

論文 (Original article)

Effect of drying methods on volatile organic compound emission from sugi wood

Atsuko ISHIKAWA^{1)*}, Tatsuro OHIRA²⁾, Isao KOBAYASHI¹⁾,
Kohta MIYAMOTO³⁾, Shin-ichiro TOHMURA³⁾, and Akio INOUE³⁾

Abstract

Recently, as demand for dried lumber has been increasing in Japan, several drying methods have been applied to sugi (*Cryptomeria japonica* D. Don) wood. Meanwhile, VOCs (volatile organic compounds) released from wood and wood products have become an issue of public concern. The purpose of this study is to investigate the effects of drying method on VOC emissions from sugi wood. Sugi specimens were treated with high-temperature-, radio frequency / vacuum (RF/V)-, and air-drying. Emissions of VOCs and aldehydes from dried wood were measured using the small chamber method (JIS A1901), and analyzed by gas chromatography / mass spectroscopy (GC/MS) and high performance liquid chromatography (HPLC). The emissions of formaldehyde and acetaldehyde from dried sugi wood were less than the guideline values proposed by the Ministry of Health, Labour and Welfare, and no significant differences were found among the drying methods. The air concentration of TVOCs (total volatile organic compounds) released from RF/V-dried sugi wood was the highest, followed by air-dried wood, and the lowest was high-temperature-dried wood. The amount of VOC emission differed depending on the drying method. These results can serve as references when using dried sugi wood as interior materials, and when investigating the effect of drying on VOC emissions from wood.

Key words : aldehydes, high-temperature drying, radio frequency / vacuum drying (RF/V), small chamber method, sugi (*Cryptomeria japonica* D. Don), volatile organic compounds (VOCs)

1. Introduction

With the recent shift in house construction trends, demand for dried lumber has been increasing in Japan (Kuroda, 2005; Kuroda, 2007). Sugi (*Cryptomeria japonica*, D. Don.) constitutes more than half of the lumber produced from Japanese plantations, and is often used in the form of boxed-heart square timber for house construction. However, sugi frequently has higher moisture content than other wood species, which causes problems such as large drying checks, long drying time, and variation in moisture content after drying. Recently, several drying methods have been applied to sugi in order to solve these problems (Kobayashi et al., 2005; Kobayashi et al., 2006; Yoshida et al., 2000; Yoshida et al., 2004). For example, high-temperature drying, above 100°C, takes relatively little time, but it can lead to deterioration of the wood. Radio frequency / vacuum (RF/V) drying promotes the drying of the inner part of lumber, and is performed at lower temperature, but requires more time than high-temperature drying. With RF/V, color changes are not significant but the drying cost is higher than high-temperature drying. The properties of lumbars dried with

these methods are still not well understood. Therefore it is very important to study the influence of these drying methods on wood quality in order to use sugi wood safely.

VOCs (volatile organic compounds) and aldehydes released from wood and wood products have become an issue of public concern in Japan. In response, the Ministry of Health, Labour and Welfare implemented an interim target value of 400 µg/m³ for TVOCs (total volatile organic compounds) and guideline values of 100 µg/m³ for formaldehyde and 48 µg/m³ for acetaldehyde as indoor air concentration (Ministry of Health, Labour and Welfare, 2002). After that, the Japanese Building Standards Law restricted the usage of formaldehyde-emitting materials (Ministry of Land, Infrastructure, Transport and Tourism, 2003). Though solid wood was excluded from the regulations, the amount of emissions from natural wood is still of great concern because it is used as components of wood-based products, which are subject to the regulations.

It is possible that drying wood changes the emission of VOCs and aldehydes from wood since the release of these compounds during drying has been reported (Fritz et

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1) Department of Wood Processing, Forestry and Forest Products Research Institute (FFPRI)

2) Department of Biomass Chemistry, Forestry and Forest Products Research Institute (FFPRI)

3) Department of Wood-Based Materials, Forestry and Forest Products Research Institute (FFPRI)

* Department of Wood Processing, Forestry and Forest Products Research Institute (FFPRI), 1 Matsunosato, Tsukuba, Ibaraki 305-8687, Japan; e-mail: aishi@ffpri.affrc.go.jp

al., 2004; McDonald et al., 2002; Milota, 2003). However, there has been little investigation about the effect of drying method on the emissions of VOCs and aldehydes from sugi wood.

