Effects of the Manufacturing Conditions on the VOCs Emissions of Particleboard

Shijing Sun,[a] Zhongyuan Zhao,[b] and Jun Shen [c,*]

The volatile organic compounds (VOCs) emitted from wood-based panels are hazardous to indoor air quality. Usually, the VOCs are derived from the adhesive, chemical compounds, and wood components. However, there has been little research focusing on the effects of manufacture conditions on the VOC emissions. In this study, the effects of density, thickness, and resin content on total VOC (TVOC) and individual VOCs were investigated by the small chamber method and gas chromatography and mass spectrometry (GC/MS). The TVOC emission from the particleboard of each manufacturing condition decreased with extended exposure time. The higher density, thickness, and resin content of particleboard at each measured time caused higher concentrations of TVOC emissions. Most of the detected VOCs were aromatics. The esters, aldehydes, and ketones showed a high increasing level with increasing particleboard density, thickness, and resin content. This result indicated that these chemical compounds were most sensitive to changes in manufacturing conditions.

Keywords: VOC; Particleboard; Manufacturing condition; GC/MS

*Contact information: a: College of Material Science and Engineering, Nanjing Forestry University, Nanjing 210037, China; b: College of Furnishings and Industrial Design, Nanjing Forestry University, Nanjing 210037, China; c: College of Material Science and Engineering, Northeast Forestry University, Harbin 150040, China; *Corresponding author: shenjunr@163.com*

INTRODUCTION

As fossil resources decrease, the development of bio-based materials has been a significant topic in material science, but most bio-based advanced materials are still in the laboratory phase, a long way from application (Xiong *et al*. 2018; Wu *et al*. 2019; Zheng *et al*. 2019). Thus, traditional bio-based materials such as particleboard, plywood, and fiberboard are typically utilized in living environments (Navarrete *et al*. 2013; Du *et al*. 2014; Jiang *et al*. 2017). These materials are manufactured by bonding the wooden elements with synthetic resin adhesives, which are mostly synthesized by formaldehyde and other petroleum related chemical compounds; free formaldehyde and volatile organic compounds (VOCs) are emitted from these materials during their use. These chemical compounds often negatively affect human comfort and health (Brightman *et al*. 2008; Norback *et al*. 2009). For instance, released formaldehyde can cause irritation of the eyes and upper respiratory tract, and it has been classified as a Group 1 human carcinogen by the International Agency for Research on Cancer (Salthammer *et al*. 2010). Benzene is another carcinogen that can cause acute leukemia (Smith 2010). Hence, both the perspective of environmental sustainability and the consumer demand for non-hazardous materials contribute to the improvement of indoor air quality (IAQ).

Based on the research of this issue, there are two main directions; developing eco-friendly adhesive synthesized by harmless and renewable materials (Zhao *et al*. 2018a,b),

and controlling VOC emissions. However, the VOCs emitted from bio-based materials are derived from both the adhesive and the wood components, so it is necessary to illuminate the VOC emission characteristics. There are some reports on the effects of environmental conditions (such as temperature, relative humidity (RH) and air exchange rate (AER)) on the VOC emissions (Kim and Kim 2015; Liang *et al*. 2015, 2016; Wolkoff 2018), but most of these studies are related to the emission of formaldehyde and total volatile organic compounds (TVOC), which limit the analysis of pollution source. In reports on the emission of individual VOCs from wood-based materials (Lin *et al*. 2009; Yrieix *et al*. 2010), the utilized materials were purchased from wood based material company, and this method ignored the manufacture conditions and storing time on VOCs emission. Thus, there is still a gap in the knowledge of VOCs emission characteristics and discipline, especially the relationship between emission of VOCs and manufacture conditions.

