Influence of Thermal Treatment Conditions on the Release of Volatile Organic Compounds from Bamboo

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Large quantities of volatile organic compounds (VOCs) are released from heat-treated bamboo during the manufacturing process of recombinant bamboo, which affects the environment and human health. In this study, bamboo was treated at 150 °C, 180 °C, and 210 °C for 3 h, and VOCs were collected every hour using a Tenax tube. The VOCs were analyzed with gas chromatography-mass spectrometry (GC-MS) to explore the effect of temperature and time on weight loss ratio, main components, and their relative proportions. The results showed that temperature considerably influenced weight loss ratio, and weight loss ratio increased rapidly at high temperature. Massive quantities of VOC were emitted during the first hour of treatment, and emissions decreased as the time and temperature increased. Terpenes were the primary component of the VOC emissions. Temperature and time exhibited minimal effects on the type of primary components, and the relative proportion of some components exhibited negligible changes over a range of temperatures and times.

Keywords: Recombinant bamboo; Thermal treatment; Volatile organic compounds

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INTRODUCTION

China has the largest resource of natural bamboo in the world. With recent advances in bamboo processing technology, a variety of new products are rapidly emerging. Recombinant bamboo products are commonly used in the bamboo industry. The manufacture of recombinant bamboo includes defibering, heat-treating, drying, gluing, laying-up, and hot-pressing (Qing and Yu 2009). Recombinant bamboo has good strength, density, water resistance, and environment resistance characteristics, and it is widely used for furniture, building materials, decorative panels, and other exterior timber products (He *et al.* 2014). Heat treatment is important during the production of recombinant bamboo, and the process improves the wood resistance to decay (*i.e.*, weather resistance) and dimensional stability. In addition, heat treatment changes the surface color to enhance the appearance of bamboo products. Massive quantities of volatile organic compounds (VOCs) are emitted during the thermal treatment process and contribute to environmental pollution that is harmful to human health.

Presently, studies investigating the VOC emissions from heat-treated wood have been reported locally and worldwide. There are many factors that affect the release of VOCs from treated wood, including the wood-related factors: species, location (*i.e.*, heartwood *vs*. sapwood) (Lljr *et al*. 2000; Dahlen *et al.* 2010), dimension, and time of harvest. Milota (2006) found that hydrocarbons and hazardous air pollutants, such as methanol and formaldehyde, varied considerably among different wood species. Graf *et al*. (2005) treated six different types of wood (*i.e.*, *Picea* (spruce), *Abies* (fir), *Larix* (larch), *Quercus* (oak), *Fraxinus* (ash), and *Robinia* (locust)) at 150 to 230 °C and concluded that the composition of the emissions was strongly dependent upon the wood species. The wood dimensions did not affect the VOC emissions from kiln-dried loblolly pine; however, the harvest season notably influenced the quantity of VOCs (Shmulsky 2000).

Process parameters, such as temperature, moisture content, and drying medium, influence the release of VOCs from wood (Banerjee *et al*. 1995; Danielsson and Rasmuson 2002). During high temperature drying, the thermal degradation of wood yields acetic acid, alcohols, aldehydes, furfurals, and carbon dioxide (Bridgwater *et al*. 1995). Schäfer and Roffael (2000) treated wood particles at 40 °C, 100 °C, and 150 °C for 3 h and found that formaldehyde emissions increased with rising temperature. In an analysis of the emissions of Norway spruce sawdust at three different temperature treatments (140, 170, and 200 °C), the concentration of VOCs and the amounts of monoterpene increased with increasing drying medium temperature (Granstrom 2003). Otwell *et al*. (2000) found that the release of methanol and formaldehyde were notably influenced by temperature. VOC emissions increase exponentially when the sawdust moisture content of treated wood is 15% (Granström and Månsson 2008). However, the effect of different drying mediums (*i.e.*, hot air or steam) on the quantity of monoterpene was negligible (Rupar and Sanati 2003).

Some VOCs from heat-treated wood, such as methanol and formaldehyde, are health hazards. Additionally, terpenes in VOCs can form atmospheric ozone and other photochemical oxidants in the presence of nitrogen oxides (Sillman 1999). The photo-oxidants are harmful to the respiratory system of humans (Burnett *et al*. 1999; Levy *et al*. 2001) and the lungs (Kampa and Castanas 2008), and it can be detrimental to vegetation by reducing photosynthesis (Heath 2003; Felzer *et al*. 2007).

