

**INVESTIGATION OF VOLATILE PRODUCTS RELEASED  
DURING VACUUM HEAT TREATMENT OF LARCH WOOD**

ZHE WANG, BAILING SUN, JUNLIANG LIU  
CHINESE ACADEMY OF FORESTRY, RESEARCH INSTITUTE OF WOOD INDUSTRY  
BEIJING, P. R. CHINA

(RECEIVED JULY 2016)

**ABSTRACT**

The aim of this study was to investigate the components of volatile by-products released at different treatment temperatures. For this objective, the aldehydes and ketone were trapped in DNPH solution and the aldehyde and ketone derivatives were analyzed by HPLC. The acids and alcohols were trapped in deionized water and analyzed by HPLC and GC. The other volatile organic compounds were trapped on Tenax TA tubes and analyzed by GC-MS. The results showed that there was an increasing trend in the concentrations of aldehydes, acids, and alcohols with the increasing treatment temperature. The heat treatment at higher temperature resulted in more kinds of volatile organic compounds.

**KEYWORDS:** Larch wood, vacuum heat treatment, aldehydes, acids and alcohols, VOC, HPLC, GC, TD-GC-MS.

**INTRODUCTION**

Larch (*Larix kaempferi*) is one of the most important plantation tree species in northeast China. Larch wood is widely used for outdoor applications because of its high hardness, beautiful texture, and strong decay resistance (Li 2006). However, untreated larch wood exposed to the weather outside has a disadvantage due to warp deformation, which is a limitation for its utilization. Thus, it is indispensable to reduce its hygroscopicity and improve its dimensional stability prior to the manufacturing process. Heat treatment is a promising method for this purpose.

Wood heat treatment technology has been developed for nearly half a century and up to now there are several different industrial heat treatment processes: thermowood in Finland by the use of steam (Viitanen et al. 1994), Platowood in the Netherlands with a combination of steam and heated air (Tjeerdsma et al. 1998), oil heat treatment in Germany (Rapp 2001).

In recent years, the thermo-vacuum treatment has been considered as a novel thermal modification technology of wood. Damage to the mechanical properties of wood is less pronounced

during thermo-vacuum treatment compared to other thermal modification technologies because the volatile compounds that contribute to accelerated degradation of polysaccharides in the wood cell wall are removed through the vacuum (Allegratti et al. 2012, Ferrari et al. 2013). However, the mechanisms of thermo-vacuum treatment have not been comprehensively studied.

The aim of this study was to better understand the wood thermodegradation mechanisms during thermo-vacuum treatment by the investigation of the components of volatile by-products of wood. For this purpose, the volatile by-products induced during heat treatment were collected and analyzed by HPLC and GC-MS.

## MATERIAL AND METHODS

### Materials

Larch (*Larix kaempferi*) wood was obtained from Qingyuan in Liaoning Province, China. Larch wood was sawn and processed with a planer to obtain specimens with a length of 400 mm (longitudinal), a width of 40 mm (radial), and a thickness of 40 mm (tangential). The specimens were free of macroscopic defects such as knots and splits. Fifteen samples were used for each of heat treatment.

### Methods

Prior to heat treatment, all specimens were oven-dried at  $103 \pm 2^\circ\text{C}$  to 0% moisture content and then placed in a vacuum pressure furnace. Heat treatment was conducted at the temperatures of 160, 200, and  $240^\circ\text{C}$  under  $-0.09\text{MPa}$ . When the vacuum pressure was dropped to the atmospheric pressure, the air released during heat treatment in the furnace was sampled for 30 min at  $500\text{ ml}\cdot\text{min}^{-1}$  by a pump.

Three parallel sampling trains were used to collect different volatile degradation products as following:

- (1) acidified 2, 4-dinitrophenylhydrazine (DNPH) was used for sampling for aldehydes (EPA method 0011 1990),
- (2) acids (formic acid, acetic acid, propionic acid, and butanoic acid) and alcohols (methylalcohol, ethylalcohol, n-propyl alcohol, and n-butanol) were collected in deionized water,
- (3) other volatile organic compounds were trapped on Tenax TA tube.