In this study, we treated sugi wood with high-temperature-, RF/V-, and air-drying, and measured emissions of VOCs and aldehydes from dried wood using the small chamber method (JIS A1901) (Japanese Industrial Standard, 2003) followed by gas chromatography / mass spectroscopy (GC/MS) and high performance liquid chromatography (HPLC).

2. Materials and methods

2.1 Sample preparation

Green sugi (*Cryptomeria japonica* D. Don) boxed-heart square timber grown in Tochigi Prefecture, Japan was used. Drying samples having dimensions of 10.8 × 10.8 × 60 (L) cm were prepared, as shown in Fig. 1. The initial moisture content of the drying samples was calculated as the average of two MC specimens, one cut from each end of the samples. The moisture content of the MC specimens was obtained after oven drying them at 105°C.

As a control, air drying was conducted in a temperature-

and humidity-controlled room at 20°C and 45 % RH for 120 days. High-temperature (HT) and radio frequency / vacuum (RF/V) drying were carried out with a superheated-steam-treatment apparatus (Takahashi Kikan Co., Nagoya) and an RF/V dryer (Yasujima Co., Ishikawa), respectively. Fig. 2 shows the drying conditions of HT drying. The input power of RF/V drying was adjusted to 5 kW/m³ by regulating the oscillating time. The pressure in the dryer during the vacuum phase was 9.3-10.7 kPa. A hole having dimensions of 2 (diameter) × 30 (depth) mm was drilled in the center of the lateral side of each sample, and a thermocouple (T-6F, Kyowa Electronic Instruments Co., Ltd., Tokyo) was fixed in the hole with epoxy resin (Konishi Co., Ltd., Osaka). Changes in the temperatures of the samples that occurred during the RF/V drying are shown in Fig. 3.

These dried samples were planed, and specimens for the small chamber method (0.9 × 6 × 15 (L) cm) were cut from the lateral surface of the samples. Specimens for moisture content measurements and ether extraction (cross section, 2-3 (L) cm) were also prepared from the center of the dried samples. The moisture content was obtained after oven drying the MC specimens at 105°C. The MC values of the samples before and after drying are listed in Table 1.

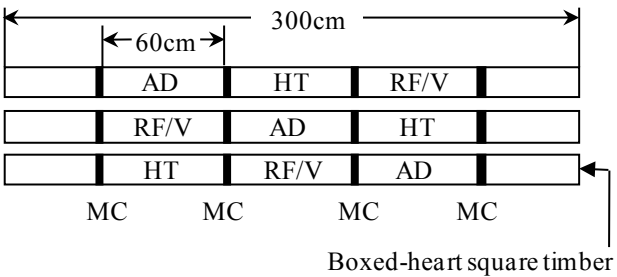


Fig. 1. Preparation of drying samples.
AD: air drying; HT: high-temperature drying;
RF/V: radio frequency / vacuum drying;
MC: specimens for moisture content measurement.

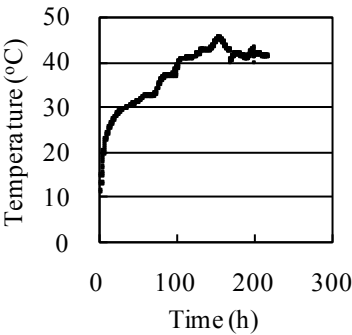


Fig. 3. Sample temperature during RF/V drying.

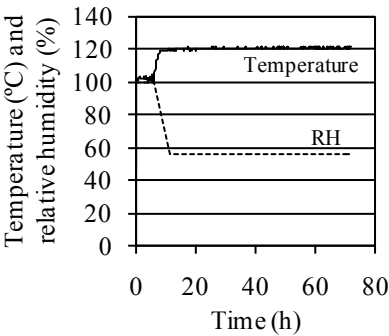


Fig. 2. High-temperature drying conditions.

Table 1. Moisture content of samples before and after drying.

