

Analysis of Gas Chromatography-Mass Spectrometry Coupled with Dynamic Headspace Sampling on Volatile Organic Compounds of Heat-Treated Poplar at High Temperatures

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Thermal modifications tend to darken wood color and enhance dimensional stability, erosion resistance, weather resistance, and product value. To investigate the chemical characteristics of VOCs influenced by the heat treatment process, air-dried poplar wood was heat-treated at four treatment temperatures (160, 180, 200, and 220 °C) for 2 h. Near-infrared spectroscopy (NIR) was used to investigate the changes in sample hemicellulose, cellulose, and lignin composition. Acid-insoluble lignin and holocellulose were determined using wet chemistry methods. Volatile organic compounds of the poplar wood were analyzed for composition using gas chromatographic-mass spectrometry coupled with dynamic headspace sampling. The results showed that the most significant volatiles in heat-treated poplar were aldehydes, which were the most abundant compound at 180 °C, in the furfural form. The amount of aromatic compounds and esters increased with increasing temperature. In addition, alcohol benzene extractives and acid-insoluble lignin increased, while holocellulose content decreased.

Keywords: Poplar wood; Thermal treatment; Volatile organic compounds; Gas chromatographic-mass spectrum; Near infrared spectroscopy (NIR)

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INTRODUCTION

Thermally treated wood is widely used for decoration, furniture, and construction materials, which results in value-added materials. Thermal modification darkens wood's color and enhances the dimensional stability, erosion resistance, and weather resistance, among others (Temiz *et al.* 2006). In addition, thermal modification permanently alters wood's construction and chemical composition, resulting in the emission of large quantities of volatile organic compounds (VOCs) during the treatment process, which contributes substantially to environmental pollution.

The process of heat-treatment dates back to the 1930s and was further developed in the 1990s. Since then, Finland, the Netherlands, France, Germany, and Japan have continued to research and develop the heat-treatment process. Finland is the earliest country to develop a steam heat-treated wood process that was applied in the industry; the process was performed under a steam atmosphere, while the process in France was performed under a nitrogen atmosphere (Cao *et al.* 2007). The process used in Japan used a smoke heat-treatment technology (Liu and Zhang 2010). The PLATO process was developed in the 1980s and was used in Netherlands (Xie *et al.* 2002), and the heat-

treatment process in Germany was carried out using hot oil (Andreas *et al.* 2001). The most common process in China involves three stages, and the methodology was introduced by Li and Tang (2008).

Hemicelluloses are characterized by an inhomogeneous structure and a low crystallinity. Hemicelluloses decompose readily during the thermal treatment process and produce large quantities of volatiles at 200 °C (Kotilainen 1999, 2000). Peters *et al.* (2008) characterized the volatiles emitted from four different heat-treated woods at 180 and 220 °C, *i.e.*, spruce, beech, maple, and ash, using chromatographic and spectroscopic methods. The results demonstrated that the main VOCs were furfuraldehyde and 5-methyl-2-furaldehyde, which were the degradation products of hemicelluloses. Long and Wang (2007) investigated the emissions from four common woods (spruce, poplar, masson pine, and *Eucalyptus urophylla*) at room temperature using high-performance liquid chromatography and gas chromatography, and the results revealed the principles of release for aldehydes and terpenes. Similarly, Hyttinen *et al.* (2010) compared the VOCs emitted from air-dried and heat-treated Norway spruce, Scots pine, and European poplar woods in an enclosed metal chamber and discovered the effect of different treatment conditions on volatile compounds. Tumen *et al.* (2010) studied the changes in the chemical structure of hornbeam and Uludag fir woods during thermal treatment at 170, 190, and 210 °C for 4, 8, and 12 h, respectively.

Various studies have investigated the physical performance, surface properties, and erosion resistance of thermally modified wood; however, few studies have focused on the volatile organic compounds retained in modified wood. In this study, poplar wood was thermally-treated in an oven at four different temperatures (160, 180, 200, and 220 °C) for 2 h. The VOCs were characterized using gas chromatographic-mass spectroscopy analysis, and the content of the holocellulose and acid-insoluble lignin were measured according to the GB/T 2677.10 (1995) and GB/T 747 (2003) testing standards, respectively.

EXPERIMENTAL

Materials

Air-dried poplar (*Populus tomentosa*) sapwood (LANDBOND Co., Ltd., Beijing, China), without cracks or knots, was selected for use in this study. The samples had an initial moisture content of approximately 15%.