According to statistics, there are huge production of recombinant bamboo in China, producing about 600,000 m^3 every year. Although there are no reports of VOCs emitted from heat-treated bamboo, it contains large quantities of sugar and starch; therefore, greater quantities of VOCs are expected to be released during processing. This study analyzed the effects of heat treatment conditions on the main components and quantities of VOC emissions from bamboo, providing theoretical guidance for further study, such as the selection of process parameters and utilization of VOC.

EXPERIMENTAL

Materials

Moso bamboo from the Zhejiang Province of China was used for the experiments. Samples were 3 to 4 years of age, with a moisture content of 5 to 6%, and were free of defects such as knots, cracks, and decay. Portions of cyan and yellow coloring on surface of the wood were removed, and the samples were cut into blocks with dimensions of 100 mm × 22 mm × 7 mm.

Methods

The bamboo samples were oven-dried to a constant weight at 103 ± 2 °C, and 5 samples were randomly selected, weighed, then input high temperature drying box with saturated steam that temperature had reached 150 °C, 180 °C, and 210 °C, respectively, heated for 1, 2, 3 h, and weighed again. The weight loss rate was obtained by the following formula, where W_1 is the weight before treatment, W_2 is the weight after treatment, and W is the weight loss ratio.

$$W = \frac{W_1 - W_2}{W_1} \times 100\% \tag{1}$$

During the heat-treatment process, VOCs were collected using a Tenax tube (Supelco Corporation, Bellefonte, PA, USA). A test hole measuring 25 mm in diameter was created for the release of gas emissions. For the complete collection of VOCs, a silicone tube was connected to the test hole, and the opposite end was connected to the VOC absorption device. The VOC absorption device included two gas bottles, a Tenax tube, and a double channel air sampler (TWA-300S, Yancheng Tianyue Instrument Co., LTD, Yancheng, China), which were all connected with silicone tubing. The first gas bottle contained ice to cool gas and lower the flow rate of VOCs. When the gas passed through the gas bottle with blue silica gel desiccant, it completely removed any water from the VOCs. The Tenax tube absorbed VOCs hourly. The double channel air sampler was connected at a flow rate of 200 mL/min. The VOC_{tot} released from the bamboo was calculated as the initial quality before bamboo treatment minus the residual.

The collected volatiles were removed from the Tenax tube using a purge & trap sample concentrator (Eclipse 4660, OI Analytical Corporation, College Station, TX, USA) and transferred into a RTx-5MS capillary column (film thickness: 30 m × 0.25 mm × 0.25 µm; Restek Corporation, Bellefonte, PA, USA) for gas chromatography-mass spectrometry (GC-MS; QP2010, Shimadzu, Tokyo, Japan). The temperature program was as follows: 40 °C for 1 min; 200 °C at a rate of 10 °C/min; 280 °C at 20 °C/min; and final hold for 5 min. The GC-MS analysis was conducted using the electron energy of 70 eV and a mass range of 40 to 650 m/e.

The relative proportion of the emission components was determined by the area normalization method.

RESULTS AND DISCUSSION

Weight Loss Ratio

Table 1 presents the weight loss ratio of bamboo at 150 °C, 180 °C, and 210 °C for 3 h during the thermal treatment. The weight loss ratio gradually decreased with increasing time and temperature. This decline in weight loss was attributed to the degradation of wood over the duration of heat treatment. The weight loss ratio was minimally affected by time at 150 °C, but notable affects were observed at a higher temperature (210 °C). At 150 °C, the weight loss ratio was only 0.22% at the beginning of thermal treatment; however, when the temperature was raised to 210 °C, the weight loss ratio dramatically increased to 5.65%.

Table 1. Weight Loss Ratio of Bamboo at Different Temperatures for 3 h

Temperature (°C)	Weight Loss Ratio (%)			
	Treatment Time			Total
	1 h	2 h	3 h	
150	0.22	0.15	0.12	0.49
180	0.92	0.8	0.72	2.41
210	5.65	3.87	2.48	11.54

The total weight loss ratio of the samples was 0.49%, 2.41%, and 11.54% for the 150 °C, 180 °C, and 210 °C heat treatments, respectively. Thus, heating contributed to the release of VOCs. The effect of temperature on the VOC emissions agreed with previous reports (Granström and Månsson 2008).