According to McDonald et al. (2002), the DNPH derivatives were prepared for further analysis. The separation of derivatives was performed on a C18 column (SUPELCO L LC-18,  $15\text{ cm}\times 4.6\text{ mm}$ ,  $5\ \mu\text{m}$ ) connected to a Shimadzu HPLC system. Samples were eluted by a mobile phase: acetonitrile/water (60/40) at the constant flow rate of  $1\text{ ml}\cdot\text{min}^{-1}$ . The DNPH derivatives were detected using UV absorbance at 360 nm. Aldehydes were quantified by using calibration curves derived from a series of standard solutions (SUPELCO, TO11/IP-6A Aldehyde/Ketone-DNPH Mix).

According to Long and Lu (2008), the acids (formic acid, acetic acid, propionic acid, butanoic acid) were quantified using calibration curves derived from a series of standard solutions by HPLC and the alcohols (methylalcohol, ethylalcohol, n-propyl alcohol, and n-butanol). The Tenax TA sampling tubes were thermally desorbed by a thermodesorber (TD) (Markes, UK) connected to a GC/MS (Agilent 7890A/5975C). The tube desorption was held at a temperature of  $300^\circ\text{C}$  for 30 min. GC-MS analysis were performed on a Agilent 7890A/5975CGC-MS equipped with a DB-5MS capillary column (30 m,  $0.25\text{ mm i.d.}$ ,  $0.25\ \mu\text{m}$  film thickness), using helium as carrier gas.

The chromatographic conditions were as follows: injector temperature 280°C; oven initial temperature 50°C (5 min); temperature increase rate 10°C·min<sup>-1</sup>; final temperature 290°C (15 min). A split ratio of 1:30 was used. The mass detector operated with ionization for electron impact (70eV) for a scan range of 30–500 m·z<sup>-1</sup>. The volatile organic compounds were identified by comparing their EI mass spectra with library spectra (NIST 2010) and the concentrations of compounds were calculated using the area normalization method.

## RESULTS AND DISCUSSION

### Aldehydes and ketone)

The concentrations of the various aldehydes in the sampled air are shown in Tab. 1. The total concentrations of aldehydes increased from 54.99 to 164.08 mg·m<sup>-3</sup> as the treatment temperature rose. The major components were formaldehyde, acetaldehyde, acrolein, and acetone in the detected aldehydes and ketone. The concentration of formaldehyde was from 15.18 to 59.17 mg·m<sup>-3</sup>, acetaldehyde was from 8.43 to 39.32 mg·m<sup>-3</sup>, acrolein was from 11.30 to 19.77 mg·m<sup>-3</sup>, acetone was from 15.32 to 30.27 mg·m<sup>-3</sup> (Tab. 1). The formation of aldehydes could result from the oxidative degradation of unsaturated lipids during the heat treatment (Makowski et al. 2005).

Tab.1: The concentrations of aldehydes at different treatment temperature.

Compounds	Concentration (mg·m <sup>-3</sup> )		
	160°C	200°C	240°C
Formaldehyde	15.18	18.33	59.17
Acetaldehyde	9.83	8.43	39.32
Acrolein	11.30	15.83	19.77
Acetone	15.32	21.02	30.27
Propionaldehyde	0.30	0.42	1.73
Crotonaldehyde	0.70	0.30	2.07
Butyraldehyde	0.22	0.37	0.78
Benzaldehyde	0.42	0.20	1.07
Isovaleraldehyde	0.47	0.50	1.15
Valeraldehyde	0.35	0.53	1.18
o-Tolualdehyde	0.45	1.63	1.80
Hexaldehyde	1.45	1.63	5.77
Total	55.99	69.19	164.08

In previous studies (Back and Allan 2000, Piispanen and Saranpaa 2002, Svedberg et al. 2004), results indicated that triglycerides and free fatty acids in the dry wood can be decomposed to aldehydes. Such reactions can be either enzyme-catalysed or occur through autoxidative reactions (Makowski et al. 2005). Schäfer and Roffael (2000) and Long and Lu (2008) reported that the thermal degradation of wood can lead to formaldehyde emission from polysaccharides. Under acidic conditions hexose degraded to hydroxymethyl furfural, which decomposed to formaldehyde and furfural (Fig. 2). In addition, under acidic conditions the degradation of lignin can also lead to formaldehyde emission (Schäfer and Roffael 2000) (Fig. 3). Acetaldehyde and acetone derived from the degradation of hemicelluloses (Omrani et al. 2009). Benzaldehyde and o-Tolualdehyde derived from the degradation of lignin because these two components contained