Thermal Treatment

The wood samples were sawn to dimensions of 500 mm × 100 mm × 20 mm (L × R × T). The thermal treatment was performed under atmospheric air in an oven at 160, 180, 200, or 220 °C for 2 h, and then the samples were ground and screened to between 40 and 60 mesh.

Near-Infrared (NIR) Spectrum Analysis

Untreated and heat-treated samples were ground into particles of 40 to 60 mesh and then oven-dried at 103 °C. Near-infrared (NIR) spectrum analysis was performed using a MPA Fourier transform near infrared spectrometer (Bruker, Germany). The resolution ratio was 8 cm⁻¹, with 32 scans per spectra, in the range of 12,800 cm⁻¹ to 4000 cm⁻¹. The spectra were analyzed by taking a second derivative.

Holocellulose and Acid-Insoluble Lignin Analysis

A Soxhlet extraction process was used for all wet chemistry methods because of its high efficiency for extraction. First, the powders were extracted with benzene:ethanol (2:1 v/v), according to the GB/T 10741-2008, wood samples are put into Soxhlet extractor after measuring, then are extracted with water bath for at least 6 hours. The contents of holocellulose and acid-insoluble lignin were measured according to the GB/T 2677.10 (1995) and GB/T 747 (2003) testing standards, respectively. All analyses were run in triplicate.

Gas Chromatography-Mass Spectroscopy Analysis with Dynamic Headspace Sampling (DHS)

Two and a half grams of the wood powders were injected into a capture tube Eclipse MODEL 4660 purge and trap sample concentrator (O.I. Analytical, America), and 4.0 mL of ultrapure water was added. Then, the gaseous compositions were read using a QP2010 gas chromatography-mass spectrometer (Shimadzu, Germany). The gas chromatography conditions were as follows: DB-1 capillary column with the dimension of 30 m × 0.25 mm × 0.25 μm, column temperature of 40 °C, heating rate of 20 °C/min to 280 °C, and injection port temperature of 250 °C. Helium was selected as the carrier gas, injected at a flow velocity of 0.8 mL/min with the split ratio of (50:1).

The mass spectrometry conditions were as follows: EI ion source and electron energy of 70 eV, and the concentrations of compounds were calculated using the area normalization method. The mass spectra obtained were compared to the mass spectra from the National Institute Standards Library (NIST, 2011).

RESULTS AND DISCUSSION

Acid-Insoluble Lignin and Holocellulose Contents

The acid-insoluble lignin and holocellulose contents are shown in Table 1. The contents of benzene-alcohol extractives and acid-insoluble lignin increased as the temperature increased, while the contents of holocellulose decreased. The hemicellulose fraction degraded as the temperature rose, while the cellulose and lignin contents degraded slightly. As a result, a large number of extractives were produced, which led to an increase in the benzene-alcohol extractive level; at the same time, the hemicellulose contents initially degraded, and then holocellulose decreased and acid-insoluble lignin increased. Additionally, the absorption and condensation reaction of carbohydrates also caused an increase in lignin content.

Table 1. Acid-Insoluble Lignin and Holocellulose Content

Groups	Benzene-alcohol extractives (%)	Holocellulose (%)	Acid-insoluble lignin (%)
Control	0.75	80.36	11.21
160 °C	1.49	78.44	11.81
180 °C	1.71	75.9	12.47
200 °C	3.98	62.25	13.34
220 °C	4.44	57.07	19.08