Relative Proportion of Compounds

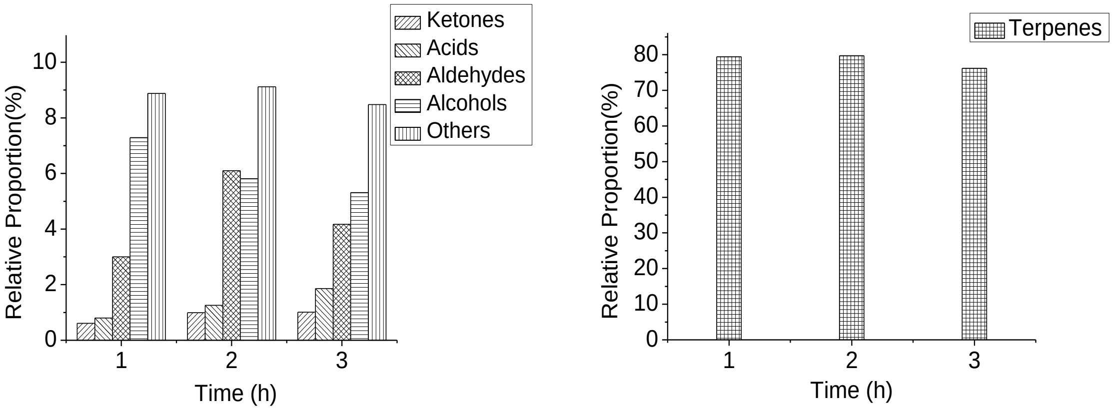
Figures 2, 3, and 4 show the relative proportions (% of total emission) of different compounds emitted from heat-treated bamboo at 150 °C, 180 °C, and 210 °C for 3 h. Table 2 presents the relative content of the main compounds, including terpenes, aromatic hydrocarbon, alkanes, aldehydes, and acids. Ketone emissions were minimal, followed by acids, aldehydes, alcohols, and terpenes, in ascending order.

The effect of temperature on the production of ketones, acids, aldehydes, and alcohols ((Fig.2(a), Fig.3(a), Fig.4(a)) was not obvious. Alcohols were emitted in a much higher proportion, increasing in quantity from 150 °C to 180 °C, and then declining at 210 °C. The amounts of methanone and ethanone were small, and these compounds were absent under certain conditions.

The acids were primarily oxalic acid and acetic acid, as well as a small amount of benzoic acid. Benzoic acid may be produced by oxidation of toluene, and benzaldehyde is the middle product, which both were collected in a small amount. Previous research on acid emissions from hardwoods during heat-treatment has shown a high amount of acetic and formic acids (Risholm-Sundman *et al.* 1998), and a large quantity of acetic acid emissions have also been reported by McDonald *et al.* (2004). Nonanal, decanal, benzaldehyde octanal, dodecanal, and 7-hexadecenal were the major aldehyde compounds. Nonanal accounted for the major proportion, followed by decanal (Table 2). However, 2-tridecenal, 2-nonenal, and furfural were also detected. Several different types of alcohols were detected, including cyclohexanol, 1-decanol, octanol, nonadecanol, and ethanol. The relative content of cyclohexanol was the highest at 150 °C, decreasing with the increase of temperature (Table 2). In some studies, the primary aldehydes and alcohols were methanol, formaldehyde, pentanal, and hexanal (Su *et al.*1999; Otwell *et al.* 2000; Barry and Corneau 2006; Milota 2006). Formaldehyde was too volatile to be collected by the Tenax tube in this study.