Drying method	Average moisture content (%) [*]	
	Before	After
Air drying	118	14
High-temperature drying	116	13
RF/V drying	116	10

^{*}n=3

2.2 Ether extraction

The amount of ether extractives included in green and dried specimens was measured in order to estimate the amount of compounds included in the samples before and after drying. Outer heartwood (outer surface to 1.5 cm from surface), middle heartwood (1.5 cm to 3 cm from surface), inner heartwood (3 cm to 4.5 cm from surface), and sapwood were cut from the wood samples (Fig. 4), excluding the pith. Undried and dried samples were cut into pieces, and ground in a mill to pass through a 2.0-mm screen. Ground samples in 5-g units were Soxhlet-extracted with diethyl ether at 40°C for 5 h. The solvents were evaporated in vacuo at 40°C. Other 1-g ground samples were oven-dried at 105°C until their weight stabilized, after which the moisture content was calculated. From these results, the rate of ether extractives relative to an oven-dried weight of wood was calculated.

2.3 Measurement of VOCs and aldehyde emission

The emission of VOCs and aldehydes from dried wood was measured based on the small chamber method (JIS A1901) (Japanese Industrial Standard, 2003) using a small chamber system (ADPAC system, ADTEC Co., Kanagawa). The temperature, relative humidity, and ventilation rate were 28 °C, 50 % RH, and 0.5/h, respectively. The chamber volume was 20 L. Before the emission test, blank air in the chamber was analyzed and confirmed to be clean. Two specimens measuring $0.9 \times 6 \times 15$ (L) cm were put in the chamber, so that the total exposure area was 435.6 cm². Sample air (5L) was collected in each of several 2, 4-dinitrophenylhydrazine (DNPH) cartridges (LpDNPH S10L, Supelco Inc., Tokyo) and Tenax-TA tubes (25090-U, Supelco Inc., Tokyo) at 1, 3, 7, and 28 days after the specimen setting. The amounts of aldehydes and VOCs were determined using high-performance liquid chromatography (HPLC) and gas chromatography / mass spectroscopy (GC/MS).

The DNPH derivatives in a DNPH cartridge were desorbed and diluted up to 5 mL using HPLC-grade acetonitrile. The solution was injected into an HPLC (LC-10 ADvp, Shimadzu Co. Ltd., Kyoto). The analysis conditions are listed in Table 2. Standard reagent (CARB 1004 DNPH Mix 2, Supelco Inc., Tokyo) was used for the quantitative determination.

The collected volatiles were removed from the Tenax tube by heating the trap with an automatic thermal desorption system (ATD400, Perkin Elmer Japan Co., Ltd., Kanagawa) at 280°C for 15 min. The compounds were cryofocused in a cold trap (air monitoring trap) at 5°C. By heating the cold trap, volatiles were transferred to an HP-5MS capillary column (30 m \times 0.25 mm i.d. \times 0.25 μ m

film thickness, Agilent Technologies Japan, Ltd., Tokyo) and analyzed by GC/MS (GC 6890, MSD 5973, Hewlett-Packard Japan, Ltd., Tokyo). The temperature program began at 40°C (hold 15 min), thereafter rising to 180°C at 4°C/min (hold 15 min), and to 280°C at 5°C/min (hold 15 min). All mass numbers between 15 and 550 m/z were recorded (SCAN technique). Individual compounds were identified by comparing their mass spectra with the NIST (National Institute of Standard and Technology) Library, published values (Adams, 2007) and NMR spectra as detailed in a previous report (Yatagai et al., 1985). The total volatile organic compound emission was first calculated by combining the peak areas of all identified compounds, after which the relative proportions of individual compounds from the total emission were calculated. Standard toluene reagent (Kanto Chemical Co., Inc., Tokyo) was used, and the amounts of VOCs were indicated as toluene equivalents.

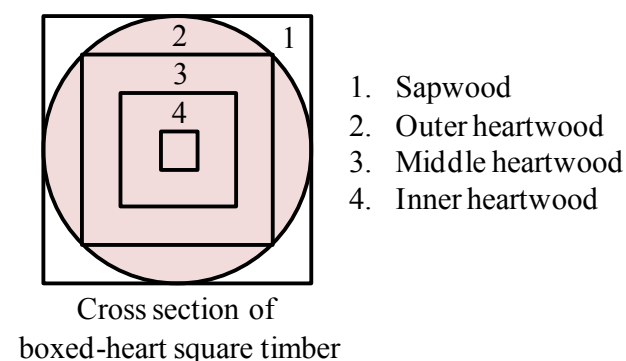


Fig. 4. Sample division for ether extraction.

Table 2. Analysis conditions of HPLC.