Based on previous research, the effects of hot pressing temperature and hot pressing time on the TVOC and VOCs emission were evaluated (Liu *et al*. 2010). However, some fabrication parameters can also affect the VOC emissions; therefore, the relationship between these conditions, TVOC emission, and VOCs needs to be clarified (Wang and Gardner 1999; Baumann *et al*. 1999; Jiang *et al*. 2002). In this study, the effects of particleboard density, thickness, and resin content on the TVOC and VOCs emission were studied by the method of dryers for collection, Tenax-TA tubes for absorption, thermal desorption, and gas chromatography and mass spectrometry (GC/MS) analysis.

EXPERIMENTAL

Materials

The *Larix gmelinii* wood particles were obtained from Langxiang Forestry Corp., Heilongjiang. The particles were dried at 105 °C until the moisture content was approximately 4%. The average size of the particles was 18.7 mm × 2.5 mm × 0.3 mm. The urea-formaldehyde (UF) resin was purchased from Bond Corp., Harbin, China. The UF resin was described as follows: pH 7.8; curing time, 76.8 s; formaldehyde content, 0.6%; and solid content, 51.9%. The resin mixed with 1.0% liquid paraffin as waterproof agent and 1.5% ammonium chloride as curing agent. Toluene-D8 (200 ng/μL; Toronto Research Chemicals, Toronto, ON, Canada) was prepared as internal standards that were dissolved with dichlormomethane (Dingshengxin Chemical Ltd., Tianjin, China).

Manufacture of Particleboards

The UF resin prepared by adding paraffin and NH_4Cl was sprayed onto wood particles in a drum blender. The sprayed particles were mat-formed in a box with dimensions of 340 mm × 320 mm for single layer particleboard. The mats were hot pressed at 140 °C and 2.5 MPa for 5 min. The particleboards were prepared with different density, thickness, and resin content. The detailed information of fabrication parameters is shown in Table 1, and three boards were manufactured under each condition. All particleboards were cut into 155 mm × 155 mm dimensions. The ends and non-testing surfaces of the small particleboards were wrapped in clean aluminum foil, and the uncovered size was 125 mm × 120 mm (the total exposed surface area for one sample was 150 cm^2). The prepared specimens were sealed in polyethylene plastic bags and stored at -30 °C.

Table 1. Manufacture conditions of the particleboards

Variable	Density (g/cm^3)	Thickness (mm)	Resin Contents (%)
Density	0.60/0.65/0.70/0.75/0.80	8	7
Thickness	0.70	8/12/16/19/22	7
Resin contents	0.70	8	7/8/9/10/11

VOCs Collection

The room temperature was controlled to be 23 °C ±0.5°C by air conditioner, and the relative humidity was maintained at 50 ± 5% with air humidifier. The particleboard specimen was quickly placed into a 15-L clean dryer with a loading of 1.0 m^2/m^3. The dryer should be clean with distilled water and placed at ventilated condition. Three samples of each manufacture condition was analyzed. The board was kept in the dryer for 24 h. An ANB3025 intelligent vacuum pump (New Weicheng Technology Ltd., Chengdu, China) was used to receive the gas emission from particleboards in the dryers. The carrier gas nitrogen was passed through, and the air inside of dryer was absorbed by Tenax-TA tubes (89 mm long with 6.4mm O.D. , with 200 mg of fillers inside to absorb VOCs including n-hexane to n-hexadecane, Perkin Elmer, City, US), and the collection process maintained 2 h with 0.2 L/min to receive 24 L sample volume. The experimental system is shown in Fig. 1. These absorbed VOCs were analysed as the first day emission from boards, and after collection the specimen was laid on room until next pre-design test day. The time intervals were set as 1, 3, 5, 7, 14, 28, and 60 days. The VOCs absorbed by Tenax-TA tube was injected with 2μ L of 200 ng/μL Toluene-D8 for quantify the concentrations of VOCs. Afterwards, the VOCs with internal standard were desorbed for 5 min at 300 °C from the tube by thermal desorption system (Beifen Instrument Ltd., Beijing, China) followed by auto injecting 1min into GC/MS.