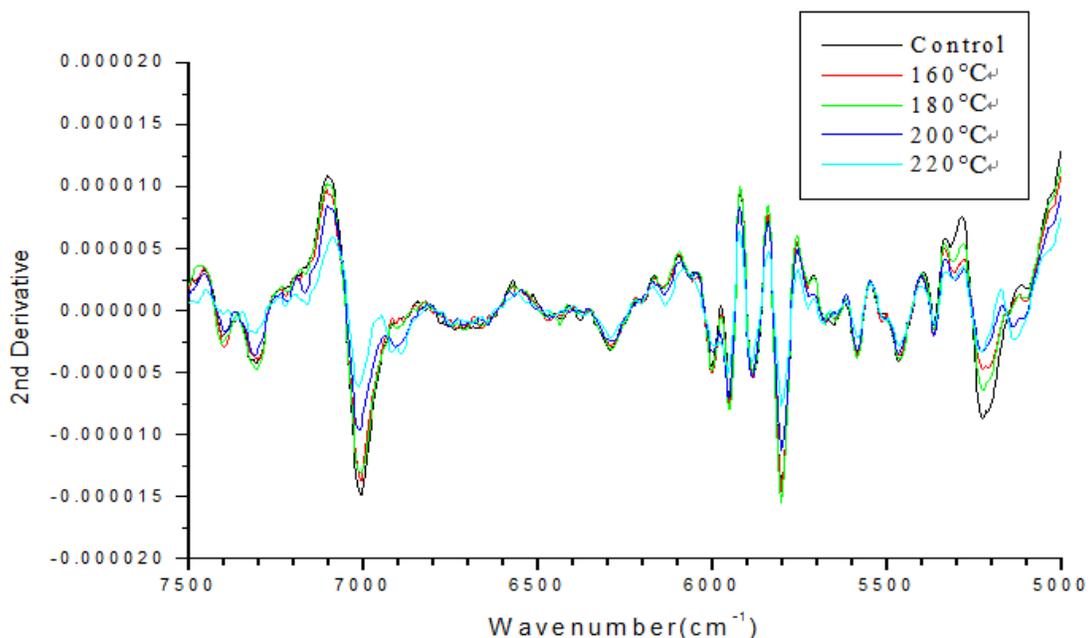


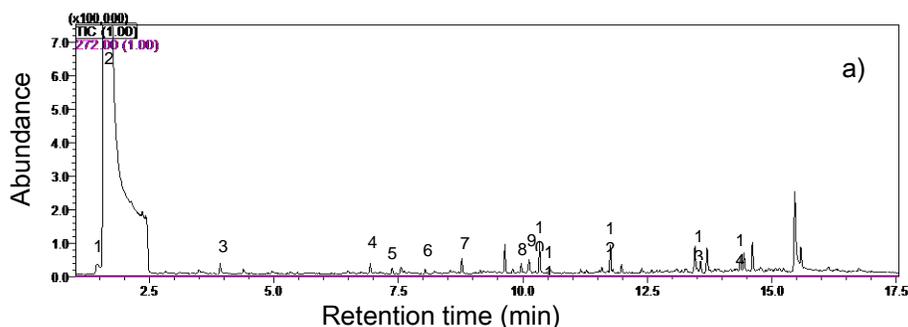
Fig. 1. Second-derivative FTNIR spectra for untreated and thermally treated wood samples

Figure 1 presents the average second-derivative FTNIR spectra of untreated and thermally treated wood samples. Some of the bands have already been referenced in the literature. The band at 7000 cm^{-1} is attributed to the amorphous region of cellulose (Tsuchikawa and Siesler 2003), and the absorption peak decreased as the temperature increased. The band at 6900 cm^{-1} is attributed to the O-H stretching vibration of lignin (Siesler *et al.* 2002), and it remained relatively unaffected by the thermal treatment because degradation was minimal. The band at 6287 cm^{-1} corresponds to the crystalline regions of cellulose (Tsuchikawa and Siesler 2003); however, there was no change in these peaks with thermal treatment. The band at 5800 cm^{-1} is attributed to the furanose/pyranose functional groups of hemicelluloses, and these absorption peaks decreased as the temperature increased. The band at 5587 cm^{-1} corresponds to the crystalline and semi-crystalline structure of cellulose (Yonenobu and Tsuchikawa 2003).

During the thermal treatment, lignin was minimally degraded. The amorphous regions of cellulose and hemicelluloses were degraded, with the severity of degradation increasing as the temperature rose.

VOCs Emitted

Chromatograms of the total ions of VOCs emitted from wood samples are shown in Fig. 2, and the volatile chemical compositions of wood samples are shown in Table 2.