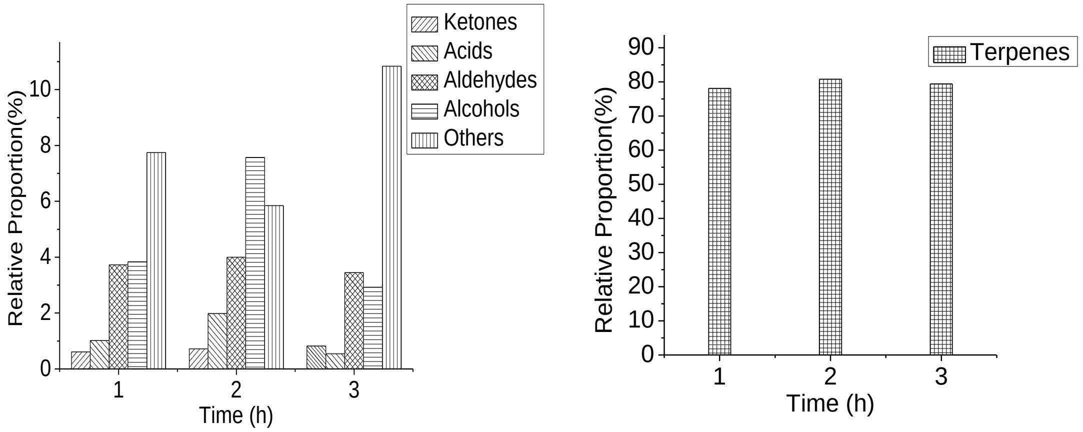
Terpenes (Figs. 2(b), 3(b), and 4(b)) constituted the largest proportion of VOC emissions from treated bamboo (approximately 80%). The effect of temperature and time on the composition of terpenes was negligible. As can be seen in Table 2, species and amount of terpenes dominated majority of all compounds. The major terpene compounds were cedr-8-ene, α-copaene, β-cedrene, D-limonene, cis-thujopsene, longifolene, α-pinene, β-myrcene, and *γ*-muurolene, of which the relative content of cedr-8-ene was about 10%. Sesquiterpenes $(C_5H_8)_3$, such as α-cedrene, α-copaene, β-cedrene, cis-thujopsene, and longifolene, accounted for the largest proportion of terpenes, while the monoterpenes$(C_5H_8)_2$, including D-limonene, α-pinene, and β-myrcene, were minimally represented.

A study on monoterpene emissions showed their dominance during the heat-treatment of wood (Milota 2000; Banerjee 2001). Similar results were reported for heat-treated eucalyptus wood (Granström 2009). The temperature of the heat-treatment exhibited a notable effect on the terpene content. The relative proportion of terpenes was around 70% per hour at 150 °C and 180 °C, but when the temperature rose to 210 °C, the



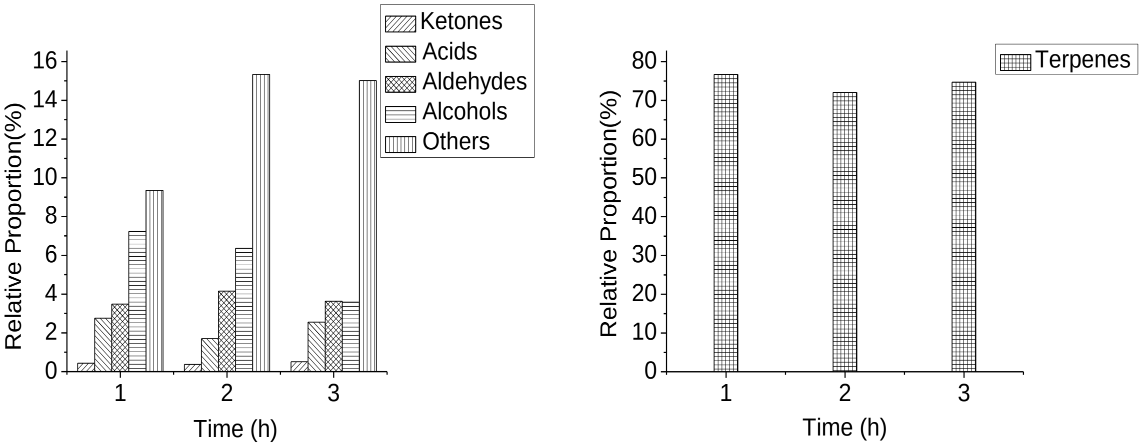
(a) (b)

Fig. 2. Relative proportion (%of total emission) of the compounds emitted from heat-treated bamboo at 150 °C



(a) (b)

Fig. 3. Relative proportion (% of total emission) of the compounds emitted from heat-treated bamboo at 180 °C



(a) (b)

Fig. 4. Relative proportion (% of total emission) of the compounds emitted from heat-treated bamboo at 210 °C

Table 2. Relative Proportions (% of total emission) of Main Individual Compounds at 150 °C, 180 °C, and 210 °C for 3 h

