

Influence of Environmental Factors on Volatile Organic Compound Emissions from Plywood Tested by a Rapid Detection Method

Wang Qifan
Shen Jun
Zhao Yang
Liu Wanjun

Abstract

At certain concentrations, volatile organic compounds (VOCs) may harm people's health. This article introduces a new rapid detection method for testing VOCs released from three-layer plywood. A Micro-Chamber/Thermal Extractor was used to analyze the effect of environmental factors on release characteristics of VOCs in the stable phase, and a single-factor experiment was used to analyze the release of VOCs under different temperatures, relative humidity levels, and ratios of air exchange rate-to-loading factor, by using the rapid sampling device together with gas chromatography-mass spectrometry (GC-MS). Results showed that aromatic hydrocarbons, alkanes, and esters were the main components of VOC emissions released from three-layer plywood. The percentage of VOC components in the stable phase changed as the single factors changed. Temperature has the greatest impact on the percentage of VOC components. The VOC concentration increased as temperature and relative humidity increased but decreased as the ratio of air exchange rate-to-loading factor increased. Temperature had a greater impact on VOC release from three-layer plywood than did relative humidity or the air exchange rate-to-loading factor ratio.

In recent years, plywood, particleboard, and fiberboard have been extensively used in interior decoration. Indoor air pollution caused by interior furnishings has been a matter of increasing concern (Chen 2010). For class I construction (e.g., homes, hospitals, old buildings, and school classrooms), volatile organic compounds (VOCs) are considered safe at levels under 0.50 mg/m^3 ; for class II construction (e.g., office buildings, stores, and libraries), levels should be under 0.60 mg/m^3 (see the national standard for indoor environment GB 50325-2010 [Standardization Administration of the People's Republic of China 2011]).

VOC emissions from three-layer plywood arise mainly from the product's film and its manufacturing process (such as the adhesive used in the overlaying process). Various studies (Wolkoff 1998, Wiglusz et al. 2002, Afshari et al. 2003, Li et al. 2013) have pointed out the impact of external conditions on VOC release. Environmental factors, such as temperature, relative humidity, and flow rate, affect the rate of VOC release from materials (Sollinger et al. 1993, Wal et al. 1997, Zhou 2007). Some studies have indicated that the impact of environmental

factors varies depending on the type of construction materials. For instance, the effect of relative humidity on VOC release is only significant with wet materials (Fang et al. 1999), and the effect of change in temperature depends on the boiling point of the VOC (Sollinger et al. 1993). Other studies have shown that the hot extraction method can be used to evaluate VOC emissions from flooring

The authors are, respectively, Master Degree Candidate and Professor, College of Material Sci. and Engineering, Northeast Forestry Univ., Harbin, China (wangqifan66@163.com, shenjunr@126.com [corresponding author]); Professor, College of Material Sci. and Engineering, Northeast Forestry Univ., Harbin, China, and Ningbo Fotile Kitchen Ware Co. Ltd, Ningbo, Zhejiang, China (706517760@qq.com); and Research Development Engineer, College of Material Sci. and Engineering, Northeast Forestry Univ., Harbin, China (liuwanjun1990@126.com). This paper was received for publication in January 2016. Article no. 16-00008.

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materials and some plastics (Hughes et al. 2006, Schmohl et al. 2006, Kieliba et al. 2007).

At present, there are three methods for VOC collection from wood-based panels: the traditional 1-m³ climate chamber method, the small space release method (field and laboratory emissions cell [FLEC]; Kim et al. 2010), and the Dying ware method (a modification of FLEC developed by Casco, Co. Ltd., Switzerland). The traditional 1-m³ climate chamber method is an international standard and has been used widely in America and Germany (see ASTM standards D5116 [ASTM International 2010] and D6330 [ASTM International 2014]). VOC emissions from wood-based panels are determined under defined conditions of temperature, relative humidity, and air exchange rate. The result is determined when the VOC content arrives at a steady value, generally after 28 days, compared with the rapid detection method, which takes about 7 days. The traditional climate chamber method is time-consuming and requires specialized equipment that occupies a large space; thus, it is important to explore an efficient, quick, and easy detection method for collecting VOC emissions from wood-based panels (Shen et al. 2012, Qi et al. 2013).