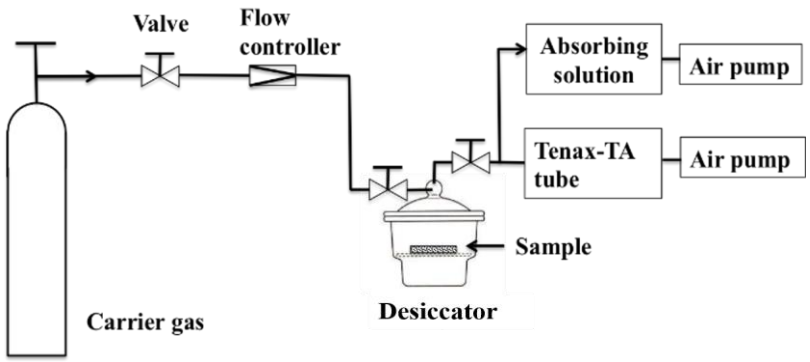

Fig. 1. Experimental system for volatile organic compounds (VOCs) collection from particleboard

VOCs Analysis

The components of VOCs emissions from particleboards were analysed using a GC/MS (Trace DSQ II, Thermo Scientific, Waltham, MA, USA) system consisting of a Trace gas chromatographic and a DSQ °C mass selective detector. TR-V1 capillary column was used with 0.25 millimetre ID, 30 meters and 1.4 μm film thickness to separate the chemical compounds. The GC inlet temperature was set at 250 °C with a split ratio of 1:40. The GC oven temperature started at 40 °C and was held for 2 min. The temperature program was from 40 to 150 °C at a rate of 4 °C per minute and then heated to 250 °C at a rate of 10 °C per minute. The ionizer voltage of the MS detector was set at 70 eV, and the temperature was set to 230 °C. The mass scan range was 40 to 450 amu. The carrier gas

was high-purity helium with a flow rate at 1.0 mL/min. The interface temperature was set at 270 °C. The compounds were identified by the retention time and comparison with mass spectra library. The number of carbon atoms between 6 and 16 with the similarity index more than 700 were selected. The concentrations of volatile components were quantified with the peak area of Toluene-D8. TVOC were calculated as the total concentration of each VOCs components.

RESULTS AND DISCUSSION

Effects of Particleboard Density on the TVOC Emission

Figure 2 shows the effects of the density of particleboards on TVOC emission from 1 to 60 exposure days. In general, the TVOC emission of each density particleboard decreased by prolonging the exposure time. However, the TVOC emissions of each density board on the first day were slightly lower than the results obtained from the third day. This was possibly due to the fact that the samples for detecting in the first day were taken out from refrigerator, so that the low temperature decelerated the release rate of TVOC. From 3 to 14 days, the TVOC of all the particleboards rapidly decreased with the increasing of the exposure time, but this emission level decreased from 14 to 60 days. At each measure time, the TVOC amount increased with increasing density of the particleboards. This phenomenon was attributed to the rising of density required more wood particles and resins, while the thickness and resin content were fixed. The highest TVOC volume was 481 μg/m^3 at 3 days derived from 0.80 g/cm^3 density particleboard. In contrast, the TVOC emission from 0.60 g/cm^3 density particleboard (341 μg/m^3) was 29% lower than highest density board. The lowest TVOC (72.6 μg/m^3) was obtained from 0.60 g/cm^3 density particleboard at 60 days, which was 78% lower than the result of 3 days. However, the TVOC decrement of 0.80 g/cm^3 density particleboard from 3 to 60 days was 72%, indicating that increasing the particleboard density decreased the TVOC emissions of the particleboard.