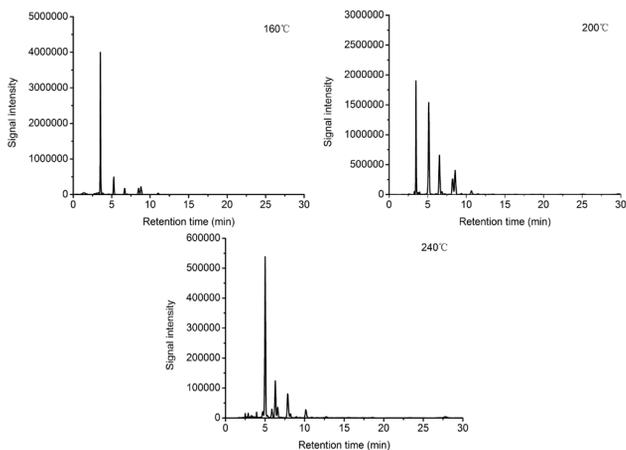


Fig. 1: Chromatograms of released aldehydes products of larch wood during heat treatment.

aromatic ring structure. In summary, the aldehyds and ketone was as a result of the degradation of extracts, hemicelluloses and lignin. The result that concentration of aldehyds and ketone was higher at higher temperature was caused by two reasons. On the one hand, with the increase of temperature, higher degree of degradation of extracts and hemicelluloses resulted in the increase of concentration of aldehyds and ketone. On the other hand, lignin was relatively stable at low temperature and gradually degraded as the treatment temperature rose. Furthermore, more acids derived from the degradation of hemicelluloses can also lead to accelerated degradation of lignin at higher temperature, which resulted in the increase of concentration of aldehyds and ketone.

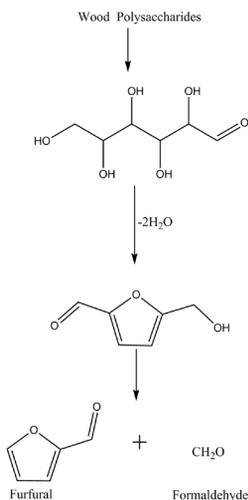


Fig. 2: Possible formation of formaldehyde from wood polysaccharides.

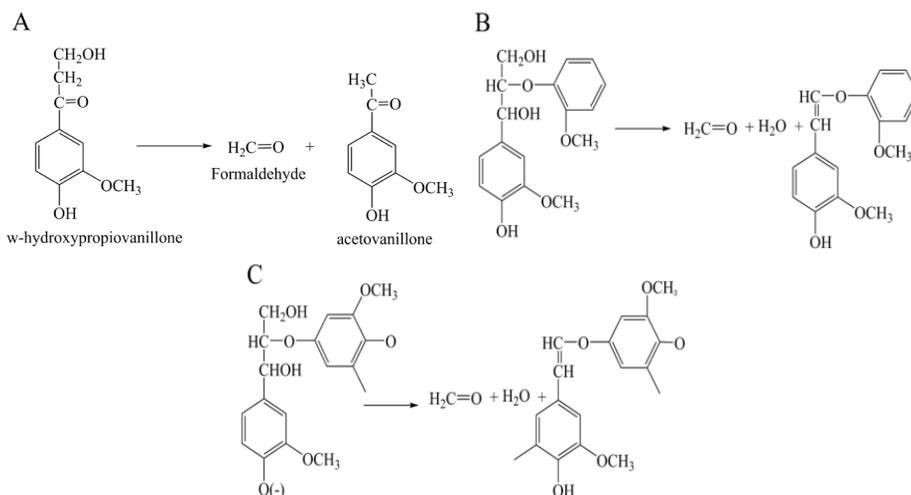


Fig. 3: Three possible pathway for the formation of formaldehyde from lignin.

### Acids and alcohols

The concentrations of the acids and alcohols in the sampled air are shown in Tab. 2. The main components were formic acid and acetic acid in the detected acid samples and methyl alcohol and n-propyl alcohol in the detected alcohol samples. The concentrations of formic acid, acetic acid, methyl alcohol and n-propyl alcohol increased from 1.49 to 2.69 mg·m<sup>-3</sup>, 17.37 to 31.85 mg·m<sup>-3</sup>, 29.45 to 38.22 mg·m<sup>-3</sup> and 14.27 to 19.09 mg·m<sup>-3</sup> (Tab. 2), respectively.

Tab. 2: The concentrations of acids and alcohols at different treatment temperature.