In related research, data obtained using the rapid detection method and the traditional climate chamber method were compared, and a good correlation was found between the two methods (Du and Shen 2015). This study used a rapid sampling device, the Micro-Chamber/Thermal Extractor M-CTE250 connected to a cylindrical volumetric flask, together with gas chromatography–mass spectrometry (GC-MS) to analyze VOC emissions from three-layer plywood under different temperatures, relative humidity levels, and ratios of air exchange rate–to–loading factor.

Materials and Methods

Experimental materials

A three-layer plywood sample, produced in Zhejiang, was chosen as our experimental material. The essential parameters of this three-layer plywood are presented in Table 1. The plywood was cut in round pieces (60 mm in diameter) for the rapid detection method and in rectangular pieces (1,000 by 500 mm) for the climate chamber method. After the specimen edges were sealed with aluminum foil to prevent the release of VOCs, they were stored in Teflon bags and placed in the refrigerator until needed.

Experimental equipment

The following equipment was used in the experiments. (1) A Micro-Chamber/Thermal Extractor M-CTE250(T)(i) (Markes International Inc., UK) was used with a TY9700 digital hygrothermograph (Tianyue Environmental Protection Technology Co., Ltd., Beijing, China). The carrier gas was nitrogen, with a temperature range of 0°C to 250°C. (2) A 1-m³ VOC/formaldehyde climate chamber (Simplewell Scientific Co., Dongguan, China) was used with a Zhiheng IAQ-Pro Constant Flow Air Sampling Pump (Sensidyne, USA). (3) A TP-5000 Thermal Analysis Desorber (Beifen Instrument Technical Co., Beijing, China) was used. The carrier gas was nitrogen, with the following settings for related parameters: resolution temperature, 45°C; pipeline temperature, 100.0°C; thermal analysis time, 5 minutes; injection time, 1 minute. (4) A DSQ II series GC-MS (Thermo Scientific, Germany) was used. Chromatography was performed with a DB-5 quartz capillary column (3,000

Table 1.—Essential parameters of the three-layer plywood.

| Parameter | Condition |
|------------------------|---|
| Tree species | |
| Surface layer | <i>Fraxinus mandshurica</i> Rupr. |
| Sandwich layer | <i>Populus ussuriensis</i> Kom. |
| Back layer | <i>P. ussuriensis</i> Kom. |
| Production time | 2014 |
| Plywood thickness | 12 mm |
| Adhesive | Urea-formaldehyde resin adhesive with the molar ratio of 1:1.6 |
| Adhesive pH | 7.0–8.5 |
| Adhesive solid content | 53%–57% |
| Resin content | 320 g/m ² |
| Moisture content | 6.94% |
| Pressing pressure | 1.4 MPa |
| Pressing temperature | 115°C |
| Pressing time | 1.0 min mm ⁻¹ |

mm by 0.26 mm by 0.25 μm). The chromatographic column was initially at 40°C for 2 minutes, it was then elevated to 50°C (at 2°C/min) and held for 4 minutes, and finally, it was elevated to 250°C (at 10°C/min) and held for 8 minutes. The injection port temperature was 250°C, the distributary flux was 30 ml/min, and the distributary ratio was 30. The following GC-MS conditions were applied: ionization mode, electron ionization (EI); transmission line temperature, 270°C; ion source temperature, 230°C; mass scan range, 50 to 650 atomic mass units (amu). (5) Tenax-TA sampling tubes were obtained from Beifen Tianpu Instrument Technology Co., Ltd. (Beijing, China). (6) Cylindrical stainless steel volumetric flasks were used (100 mm in diameter, 650 mm in height).