Apparatus	SHIMADZU LC-10 Avp System
Column	two STR-ODSI (150 mm \times 4.6 mm ϕ) (Shinwa Chemical Industries, Ltd.)
Mobile phase	Acetonitrile/Distilled water
Gradient	40:60 (0-5 min), 100:0 (5-30 min), 100:0 (30-35 min), 40:60 (35-36 min), 40:60 (36-50 min)
Flow rate	1.0 mL/min
Injection volume	20 μ L
Oven temp.	40 °C
Detector	UV 360 nm

The air concentration in the small chamber C and emission rate E of VOCs and aldehydes were calculated using the following equations:

$$C = (W_s - W_t)/V \dots (1)$$

$$E = C \times Q/S \dots (2)$$

where C : air concentration in the small chamber ($\mu\text{g}/\text{m}^3$), W_s : mass values of sampled compounds (μg), W_t : mass values of travel blank (μg), V : volume of collected air (m^3), Q : air flow rate (m^3/h), S : surface area of a specimen (m^2).

3. Results and discussion

Fig. 5 shows the formaldehyde emissions from air-, HT-, and RF/V-dried sugi wood. According to the Building Standard Law, materials emitting less than $5 \mu\text{g}/\text{m}^2/\text{h}$ of formaldehyde are not restricted for use in houses. Formaldehyde emissions for all samples in this study were less than this value. The emission rate $5 \mu\text{g}/\text{m}^2/\text{h}$ is equal to an air concentration of $36 \mu\text{g}/\text{m}^3$, and this is also lower than the guideline of $100 \mu\text{g}/\text{m}^3$ for indoor air concentration of formaldehyde proposed by the Ministry of Health, Labour and Welfare. It has been reported that natural wood itself contains detectable formaldehyde (Weigl et al., 2009), and thermal degradation of lignin and hemicelluloses could produce formaldehyde (Schäfer and Roffael, 2000; Roffael, 2006). However, it appears that the drying conditions used in this study did not affect the formaldehyde emission from sugi wood, since the amount of formaldehyde emission did not significantly differ among the samples.

The air concentration of acetaldehyde released from the dried specimens is shown in Fig. 6. No significant differences in acetaldehyde emission were found among the drying methods, though one of the RF/V-dried specimens showed a somewhat higher value than the others. The air concentration values were less than the $48 \mu\text{g}/\text{m}^3$ guideline proposed by Ministry of Health, Labour and Welfare.

The air concentration of TVOCs (total volatile organic compounds) emitted from HT-dried specimens was lower than that from the others (Fig. 7). This might have been due to the removal of essential oil from the wood by the high-temperature drying (Fritz et al., 2004; McDonald et al., 2002; Milota, 2003). As for the RF/V-dried specimens, TVOC emissions were expected to be lower than from air-dried specimens, since the former were treated at a higher temperature than the latter. However, RF/V-dried sugi wood showed a higher air concentration than the air-dried samples. One possible explanation is that air drying took much more time than the RF/V drying, and a much greater amount of VOCs might have been removed during the air drying than during the RF/V drying.

Uneven distribution of extractives in wood might also have affected the experimental results. Therefore, the distribution of extractives in specimens before and after drying was investigated, and the results were plotted in Fig. 8. The distribution of extractives tended to be almost the same for the two green-wood samples but different for the dried ones. The extractive content of HT-dried wood was lower than that of the others for both samples 1 and 2, while that of RF/V-dried wood was lower for sample 1 and higher for sample 2 compared with the respective air-dried samples. Removal of extractives might easily occur during high-temperature drying, while it depends on the location in the wood, individuals, and so forth during lower temperature drying. The RF/V-dried samples used in the emission test might have had a distribution pattern of extractives similar to that of sample 2 in Fig. 8, and thus showed high TVOC emission as shown in Fig. 7. Further studies will be needed to clarify the details.

The major VOCs released from the dried specimens are listed in Table 3. The dominant compounds were δ -cadinene and cubenene for all the samples. Many of the compounds