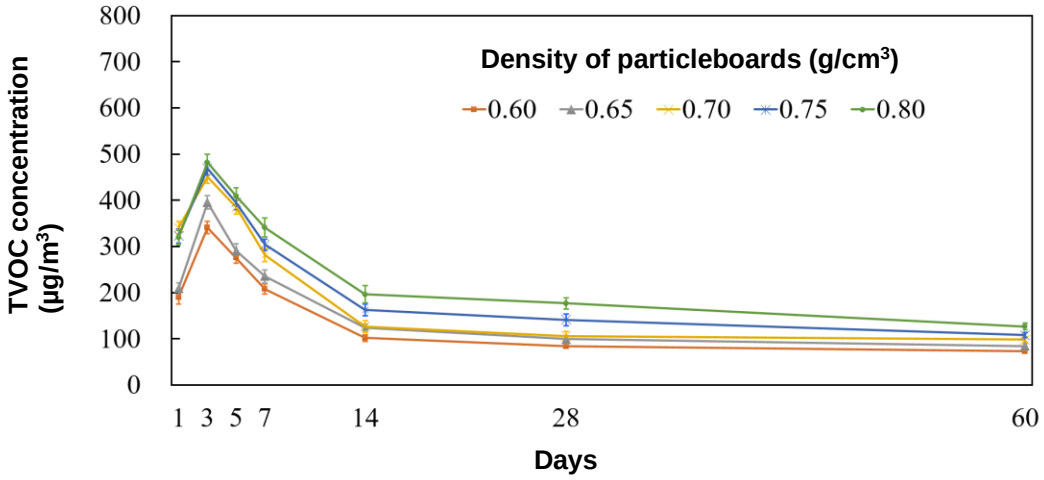

Fig. 2. Effects of particleboard density on the total volatile organic compounds emission

Effects of Particleboard Thickness on the TVOC Emission

Figure 3 shows the effects of particleboard thickness on TVOC emission during the exposure time from 1 to 60 days. A similar trend was obtained compared with the effects

of particleboard density. As the exposure time was increased, the TVOC emission of each thickness type particleboard decreased from 3 to 60 exposure days. The highest TVOC emission obtained from the 16 mm thickness particleboard (631 μg/m^3). Compared with the 16 mm thickness particleboard, the TVOC emission of 8 mm thickness particleboard decreased by 28% (450 μg/m^3). When the exposure time was longer than 28 days, the TVOC amount stabilized. At 60 days, the lowest TVOC emission was obtained from the 8 mm thickness boards (98 μg/m^3), and compared with 3 days was 78% decreased. However, the decrement of the board with 16 mm thickness from 3 to 60 days was 67%, which indicated that the thickness of the particleboard exhibited a negative correlation with TVOC emission efficiency. As the thickness increased, the TVOC amount increased at each detected days. Considering the density and resin content of each particleboard was constant (0.7 g/cm^3 and 7%, respectively), this was due to the increasing of utilization of adhesive and wood particles.

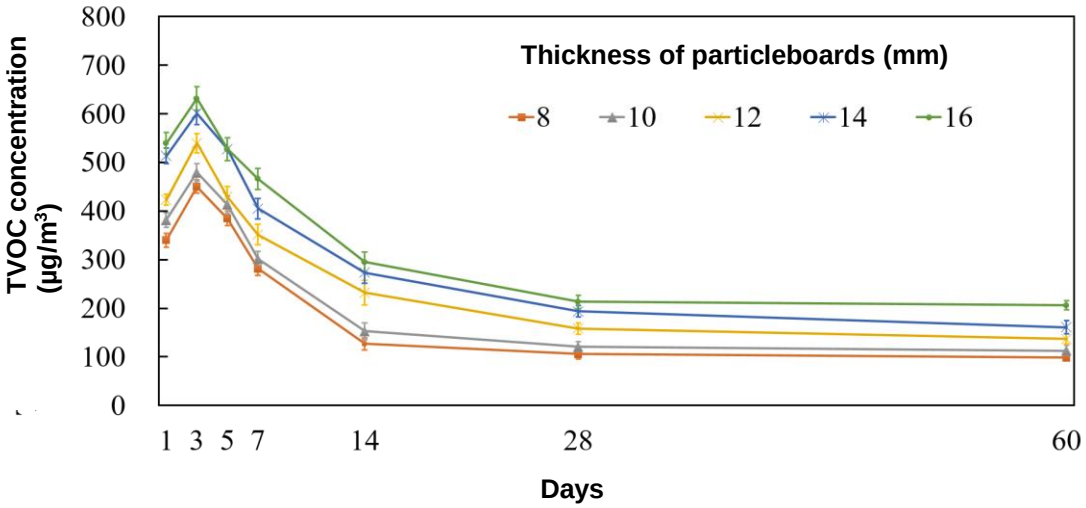

Fig. 3. Effects of particleboard thickness on the total volatile organic compounds (TVOC) emission