Experimental design

Rapid detection method.—The experiment used the single-factor method to test the VOC emissions of three-layer plywood under different experimental conditions (the conditions are noted in “VOC emissions analysis” section); three samples were tested under each condition. The rapid test sampling device was based on the Micro-Chamber/Thermal Extractor M-CTE250 (Markes International), connected to a cylindrical volumetric flask to provide moisture and regulate the carrier gas humidity; a handheld thermometer was also used. With constant air flow and low background concentration, the temperature could be adjusted to between 0°C and 250°C and the relative humidity to between 30 and 80 percent. Clean, humidified nitrogen was used as the carrier gas. The total test period was 7 days (168 h). Table 2 shows the operating parameters during the experiment.

Traditional climate chamber method.—Sampling was done using the 1 m³ traditional climate chamber and method, based on International Organization for Standardization (ISO) standards ISO 16000-9 (2006) and ISO 16000-6 (2011). The climate chamber parameter values were set according to ASTM standard D5116 (ASTM International 2010). Before the experiment, the climate chamber was cleaned once with drinking water and twice with deionized water. Meanwhile, the three-layer plywood samples were kept at 23°C and 45 percent relative humidity for a week.

Table 2.—Micro-chamber/thermal extractor operating parameters of the rapid test method.

| Variable | Condition |
|-----------------------------|--|
| Specimen area | $5.65 \times 10^{-3} \text{ m}^2$ |
| Cell volume | $1.16 \times 10^{-6} \text{ m}^3$ |
| Loading factor | $4.87 \times 10^3 \text{ m}^2 \text{ m}^3$ |
| Area specific air flow rate | 0.2, 0.5, 1.0 $\text{m}^3 \text{ m}^{-2} \text{ h}^{-1}$ |
| Temperature | 23°C, 60°C, 80°C |
| Relative humidity | 40%, 60% |

After a week, the same three samples were taken out and were placed horizontally in the center of the climate chamber; the door was closed after ensuring that the inside air could flow around the two sides of the samples. The VOCs released from the specimen surfaces were absorbed by Tenax-TA tubes and were recorded on days 1, 3, 7, 14, 21, and 28. Purified, humidified air was supplied throughout the experiment.

VOC emissions analysis.—Thermal desorption sample injector TP-5000 was used to thermally desorb the VOC samples. The temperature was kept at 280°C for 5 minutes, after which the VOC samples were characterized and quantified by DSQ II GC-MS. Table 3 lists the basic GC-MS parameters. This experiment included groups A, B, C, and D; the scheme of the experiment is shown in Table 4.

Results and Discussion

The effect of environmental factors on the components of VOC emissions

The main components emitted from the three-layer plywood are listed in Table 5. Note that there were more components in the aromatic hydrocarbon and alkane categories than in the others. Components were also found in these categories: alkenes, aldehydes and ketones, esters, and ethers (small amounts).

Figure 1 shows the percentage of different components in stable phase under different environmental conditions and environmental methods. Figures 1a through 1c show the impact that different temperatures, relative humidity levels, and ratios of air exchange rate-to-loading factor had on the percentages of VOC components. The percentages of VOC components changed with changes in single factors. When relative humidity and the ratio of air exchange rate-to-loading factor were held steady, the percentage of arenes and esters steadily increased as the temperature rose. Alkanes reached the highest value at 80°C, but alkenes and aldehydes and ketones reached their highest values at 60°C and 23°C, respectively. Increases in temperature increased the differences among various components (Fig. 1a). When temperature and ratio of air exchange rate-to-loading factor were held steady, the changes in relative humidity had a relatively small effect on the percentage of each component, especially alkanes and alkenes. The changes of VOC components at 50 to 60 percent relative humidity were obviously less than at 40 to 50 percent relative humidity. Aldehydes and ketones reached their highest values at 40 percent relative humidity (Fig. 1b).