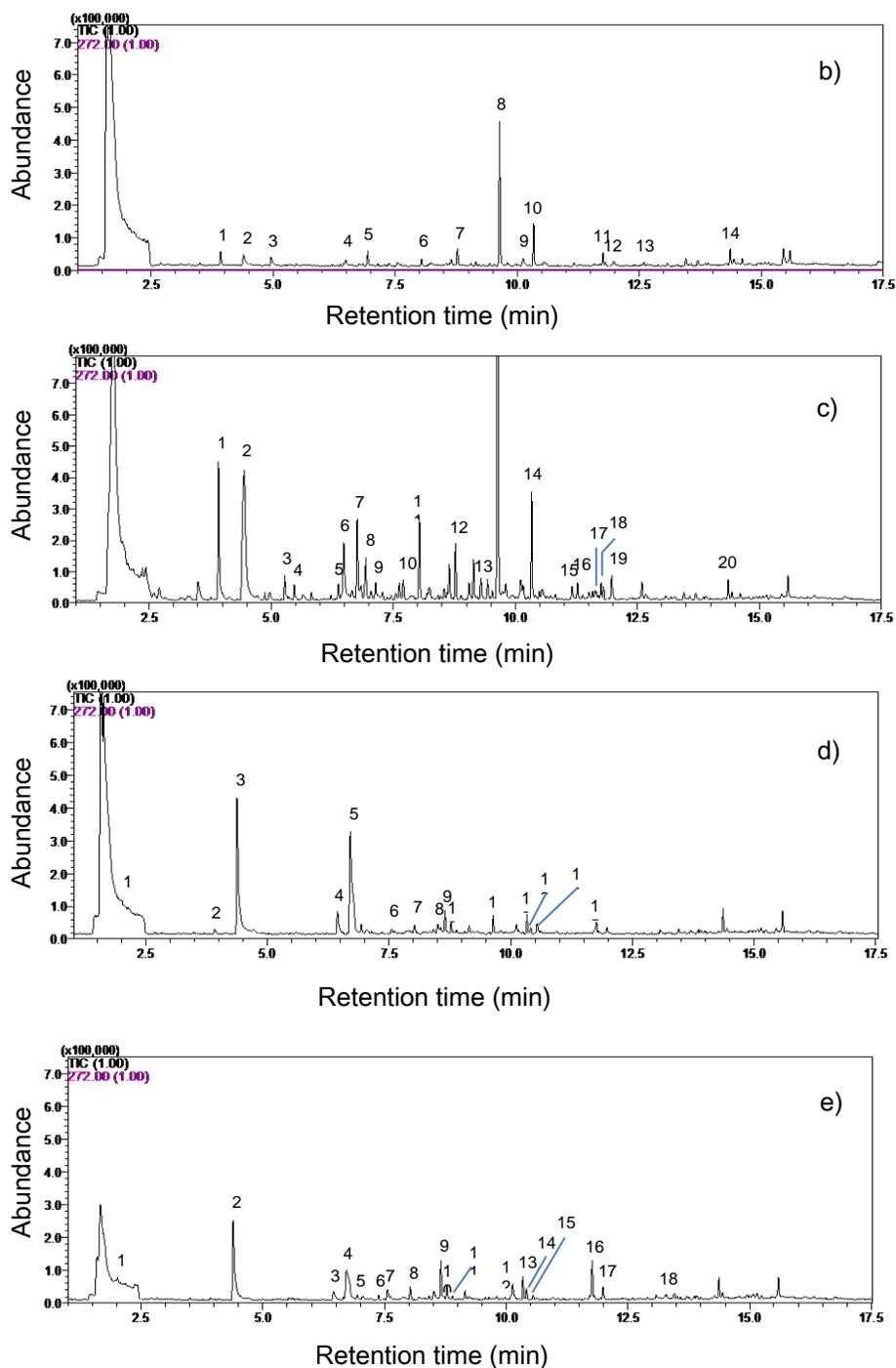


Fig. 2. The total ion chromatograms of VOCs emitted from: (a) untreated wood samples; (b) samples heat-treated at 160 °C; (c) samples heat-treated at 180 °C; (d) samples heat-treated at 200 °C; and (e) samples heat-treated at 220 °C

The compounds in untreated poplar samples were relatively lower than those of thermally treated ones. Large quantities of carboxylic acids were found in untreated poplar wood, and there were minimal aromatic compounds present, such as naphthalene and methylnaphthalene, in the poplar wood samples; these compounds exist in wood

extractions and are released during the heating process. Aldehydes are generally less present in the emissions from natural poplar wood.