Compounds	Concentration (mg·m <sup>-3</sup> )		
	160°C	200°C	240°C
Formic acid	1.49	2.99	2.69
Acetic acid	17.37	20.19	31.85
Propionic acid	-	-	0.74
Butanoic acid	0.31	0.21	1.04
Methyl alcohol	29.45	35.09	38.22
Ethyl alcohol	3.83	3.55	5.53
n-Propyl alcohol	14.27	19.02	19.09
n-Butanol	7.56	3.85	8.77

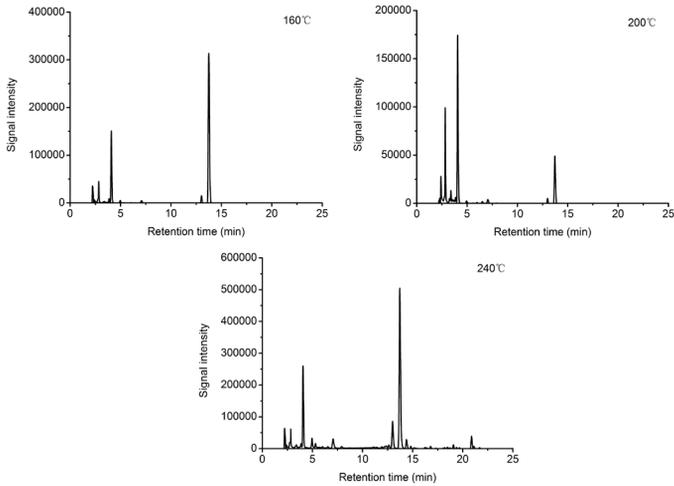


Fig. 4: Chromatograms of released acids of larch wood during heat treatment.

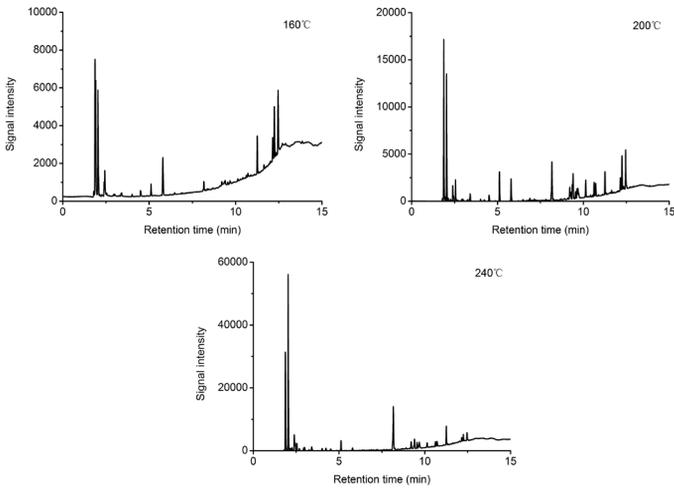


Fig. 5: Chromatograms of released alcohols of larch wood during heat treatment.

**Volatile organic compounds on Tenax TA** major aliphatic carboxylic acids (formic acid and acetic acid) formed during heat treatment resulted from hemicelluloses degradation (Candelier et al. 2013). The formation of formic acid and acetic acid originated from formate esters in the wood and acetate groups in the methylglucuronoxylan, respectively (Sundqvist et al. 2006). The formation of methylalcohol resulted from de-O-methylation of 4-O-methyl-D-glucuronic acid (Kosik et al. 1968, McDonald et al. 2002). The concentrations of aliphatic carboxylic acids increased with the increase of treatment temperature, which resulted from higher degradation degree. The volatile organic compounds trapped on Tenax TA at different treatment temperatures were identified by thermodesorption-GC-MS. The identities of the ten principal compounds released during heat treatment and their relative abundances are shown in Tab. 3.

There were 48, 63 and 68 kinds of the volatile organic compounds identified on the Tenax TA, respectively (not shown in Tab. 3).

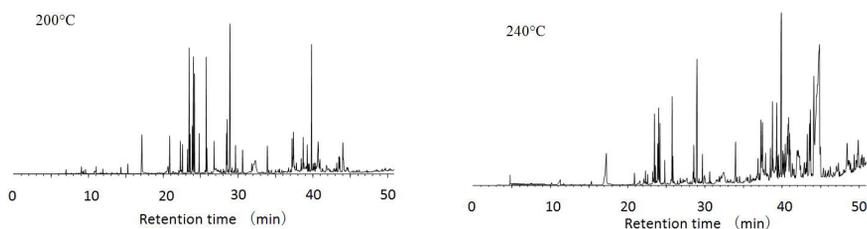


Fig. 6: Chromatograms of degradation products identified by TD-GC-MS.