When the temperature and relative humidity were held steady, the percentage of arenes increased as the ratio of

Table 3.—The basic parameters of gas chromatography–mass spectrometry.

| Variable | Condition |
|------------------------|---|
| Column | DB-5 (3 m by 0.26 mm by 0.25 μm) |
| Carrier gas | He (99.99%) |
| Temperature program | 40°C (2 min) \rightarrow 50°C (4 min) \rightarrow 150°C (4 min) \rightarrow 250°C (8 min) |
| Ion source | EI (electron ionization) |
| Ion source temperature | 230°C |
| Scan mode | Full scan (40–450 amu) |

air exchange rate-to-loading factor increased, but the percentage of alkenes and of aldehydes and ketones decreased at the same rate as this ratio increased (Fig. 1c). In summary, temperature has the greatest impact on the percentage of different VOC emissions. An increase in temperature and relative humidity can increase the change in the proportion of each component, such as lowering the proportion of aldehydes and ketones and increasing that of esters. Figure 1d shows the percentage of various components detected by two different methods. Although the methods used analogous environmental conditions, the percentages found were obviously different, but the species were the same. Significant differences include the higher percentage of arenes found by the rapid detection method compared with the traditional climate chamber method and the much lower percentage of alkanes detected by the rapid detection method compared with the traditional climate box method. The differences seen in the two detection methods may be explained by the different samples used. The samples for the rapid detection method were cut in round pieces (60 mm in diameter), whereas the samples used in the climate chamber method were cut in rectangular pieces (1,000 by 500 mm). Different sample sizes may affect VOC emissions, with greater stability of VOC emissions seen in larger samples. However, because the rapid detection method is much faster and the difference in results between the two methods is small, the rapid detection method can be used with convenience to monitor VOC emissions in factories.

The effect of environmental factors on VOC emissions

The emissions rate of VOCs gradually decreased with time, until it reached a stable phase. The VOC concentrations sharply decreased from Day 1 to Day 3, after which the rate of decline slowed.

Figure 2a shows the changes in VOC concentrations under different temperatures from Day 1 to Day 7. When the temperature increased, the VOC concentrations also increased. As time went on, the distinctions in VOC concentrations gradually diminished, and they finally reached equilibrium. At 23°C, 60°C, and 80°C, from Day 1 to Day 4, the average rates of decline of VOCs, respectively, were 88.03, 121.53, and 141.82 $\mu\text{g}\cdot\text{m}^{-3} \text{ d}^{-1}$. Thus, in the first day of the experiment, temperature had a distinct influence on VOC concentration: the higher the temperature, the faster the decline in VOC concentration. Meanwhile, the VOC equilibrium concentration at high

Table 4.—Experimental scheme under different methods and environment conditions.

| Experimental scheme | Temperature (°C) | Relative humidity (%) | Ratio of air exchange rate-to-loading factor (m ³ h ⁻¹ m ⁻²) | Experimental condition |
|------------------------|------------------|-----------------------|--|---|
| Climate chamber method | | | | |
| A | 23 | 45 | 1 | Standard conditional |
| Rapid detection method | | | | |
| B | 23, 60, 80 | 40 | 0.2 | Different temperatures |
| C | 23 | 40, 50, 60 | 0.2 | Different humidity levels |
| D | 23 | 40 | 0.2, 0.5, 1.0 | Different ratios of air exchange rate-to-loading factor |

Table 5.—The main components of volatile organic compounds emitted from the three-layer plywood by rapid test method and traditional climate chamber method.

| Category | Main components |
|-----------------------|---|
| Aromatic hydrocarbons | Ethylbenzene, 1,3-dimethyl benzene, 1-methylene 1H-indene, butylated hydroxy toluene, 1-methylnaphthalene, 2-methylnaphthalene |
| Alkanes | Undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, 2,6,10-trimethyl dodecyl, 4-(prop-2-oxypropang)octane, 2,6-dimethyl decane |
| Alkenes | 2-Propenylidene cyclobutene, cedrene, Seychelles alkene |
| Aldehydes and ketones | Hexanal, nonanal, benzaldehyde, acetophenone, undecanal |
| Esters | Butyl butyrate, 3-methyl heptanol acetate, 2 acrylic acid 2 ethylhexyl ester, oxalic acid acrylate |
| Others | N-butyl ether |

temperature was slightly higher than the VOC equilibrium concentration at low temperature. In the later stages, the impact of temperature on VOC concentration became weak; the VOC concentrations in different temperatures gradually reached equilibrium. Temperature has a significant impact on VOC emissions from wood-based panels: as the temperature rises, the thermal motion of VOC molecules strengthens, the VOC diffusion coefficient increases, and the panels' adsorption capacity decreases. The relationship between temperature and VOC diffusion coefficient in the material is simplified as follows:

$$D = D_{\text{ref}} \exp \left[-E \left| T^{-1} - 296^{-1} \right| \right]$$

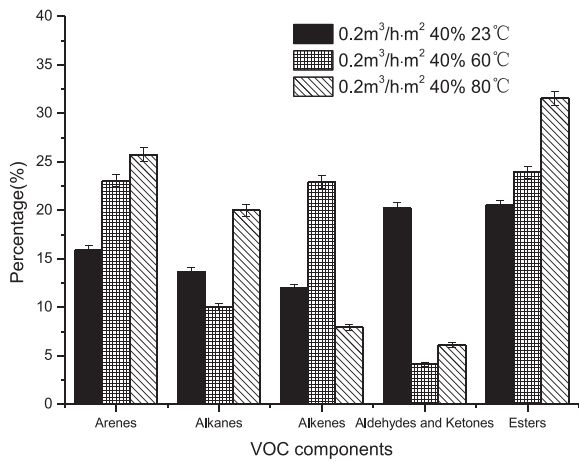
where D is the internal diffusion coefficient of the material (m² h⁻¹); D_{ref} is the internal diffusion coefficient of the material at 23°C; E is determined by the test coefficient, generally 9,000 T ; and T is the thermodynamic temperature (K). Temperature influences VOC emissions through its impact on the diffusion coefficient. Based on the mass transfer theory, as a result, the VOC emissions from the panels become fast and massive (Li et al. 2013).

Figure 2b displays the influence of relative humidity on VOC concentrations. The VOC concentration decreased fastest from Day 1 to Day 2, with decreases of about 200 µg/m³ at each of the relative humidity levels. From Day 2 to Day 5, the relative humidity showed a significant effect on VOC concentration, which declined at a rate that increased as relative humidity increased. Experiments show that, in general, VOC concentrations increase as relative humidity increases, which may be explained by the change in pore structure due to acceleration of hydrolysis. The expansion of pores in the drying layer and hygroscopicity favors the release of VOCs, as shown by Zhu et al. (2013) and Shan et al. (2013).

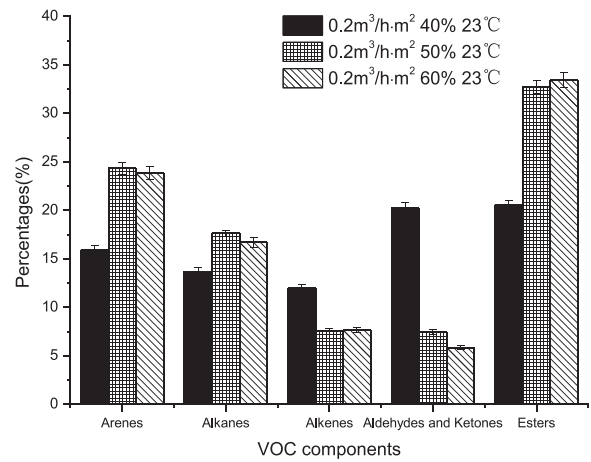
Figure 2c shows the relation between VOC concentration and the ratio of air exchange rate-to-loading factor. In general, as the ratio of air exchange rate-to-loading factor decreases, the VOC concentration increases. VOC concentration decreased significantly from Day 1 to Day 2, dropping approximately 200 µg/m³ under three different ratios of air exchange rate-to-loading factor. From Day 2 to Day 3, the rate of decrease slowed noticeably, but it still declined slowly. After Day 3, the VOC concentration gradually reached equilibrium. Yu et al. (2006) and Yang et al. (2007) studied the influence of natural ventilation on VOC emissions from interior furnishings and found that increased ventilation would reduce the VOC concentrations, similar to our findings. In short, massive amounts of fresh carrier gas dilute VOC emissions within microcell extraction and enlarge the concentration gradient between microcell extraction and panels, promoting the release of VOCs and reducing the amount of collected release.