Effects of Particleboard Resin Content on the TVOC Emission

Figure 4 shows the effect of resin content of the particleboards on the TVOC emission. The TVOC trend in each specimen increased from 1 to 3 days, and then it decreased from 3 to 60 days. With increasing resin content, the TVOC emission increased at each exposure time, indicating a positive correlation between resin content and TVOC emission. The highest value was obtained from the board bonded with 11% resin content at 3 exposure days (782 μg/m^3), and this value was 74% higher than the TVOC emission of 7% resin content (450 μg/m^3). Notably, 782 μg/m^3 was also the highest value among the 3 group experiments, indicating that the TVOC emission of the particleboard was most effected by the resin content. In addition, the TVOC decrement from 3 days of the board with 7% resin content was 78%, but this value of the board with 11% resin content was 69%, indicating that the resin content of the particleboard exhibited a negative correlation with TVOC emission efficiency.

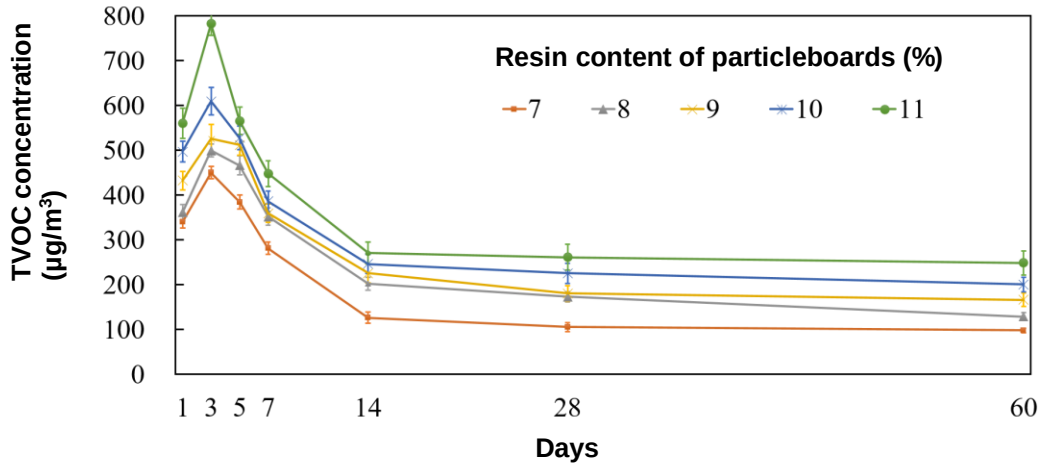

Fig. 4. Effects of particleboard resin content on the total volatile organic compounds emission

VOCs Analysis of the Particleboards Manufactured by Different Conditions

To identify the composition of TVOC, the chemical compounds were detected by the GC/MS method, and all the chemical compounds were classified into 7 types. Figure 5 shows these kinds of compounds concentrations of VOCs emission from five series of different density particleboards after exposing at room temperature 60 days. Aromatics (30 to 34%) were the most component and followed by alcohols (17 to 27%), alkanes (16 to 17%), aldehydes (6 to 12%), ketones (7 to 9%), terpenes (6 to 10%), and esters (3 to 5%). As the density of particleboards increased, the amounts of each component increased, and this was caused by the same reason as for the increasing of TVOC. The levels of each type VOC emission along with density increases are shown in Table 2. Comparing with 0.60 g/cm^3 board, the concentration of ester compounds in 0.80 g/cm^3 density boards increased 233%. The increasing levels in the second and third higher place were aldehydes (221%) and terpenes (149%).