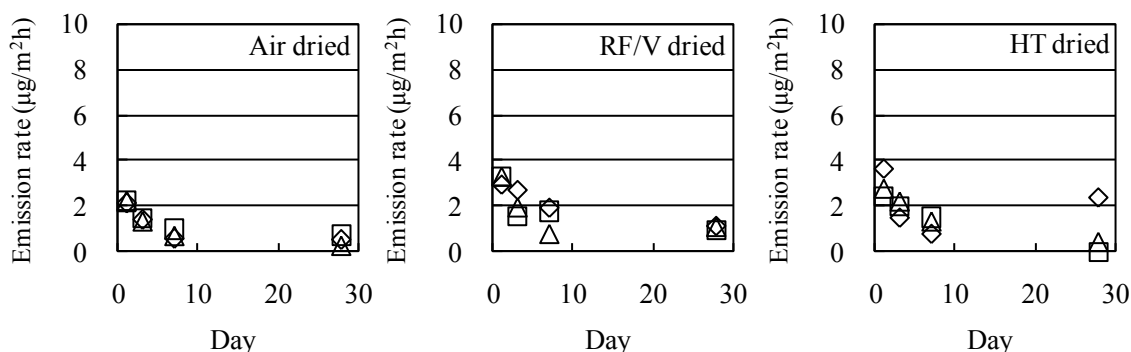


Fig. 5. Formaldehyde emission from dried sugi wood.

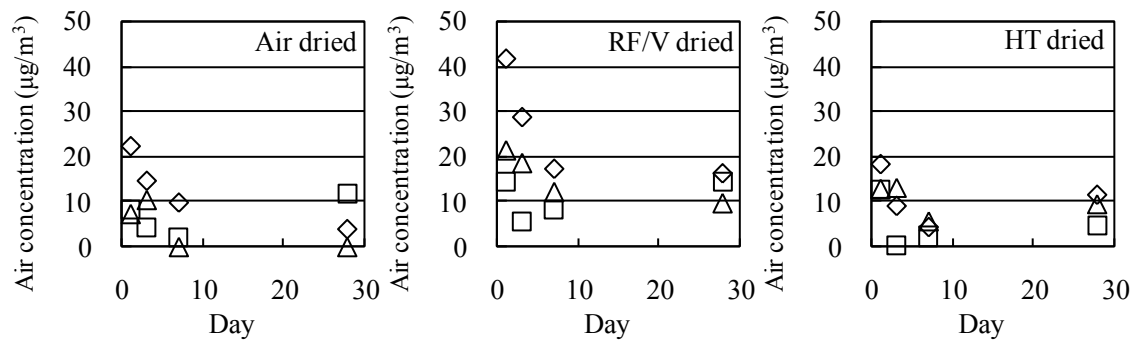


Fig. 6. Acetaldehyde emission from dried sugi wood.

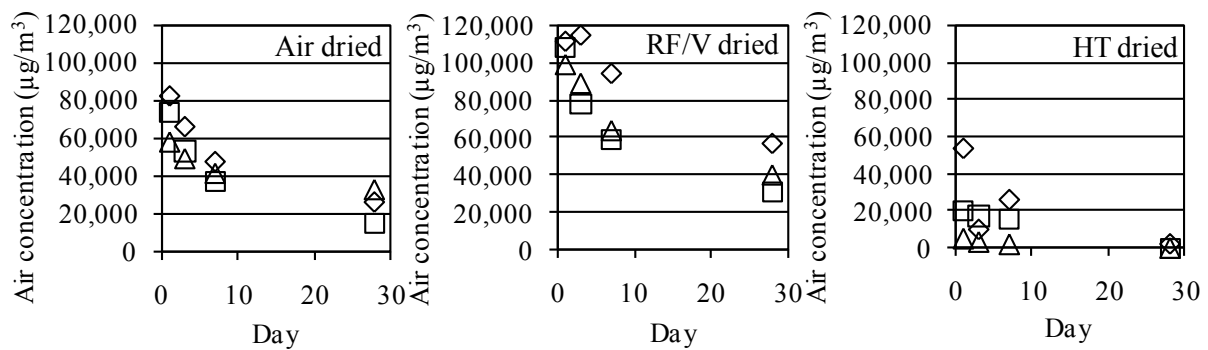


Fig. 7. TVOC emission from dried sugi wood.

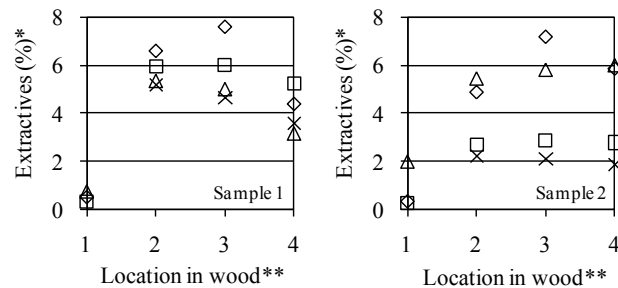


Fig. 8. Ether extractives of green and dried sugi wood.
 ◇ : green; □ : air dried; △ : RF/V dried; × : HT dried.