Conclusions

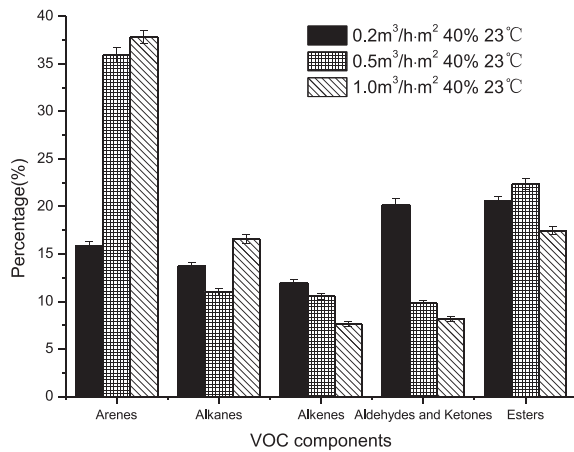
The rapid detection method and the traditional climate chamber method found similar trends in VOC emissions species from three-layer plywood. Aromatic hydrocarbons, alkanes, and esters were the main components of VOC emissions. The percentages of VOC components in the stable phase changed as single factors were changed. Temperature had the greatest impact on the percentage of VOC components. The total VOC concentration increased as temperature and relative humidity increased but decreased as the ratio of air exchange rate-to-loading factor increased. The impact was strong in the first days of the experiment and gradually reached equilibrium. Temperature always had a greater impact on VOC emissions from three-layer plywood than did relative humidity or the ratio of air exchange rate-to-loading factor.



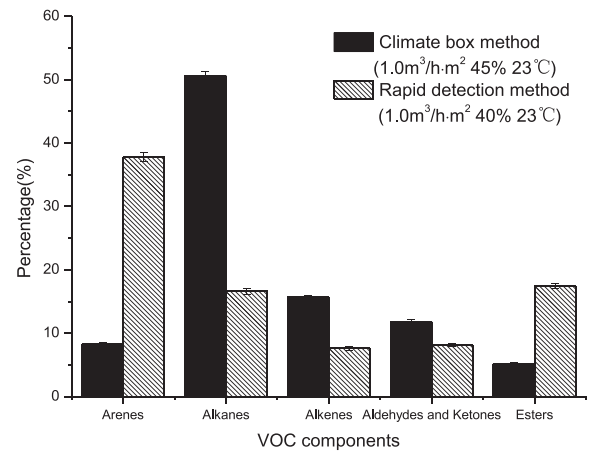
(a)



(b)

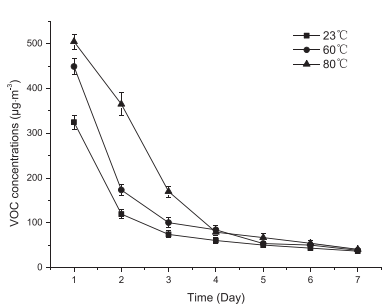


(c)

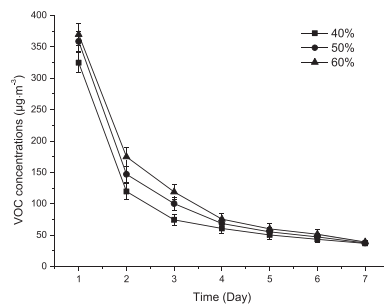


(d)

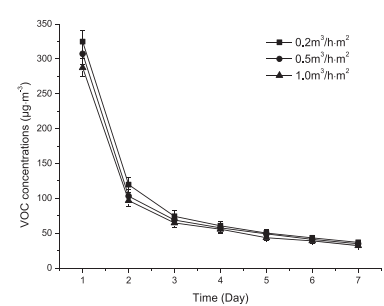
Figure 1.—The percentage of different components in stable phase under different temperatures (a), relative humidity levels (b), ratios of air exchange rate–to–loading factor (c), and detection methods (d).



(a)



(b)



(c)

Figure 2.—The relationship between concentration of total volatile organic compounds and environmental conditions of plywood: different temperatures (a), different relative humidity levels (b), and different ratios of air exchange rate–to–loading factor (c).

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