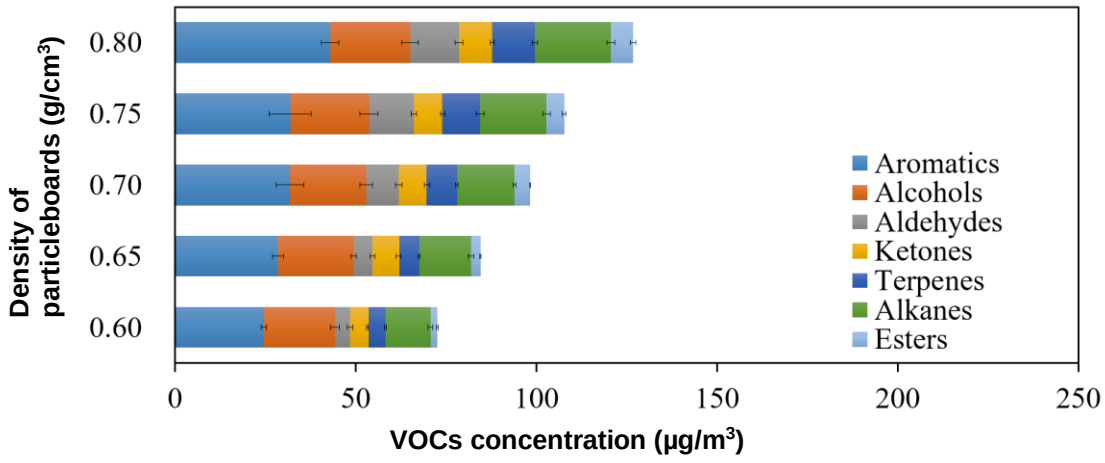

Fig. 5. Chemical compounds concentration of volatile organic compounds (VOCs) emission from five series of different density particleboards after exposure at room temperature for 60 days

Figure 6 shows the amount of VOCs emission from each thickness type particleboard with 60 days exposure time. The amounts of all compounds were increased by adding thickness, and this was attributed to the similar reason as for the increase of

TVOC. The most abundant among the detected VOCs was aromatics, accounting for approximately 30% of TVOC, followed by alcohols (20 to 23%), alkanes (14 to 16%), aldehydes (9 to 13%), terpenes (8 to 12%), ketones (6 to 8%), and esters (4 to 7%). The increment of each type compounds by increasing the thickness of particleboards is shown in Table 2. Compared with 8 mm particleboard, the emission of esters and terpenes increased by 215% and 203%, respectively, indicating that these chemical compounds were most sensitive to the thickness change.

Table 2. Increasing Level of Each Type of Compound at Exposure 60 Days

Compounds type	Increasing level of VOCs* from 0.6 to 0.8 g/cm^3 density (%)	Increasing level of VOCs* from 8 to 16mm thickness (%)	Increasing level of VOCs* from 7 to 11% resin content (%)
Aromatics	75	65	100
Alcohols	12	102	124
Aldehydes	221	151	582
Ketones	81	105	258
Terpenes	149	203	-48
Alkanes	68	111	72
Esters	233	215	306