*Relative to oven-dry weight

**See Fig.4.

Table 3. Air concentration of major VOCs emitted from dried sugi wood.*

Compounds	Air concentration ($\mu\text{g}/\text{m}^3$)		
	AD	RF/V	HT
δ -Cadinene	8031	9605	2924
Cubenene	5906	7008	2144
β -Cubebene	1521	3093	117
β -Caryophyllene	1264	3675	898
α -Cubebene	889	4609	316
α -Copaene	540	1814	2279
γ -Muurolene	517	4731	124
Cadalene	65	238	129
1(5),11-Guaidiene	13	64	27
α -Aromadendrene	9	9	31
Acetic acid	-	-	254

∴ undetected, n=3

*Results after 7 days.

detected in this study have been reported to be included in sugi wood (Nagahama and Tazaki, 1993; Nagahama et al., 1995; Nagahama et al., 1996; Nagahama et al., 1998; Nagahama et al., 2000; Arihara et al., 2004). Moreover, acetic acid, which is known to be generated by thermal degradation of hemicellulose and other wood components (Minami and Kawamura, 1958; Minami et al., 1958), was emitted only from the HT-dried wood. The air concentration of TVOCs for most of the samples was higher than the interim target value of indoor air concentration, $400 \mu\text{g}/\text{m}^3$, as shown in Fig. 7. It should be noted, however, that most of the emitted compounds were terpenes, and they are known to have many beneficial functions (for example, Yatagai, 2005).

4. Conclusions

VOCs (volatile organic compounds) and aldehydes released from air-, high-temperature-, and radio frequency / vacuum-dried sugi wood were measured at 1, 3, 7 and 28 days after drying. The following results were obtained.

- Emissions of formaldehyde and acetaldehyde from dried sugi wood were less than the guideline values proposed by the Ministry of Health, Labour and Welfare, and no significant effect of drying method on the emissions was found.

- The amount of TVOCs (total volatile organic compounds) and each compound emitted from sugi wood differed depending on the drying method. Specimens dried at high temperature showed characteristic release of acetic acid. It was considered that not only drying temperature but also drying time and distribution of extractives in wood had influence on the VOC emission from wood.

These results can be of help when using dried wood for building, and when considering the effects of drying

conditions on the changes that occur in wood components.

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スギ材から放散する揮発性有機化合物に及ぼす乾燥方法の影響

石川敦子^{1)*}、大平辰朗²⁾、小林 功¹⁾、宮本康太³⁾、塔村真一郎³⁾、井上明生³⁾

要 旨

近年、乾燥材需要の高まりに伴い、スギ材に対して様々な乾燥方法が適用されるようになった。他方、木材および木質材料から放散する揮発性有機化合物（VOC）について関心が高まっている。そこで本研究では、乾燥処理がスギ材からの VOC の放散へ及ぼす影響を検討することとした。スギ材に対して高温乾燥、高周波減圧乾燥、および自然乾燥を施した。乾燥材から放散する VOC を小形チャンバー法で測定し、ガスクロマトグラフ質量分析（GC/MS）および高速液体クロマトグラフィー（HPLC）により分析した。ホルムアルデヒドとアセトアルデヒドの放散量は厚生労働省の指針値よりも低い値であり、乾燥方法による顕著な違いは認められなかった。総揮発性有機化合物（TVOC）の放散量は、高周波減圧乾燥材で最も多く、次いで自然乾燥材であり、高温乾燥材で最も少なかった。また、個々の VOC の放散量は、乾燥方法によって異なっていた。これらの結果は、スギ材を建築内装材料として用いる際、および乾燥が VOC の放散に及ぼす影響を検討する際に役立つものである。

キーワード：アルデヒド、高温乾燥、高周波減圧乾燥（RF/V）、小形チャンバー法、スギ（*Cryptomeria japonica* D. Don）、揮発性有機化合物（VOCs）

1) 森林総合研究所加工技術研究領域

2) 森林総合研究所バイオマス化学研究領域

3) 森林総合研究所複合材料研究領域

* 森林総合研究所加工技術研究領域 〒 305-8687 茨城県つくば市松の里 1 e-mail: aishi@ffpri.affrc.go.jp