As the temperature increased to 180 °C, the amount of carboxylic acids and hemicelluloses decreased rapidly, and the production of aldehydes, mainly furfural (peak 2; Fig. 2b, peak 2; Fig. 2c, peak 3; Fig. 2d and peak 2; Fig. 2e), increased. The max concentration of aldehydes appeared at 180 °C, and increased to approximately 83% overall. Aromatic compounds and esters increased with increasing temperature. In the early phase of the decomposition of hemicelluloses, the breakage of 4-O-methyl-D-glucuronic acids formed acetic acids, ketones, and aldehydes through a secondary reaction. Secondary pyrolysis and condensation of aldehydes and ketones are enhanced by high temperatures. Furan is formulated by 4-O-methyl-D-glucuronic acid in the branched chain of xylan. Aromatic compounds are derived from the breakage in the junction between hemicellulose and lignin (Gao *et al.* 2013). As the temperature kept increasing from 180 °C to 220 °C, the concentration of aldehydes decreased gradually, and the main aldehyde produced was still furfural. Meanwhile, the concentration of aromatic compounds increased, especially phenol (peak 6; Fig. 2d and peak 4; Fig. 2e) and methylnaphthalene (peak 15; Fig. 2d and peak 16; Fig. 2e). Additionally, the content of esters also increased (peak 9; Fig. 2d and peak 8; Fig. 2e).

Table 2. VOCs from Wood Samples

Groups	Peak #	R. time	Compounds	Relative amount(%)
Untreated wood	1	1.450	Oxalic acid	31.9
	2	1.595	Ethylhexanol	2.64
	3	3.925	Hydroxyl methyl butyl aldehyde	3.47
	4	6.935	2-Pentyl-furan	3.14
	5	7.375	Dichlorobenzene	1.82
	6	8.040	2-Nonenal	9.75
	7	8.775	Nonanal	5.29
	8	9.965	Cyclohexanol	3.31
	9	10.125	Naphthalene	5.62
	10	10.335	Capraldehyde	9.92
	11	10.545	Hydroxymethylfurfural	1.82
	12	11.760	Methylnaphthalene	12.23
	13	13.510	Dimethylnaphthalene	1.49
	14	14.365	Hexadecane	4.46
160 °C	1	3.920	4-Hydroxy-3-methylbutanal	4.19
	2	4.390	Furfural	3.93
	3	4.955	Hexyl alcohol	2.96
	4	6.490	Benzaldehyde	1.96
	5	6.935	2-Pentyl- furan	4.19
	6	8.040	2-Octenal	2.23
	7	8.775	Nonanal	4.78
	8	9.640	2-Nonenal	40.47
	9	10.125	Naphthalene	2.03
	10	10.335	Decanal	10.94
	11	11.760	2-Methyl-Naphthalene	5.11
	12	11.805	Undecanal	0.92
	13	12.590	2-Undecenal	0.98
	14	14.365	Hexadecane	9.95
180 °C	1	3.920	4-Hydroxy-3- methylbutanal	6.51
	2	4.445	Furfural	17.37

	3	5.275	2-Heptanone	0.93
	4	5.470	4-Methyl-hexanal	0.62
	5	6.375	2-Heptenal	0.63
	6	6.485	Methylfurfural	3.73
	7	6.760	1-Octen-3-ol	4.28
	8	6.935	Pentyl furan	2.31
	9	7.140	Octanal	0.57
	10	7.705	3-Octen-2-one	0.92
	11	8.035	2-Nonenal	43.19
	12	8.775	Nonanal	2.58
	13	9.295	3-Nonene-2-ketone	1.10
	14	10.335	Capraldehyde	4.59
	15	11.165	2-Undecenal	1.40
	16	11.275	6-Undecanone	0.87
	17	11.760	Methylnaphthalene	0.75
	18	11.805	Undecanal	0.53
	19	11.975	2,4-Decadienal	1.31
	20	14.365	Hexadecane	1.68
200 °C	1	2.010	3-Methyl-furan	6.31
	2	3.925	2-Ethyl-Cyclobutanol	0.74
	3	4.375	Furfural	27.31
	4	6.440	5-Methyl-2-fural	4.48
	5	6.700	Phenol	29.26
	6	7.550	2-Ethyl-1-Hexanol	0.65
	7	8.020	Acetic acid phenyl ester	1.18
	8	8.500	2-Methoxy-phenol	1.58
	9	8.645	Benzoic acid methyl ester	3.00
	10	8.775	Nonanal	1.33
	11	9.640	2-Nonenal	2.04
	12	10.335	Decanal	2.38
	13	10.410	2-Ethyl-benzofuran	1.02
	14	10.545	5-Hydroxymethylfurfural	1.42
	15	11.755	2-Methyl-naphthalene	2.94
220 °C	1	2.015	Methyl furan	0.49
	2	4.390	Furfuraldehyde	25.69
	3	6.450	5-Methyl furfural	2.79
	4	6.715	Phenol	15.74
	5	6.940	Acetic acid methyl furan	0.61
	6	7.380	Dichlorobenzene	0.90
	7	7.555	2-Ethyl hexanol	2.28
	8	8.025	Phenyl acetate	2.59
	9	8.655	Methyl benzoate	8.92
	10	8.780	Nonanal	4.07
	11	8.895	2-Methyl-coumarone	1.06
	12	10.130	Naphthalene	3.99
	13	10.340	Capraldehyde	4.48
	14	10.420	2-Ethyl-coumarone	2.30
	15	10.550	5-Hydroxymethylfurfural	1.08
	16	11.765	Methylnaphthalene	10.18
	17	11.815	Undecanal	0.65
	18	13.455	Dimethylnaphthalene	1.20