Compound	Relative proportion (%)										
	150℃				180℃				210℃		
	1h	2h	3h		1h	2h	3h		1h	2h	3h
cedr-8-ene	12.57	12.3	12.7		9.85	8.7	11.81		12.45	12.47	15.34
α-copaene	8.04	8.15	8.43		6.02	5.37	7.14		8.08	9.1	9.88
β-cedrene	5.28	5.36	5.4		4.11	3.61	4.94		5.37	2.47	6.4
D-limonene	2.85	2.14	1.64		4.22	3.94	3.03		1.5	2.58	3.75
α-pinene	2.69	1.92	1.45		2.85	1.91	1.71		1.13	1.53	1.18
cis-Thujopsene	2.44	2.39	2.5		2.05	1.98	2.51		2.54	2.78	3.06
Longifolene	1	1.04	1.08		1.06	1.09	1.21		1.1	-	1.28
Dodecane	1.54	1.14	1.16		0.88	0.99	1.32		1.13	1.58	1.29
Phenol	0.25	0.25	1		2.29	1.98	1.48		0.14	0.01	-
Nonanal	1.07	1.42	1.03		1.03	1.25	0.91		0.92	1.1	0.9
Naphthalene	1.28	1.34	1.36		1.24	1.54	1.3		1.31	1.67	1.28
Toluene	0.43	0.29	0.29		0.51	0.41	0.39		0.31	0.44	0.32
Decanal	0.69	0.79	0.65		0.57	0.85	0.66		0.64	0.79	0.55
Cyclohexanol	0.86	0.93	0.96		0.42	0.9	0.13		0.97	0.13	0.11
3-Carene	1.2	0.8	0.6		0.87	0.75	0.53		0.47	0.55	0.43
Ethylbenzene	0.25	0.2	0.27		0.27	0.18	0.16		0.42	0.37	0.3
Undecane	0.84	0.89	0.1		0.05	0.11	0.12		0.91	-	0.87
1-Decanol	0.82	0.83	0.88		0.7	-	1.16		0.85	1.48	0.39
Oxalic acid	0.46	0.31	0.44		0.29	0.3	-		0.82	0.61	0.21
Benzaldehyde	0.38	0.37	0.22		-	0.5	0.27		-	-	0.24
Other compounds	55.06	57.14	57.84	100	60.72	63.64	59.22	100	58.94	60.34	52.22

terpene content was lower. For different temperature, the treatment time had disparate influences on the production of terpenes. At 150 °C, the ratio of terpenes increased steeply as the time increased. This trend was initially slight and decreased at 180 °C. In contrast, the proportion of terpenes initially increased and then decreased at 210 °C.

Other compounds, including aromatic hydrocarbon, alkanes, and esters, were detected. Toluene, o-cymene, and o-xylene were the primary aromatic hydrocarbons, which are highly carcinogenic (Yazar *et al.* 2011). They have rarely been reported as being present during heat treatment of wood. Alkanes, including dodecane, tetradecane, and pentadecane, accounted for a considerable large proportion. There are also reports of alkanes in some studies. Ethane are produced by biomass burning (Rudolph 1995), whereas alkanes and esters, come from the biogenic emissions (Kesselmeier and Staudt 1999). Whether it is high temperature or low temperature during heat-treated wood, aromatic hydrocarbon and alkanes products are not mentioned in most of the research. However, during the process of high temperature treatment of bamboo, a large amount of aromatic hydrocarbon and alkanes are found, which may be due to the high temperature or different species.

There are three reasons for differences in the primary constituents and their concentrations in heat-treated bamboo. First, the temperature necessary to produce thermal degradation is fairly dependent on wood species. Graf *et al*. (2005) showed that softwood produced an abundant quantity of terpenes. Risholm-Sundman *et al*. (1998) concluded that acetic acid was the primary substance emitted from hardwood. Bamboo is comprised of cellulose, hemicelluloses, lignin, and extractives at varying levels, depending on the type of wood (*i.e*., hardwood or softwood). Furthermore, if the test material is too small, some emissions will be lower than the detection limit. Additionally, some polar compound emissions, such as methanol, ethanol, formic acid, and acetic acid, are soluble in water. The saturated steam treatment medium could have absorbed the polar compounds, leading to a reduction in the acid and alcohol contents. The use of bamboo as a recombinant material warrants further study.

CONCLUSIONS

1. Weight loss ratio from heat-treated bamboo was found to be strongly related to temperature. As the temperature increased, a greater quantity of thermal degradation compounds was produced. However, there was no effect of temperature on the relative proportion of these compounds. With increasing temperature, some compounds increased in concentration (ester), while others decreased (terpenes).
2. Time exhibited a less apparent effect on weight loss ratio at low temperatures, but notably declined at high temperature. The relative proportions of the emissions were mostly unaffected by time.
3. In China, the application of bamboo is becoming widespread. The adverse effects of VOCs from heat-treated bamboo on the environment must be addressed. The results of this study contribute a selection of appropriate process parameters to reduce the quantity of VOC emissions.

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