Tab. 3: The relative contents of VOC at different treatment temperature.

Peak	Compounds	Retention time (min)	Relative contents (%)		
			160°C	200°C	240°C
1	Furfural	17.07	0.44	3.00	2.69
2	$\alpha$ -Pinene	20.96	20.78	8.63	6.53
3	$\beta$ -Pinene	22.63	10.06	2.83	0.56
4	(1S)-3,7,7-Trimethyl-bicyclo[4.1.0]hept-3-ene	23.48	8.18	-	1.62
5	Limonene	24.02	2.27	5.17	1.80
6	$\beta$ -Phellandrene	24.16	1.71	4.01	1.23
7	1-Methyl-4-(1-methylethylidene)-cyclohexene	25.72	0.97	5.69	1.77
8	Decamethyl-cyclopentasiloxane	25.87	2.16	-	-
9	p-Menth-1-en-8-ol	28.88	2.52	9.47	4.79
10	Dodecamethyl-cyclohexasiloxane	30.62	5.22	1.17	0.31
11	1,3,6,10-Cyclotetradecatetraene, 3,7,11-trimethyl-14-(1-methylethyl)-, [S-(E,Z,E,E)]-	32.41	-	2.92	0.72
12	Vanillin	36.88	-	-	2.16
13	Cedrene	37.44	4.41	2.67	1.66
14	$\alpha$ -Muurolene	39.25	0.60	1.37	2.17
15	$\delta$ -Cadinene	39.80	1.48	5.49	-
16	$\alpha$ -Calacorene	40.67	-	0.22	3.69
17	Abietatriene	42.09	-	-	2.27
18	tau.-Muurolol	43.67	-	-	2.33
19	$\alpha$ -Cadinol	44.01	-	1.79	4.62
20	Manool	44.46	-	-	19.49
21	Naphthalene, 1,6-dimethyl-4-(1-methylethyl)-	44.70	-	0.24	-

Results obtained clearly indicated that heat treatment resulted in more kinds of volatile organic compounds at the higher temperature (200°C and 240°C). The more kinds of volatile organic compounds could result from the more severe degradation of wood compositions at the higher treatment temperature. The main volatile organic compounds found on the Tenax TA traps were  $\alpha$ -pinene,  $\beta$ -pinene, limonene, furfural and cedrene. The presence of  $\alpha$ -pinene,  $\beta$ -pinene and limonene were expected in the volatile organic compounds during heat treatment

(Tab. 3) since these monoterpenes are common constituents of pine (McDonald et al. 2002). Peters et al. (2008) reported that the formation of furfural was the result of hemicelluloses thermal degradation. Vanillin resulting from lignin degradation was detected at 240°C (Tab. 3). In previous studies, Candelier et al. (2013) indicated that vanillin was the most abundant product of lignin phenolic degradation during heat treatment. There was a trace amount of this product below 200°C of treatment temperature. Our results are in good agreement with these researchers' findings.

## CONCLUSIONS

Volatile products released during vacuum heat treatment of larch wood were investigated by HPLC and GC-MS. In this study, the total concentrations of aldehydes and ketone showed a tendency of rising with the increase of treatment temperature. The total concentrations of aldehydes and ketone increased from 54.99 to 164.08 mg·m<sup>-3</sup>. The formaldehyde, acetaldehyde, acrolein, and acetone were the four major components in the detected aldehydes and ketone. Acetic acid was the most abundant product in the detected acid samples and methylalcohol was the most abundant product in the detected alcohol samples. The concentrations of acetic acid and methylalcohol increased from 17.37 to 31.85 mg·m<sup>-3</sup> and from 29.45 to 38.22 mg·m<sup>-3</sup>, respectively. The  $\alpha$ -pinene,  $\beta$ -pinene, limonene and furfural were the main components in the volatile organic compounds trapped on Tenax TA. More kinds of volatile organic compounds were detected as the treatment temperature rose. The higher treatment temperature could result in the more severe degradation of wood compositions.

## ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (Grant No. 31370558).

## REFERENCES

1. Allegretti, O., Brunetti, M., Cuccui, I., Ferrari, S., Nocetti, M., Terziev, N., 2012: Thermo-vacuum modification of spruce (*Picea abies* Karst.) and fir (*Abies alba* Mill.) wood, *Bioresources* 7(3): 3656-3669.
2. Back, E.L., Allan, L.H., 2000: Pitch control, wood resin and deresination, Tappi Press. Atlanta, GA Pp 151-183.
3. Candelier, K., Dumařay, S., Pétrissans, A., Pétrissans, M., Kamdem, P., Gérardin, P., 2013: Thermodesorption coupled to GC-MS to characterize volatiles formation kinetic during wood thermodegradation, *Journal of Analytical and Applied Pyrolysis* 101(5): 96-102.
4. Ferrari, S., Allegretti, O., Cuccui, I., Moretti, N., Marra, M., Todaro, L., 2013: A reevaluation of Turkey oak wood (*Quercus cerris* L.) through combined steaming and thermo-vacuum treatments, *Bioresources* 8(4): 5051-5066.
5. Kosik, M., Herain, J., Domansky, R., 1968: Pyrolysis of beech wood at low temperatures. IV. Basic views on the formation of volatile products, *Holzforschung* 20: 56-59.

6. Li, J., 2006: The study of wood protection, Science Press. Beijing.
7. Long, L., Lu, X.X., 2008: VOC emission from Chinese fir (*Cunninghamia lanceolata*) drying, *Scientia Silvae Sinicae* 44(1): 107-116. (in Chinese).
8. Makowski, M., Ohlmeyer, M., Meier, D., 2005: Long-term development of VOC emissions from OSB after hot-pressing, *Holzforschung* 59(5): 519-523.
9. McDonald, A.G., Dare, P.H., Gifford, J.S., Steward, D., Riley, S., 2002: Assessment of air emissions from industrial kiln drying of *Pinus radiata* wood, *Holz als Roh-und Werkstoff* 60(3): 181-190.
10. Omrani, P., Masson, E., Pizzi, A., Mansouri, H.R., 2009: Emission gases in linear vibration welding of wood, *Journal of Adhesion Science and Technology* 23(1): 85-94.
11. Peters, J., Fischer, K., Fischer, S., 2008: Characterization of emissions from thermally modified wood and their reduction by chemical treatment, *Bioresources* 3(2): 491-502.
12. Piispanen, R., Saranpaa, P., 2002: Neutral lipids and phospho-lipids in Scots pine (*Pinus sylvestris*) sapwood and heart-wood, *Tree Physiology* 22(9):661-666.
13. Rapp, A., 2001: Review on heat treatments of wood, COST ACTION E22-Environmental optimization of wood protection. Proc Special Seminar in Antibes, France, European Commission Research Directorate, Political Co-Ordination and Strategy, Brussels, Belgium.
14. Schäfer, M., Roffael, E., 2000: On the formaldehyde release of wood, *European Journal of Wood and Wood Products* 58(4): 259-264.
15. Sundqvist, B., Karlsson, O., Westermark, U., 2006: Determination of formic-acid and acetic acid concentrations formed during hydrothermal treatment of birchwood and its relation to colour, strength and hardness, *Wood Science and Technology* 40(7): 549-561.
16. Svedberg, U.R.A., Hogberg, H.E., Hogberg, J., Galle, B., 2004: Emission of hexanal and carbon monoxide from storage of wood pellets, a potential occupational and domestic hazard, *Annals of Occupational Hygiene* 48(4): 339-349.
17. Tjeerdsmas, B., Boonstra, M., Pizzi, A., Tekely, P., Militz, H., 1998: Characterisation of thermally modified wood: Molecular reasons for wood performance improvement, *Holz als Roh-und Werkstoff* 56(3): 149-153.
18. Viitanen, H., Jamsa, S., Paajanen, L., Nurmi, A., Viitaniemi, P., 1994: The effect of heat treatment on the properties of spruce, Technical Report IRG/WP 94-40032, International Research Group on Wood Protection, Stockholm, Sweden.

ZHE WANG, BAILING SUN, JUNLIANG LIU\*  
CHINESE ACADEMY OF FORESTRY  
RESEARCH INSTITUTE OF WOOD INDUSTRY  
BEIJING 100091  
P. R. CHINA

Corresponding author: liujunliang@caf.ac.cn  
PHONE: +86-010- 62889477