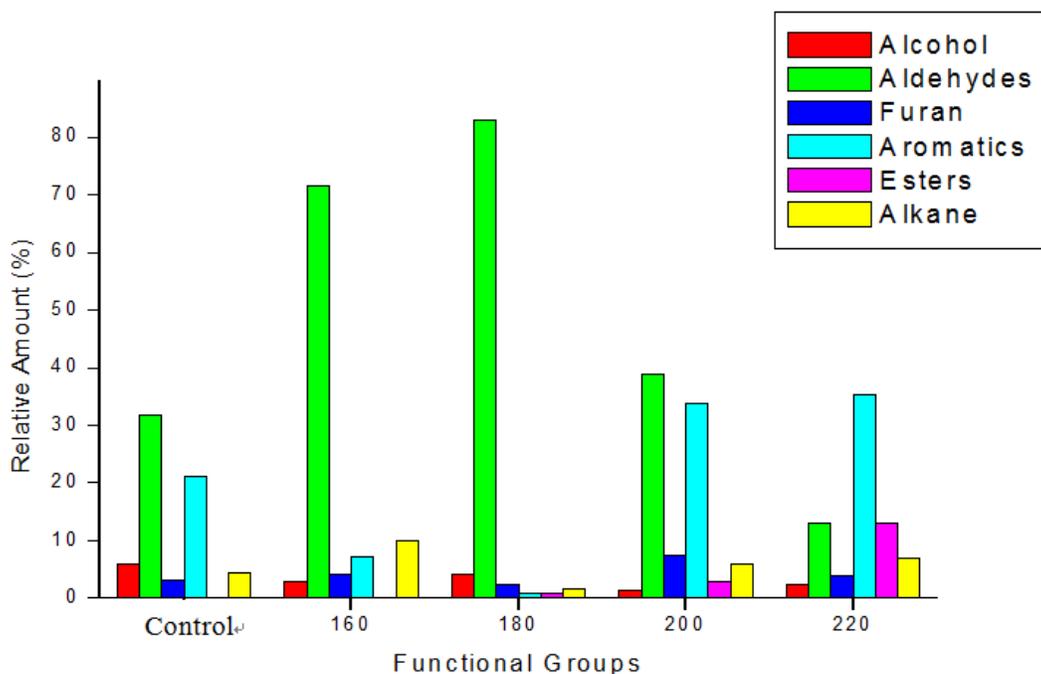


Fig. 3. VOCs emitted from wood samples

Figure 3 shows the various species of VOCs emitted from different wood samples. The different kinds of compounds in the samples included the most abundant compound, aldehyde, which initially increased, and then decreased with increasing temperatures. The content reached its maximum value of 83% at 180 °C.

The hemicelluloses content degraded the most, and the content of aldehydes decreased to 13% at 220 °C. The concentration of aromatic compounds increased with increasing temperature, which accounts for approximately 30% of the total volatiles when the temperature was relatively high. An increased content of esters appeared at temperatures above 180 °C. When the temperature was increased to 220 °C, its relative content was measured at approximately 13%. Moreover, there was a small amount of alcohol, furan, and alkane compounds that appeared after the thermal treatment at high temperatures.

Because aldehydes are the most abundant compounds in all wood samples, it is worth considering the species specificity for different wood samples. The main aldehydes emitted from untreated and thermally-treated poplar wood are shown in Fig. 4. Untreated poplar wood contained less aldehydes than thermally-treated wood. Furthermore, the main aldehydes were nonyl aldehyde, hydroxynonenal, and capraldehyde.

