples

The acid content (mainly acetic acid) of treated samples decreased significantly with increasing treatment temperature, which could be due to the fact that hemicellulose degradation occurred during heat treatment. The alcohol (3-amino-1, 2-propanediol) content of treated samples also decreased with increasing treatment temperature. The decrease in alcohol content could have been a result of a decline in the amount of accessible hydroxy groups after heat treatment (Grinins *et al*. 2013).

The pyrolysis products of lignin are complex, including aldehydes, esters, and phenols. According to the aromatic substituent groups, the pyrolysis products of lignin can be divided into four categories: guaiacyl type (G), syringol type (S), phenol type (P), and catechol type (C) (Wang *et al*. 2015). G-type products of untreated and treated samples originating from the guaiacyl units of lignin were the most abundant in this study. S-type compounds were not detected in the main products due to a lack of syringol units in larch (softwood) lignin. The variation in the contents of lignin pyrolysis products could result from the number of broken ether linkages. The results obtained by Amen-Chen *et al.* (2001) showed that guaiacol is mainly produced by the direct breaking of β-O-4 linkages. Therefore, the structural changes in lignin after heat treatment may be characterized by the differences of pyrolysis products.

CONCLUSIONS

1. Vacuum heat treatment caused clear changes in the chemical properties of larch wood. The relative percentage content of holocellulose, cellulose, and hemicelluloses decreased, whereas that of lignin and extractives increased after heat treatment.

2. The decrease in the ratios of H/C and O/C indicated the loss of functional groups containing hydrogen and oxygen during heat treatment.

3. The changes of the calorific value were related to the modifications of wood chemical components.

4. Py-GC-MS indicated that changes in pyrolysis products were mainly in the relative proportions in untreated and treated samples. The acid contents, especially acetic acid, decreased with increasing treatment temperature, which showed that hemicelluloses degraded during heat treatment.

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