The main aldehyde present in poplar wood that was heat-treated at low temperatures (160 and 180 °C) was hydroxynonenal. When the temperature was increased, the concentration of furfuraldehyde increased quickly, and then it became the main aldehyde. Furfuraldehyde, the decomposition product of hemicelluloses, was enhanced at high treatment temperatures.

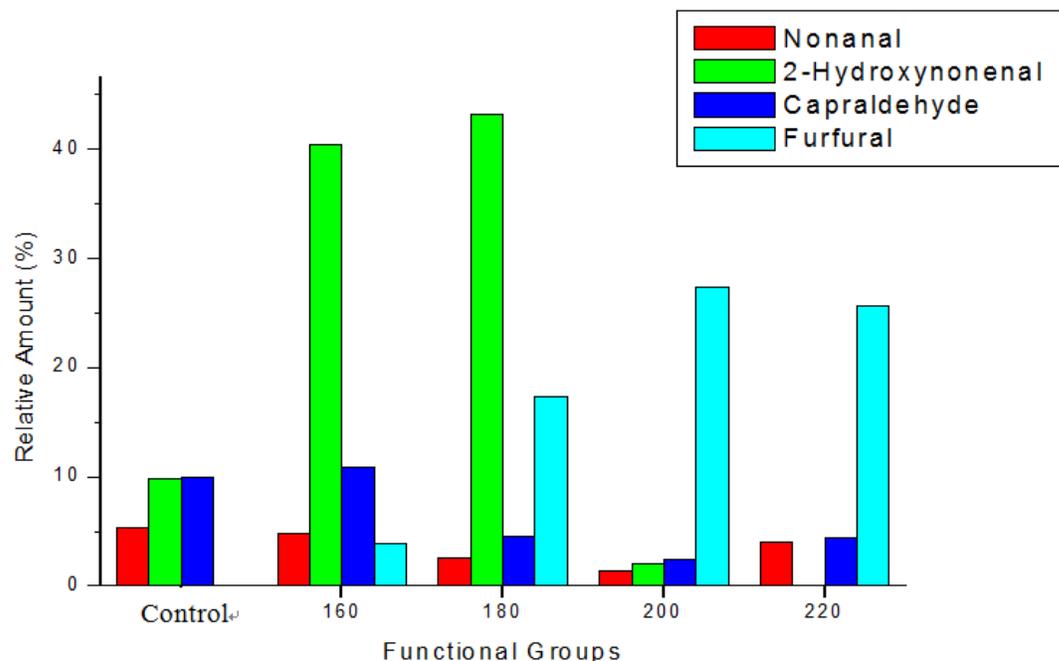


Fig. 4. Aldehydes from untreated and thermally treated poplar wood samples

CONCLUSIONS

1. Hemicelluloses initially degraded during the heat treatment process, causing a decrease in the holocellulose contents, while lignin was barely degraded. The content of acid-insoluble lignin increased with the increase in treatment temperature. In addition, a large number of extractives appeared during the treatment process.
2. Large quantities of carboxylic acids and aldehydes were emitted from untreated poplar wood samples, and the carboxylic acids disappeared with the increasing temperature. The amount of aldehydes reached a maximum of 83% at 180 °C. Meanwhile, the relative content of aromatic residues increased, and esters appeared when the temperature was increased to 180 °C, reaching a maximum of 13% at 220 °C.
3. The main aldehydes were nonanal, 2-nonenal, decanal, and furfural, at low treatment temperature phases; the 2-nonenal and decanal compounds were the most prevalent aldehydes at 50%. As the temperature increased, the content of furfural increased, reaching approximately 25% of the total aldehydes, and the content of 2-nonenal decreased and nearly vanished when the wood was heat-treated at 220 °C.

ACKNOWLEDGMENTS

The authors are grateful for the support of the Forestry Public Welfare Project Foundation of China (201404502) and the National Natural Science Foundation of China (31170533).

REFERENCES CITED

- Andreas, O. Rapp., and Sailer, M. (2001). "Oil heat treatment of wood in Germany-state of the art," in: *Review on Heat Treatments of Wood*, Proceedings of special seminar on heat treatments, 9 February 2001, Antibes, France. Office for Official Publications of the European Communities, Luxembourg, 47-64
- Cao, Y. J., Lv, J. X., Sun, Z. Y., Huang, R. F., Zhou, Y. D., and Wu, Y. Z. (2007). "Development and application of overseas heat-treated wood," *Scientia Silvae Sinicae* 43(2), 102-110. DOI: 10.11707/j.1001-7488.20070218
- Gao, N. B., Li, A. M., Quan, C., Du, L., and Duan, Y. (2013). "TG-FTIR and Py-GC/MS analysis on pyrolysis and combustion of pine sawdust," *Journal of Analytical & Applied Pyrolysis* 100, 26-32. DOI: 10.1016/j.jaap.2012.11.009
- GB/T 10741-2008. "Pulps – Determination of alcohol-benzene solubles," China Standards Press, Beijing, China.
- GB/T 747 (2003). "Fibrous raw material – Determination of acid-insoluble lignin," China Standards Press, Beijing, China.
- GB/T 2677.10 (1995). "Fibrous raw material – Determination of holocellulose," China Standards Press, Beijing, China.
- Hyttinen, M., Weijio, M. M., Kalliokoski, P., and Pasanen, P. (2010). "Comparison of VOC emissions between air-dried and heat-treated Norway spruce (*Picea abies*), Scots pine (*Pinus sylvestris*) and European aspen (*Populus tremula*) wood," *Atmospheric Environment* 44(38), 5028-5033. DOI: 10.1016/j.atmosenv.2010.07.018
- Kotilainen, R. (1999). "Changes in the chemical composition of Norway spruce (*Picea abies*) at 160 to 260 °C under nitrogen and air atmosphere," *Paperi ja Puu* 81(5), 384-388.
- Kotilainen, R. (2000). *Chemical Changes in Wood during Heating at 150 to 260 °C*, Ph.D. dissertation, University of Jyväskylä, Jyväskylä, Finland.
- Li, Y. J., and Tang, R. Q. (2008). "The preliminary study on high temperature heat-treatment technology of wood," *China Forest Products Industry* 35(20), 16-18.
- Liu, L. L., and Zhang, H. (2010). "Research and utilization of smoke heating treatment technology in China and Japan," *Journal of Zhejiang Forestry Science and Technology* 30(5), 76-81.
- Long, L., and Wang, J. L. (2007). "Aldehyde and terpene emissions from four species of wood at normal temperature," *China Wood Industry* 21(3), 14-17.
- Peters, J., Fischer, K., and Fischer, S. (2008). "Characterization of emission from thermally modified wood and their reduction by chemical treatment," *BioResources* 3(2), 491-502. DOI: 10.15376/biores.3.2. 491-502.
- Siesler, H. W., Ozaki, Y., Kawata, S., and Heise, M. (2002). *Near Infrared Spectroscopy: Principle, Instrument and Applications*, Wiley-VCH, Weinheim
- Temiz, A., Terzive, N., Jacobsen, B., and Eikenes M. (2006). "Weathering, water absorption and durability of silicon, acetylated and heat-treated wood," *Journal of Applied Polymer Science* 102(5), 4506-4513. DOI:10.1002/app.24878
- Tsuchikawa, S., and Siesler, H. W. (2003a). "Near-infrared spectroscopy monitoring of the diffusion process of deuterium-labeled molecules in wood. Part I. Softwood," *Applied Spectroscopy* 57(6), 667-674. DOI: 10.1366/000370203322005364
- Tsuchikawa, S., and Siesler, H. W. (2003b). "Near-infrared spectroscopy monitoring of the diffusion process of deuterium-labeled molecules in wood. Part II. Hardwood," *Applied Spectroscopy* 57(6), 675-681. DOI: 10.1366/000370203322005373

- Tumen, I., Ayddemir, D., Gunduz, G., Uner, B., and Cetin, H. (2010). "Changes in the chemical structure of thermally treated wood," *BioResources* 5(3), 1936-1944. DOI: 10.15376/biores.5.3.1936-1944
- Xie, Y. J., Liu, Y. X., and Sun, Y. X. (2002). "Heat-treated wood and its development in Europe," *Journal of Forestry Research* 13(3), 224-230. DOI: 10.1007/BF02871703
- Yonenobu, H., and Tsuchikawa, S. (2003). "Near-infrared spectroscopic comparison of antique and modern wood," *Applied Spectroscopy* 57(11), 1451-1453.

Article submitted: September 16, 2015; Peer review completed: January 9, 2016; Revised version received: February 1, 2016; Accepted: February 2, 2016; Published: February 29, 2016.

DOI: 10.15376/biores.11.2.3550-3560