*VOCs：volatile organic compounds

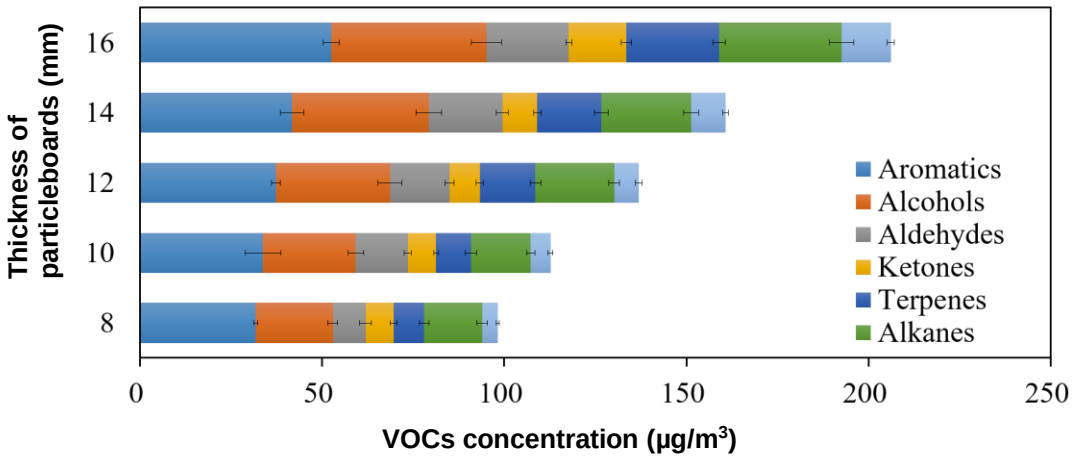

Fig. 6. Chemical compounds concentration of volatile organic compounds (VOCs) emission from five series of different thickness particleboards after exposure at room temperature for 60 days

The amounts of each compound in the TVOC emission of the particleboard manufactured with different resin content and exposure for 60 days are shown in Fig. 7. Most compounds were increased by adding resin content, but the opposite result was observed from terpenes. Aromatics was the highest content in the TVOC of each type particleboard (30 to 32%), followed by alcohols (21 to 25%), aldehydes (9 to 30%), alkanes (15 to 18%), ketones (8 to 13%), esters (4 to 8%), and terpenes (2 to 9%). Table 2 shows the increment of each compound. Comparing the particleboards bonded with 7 and 11% resin content, terpenes were decreased by 48% by adding resin content, indicating that the emission of terpenes was most influenced by the content of wood particles (the density of the particleboard was kept at 0.7 g/cm^3). The increment levels of aldehydes, ketones, and esters showed high values; these chemical compounds were most sensitive to the resin content change. In addition, aromatics, alcohols, and alkanes obtained a positive increment

by adding the resin content, implying that these compounds were also partly derived from the composition of UF adhesive, such as some auxiliaries (Wang and Gardner 1999).

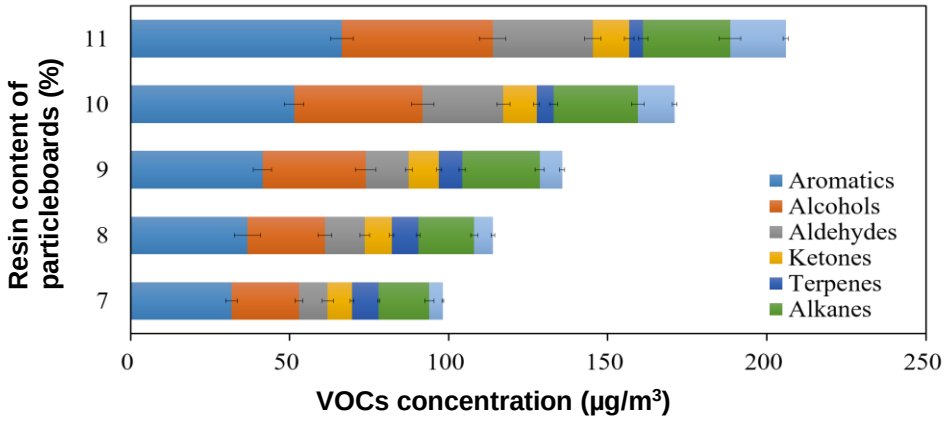

Fig. 7. Chemical compounds concentration of volatile organic compounds (VOCs) emission from five series of different resin content particleboards after exposure at room temperature for 60 days

The main detected compounds (having concentration more than 0.1μg/m^3 and detected more than 35 times.) in each chemical substance types are shown in Table 3.

Table 3. Main Compounds in Each Chemical Substances Type *

Type of Compounds	VOCs Compounds
Esters	Acetic acid, butyl ester
Terpenes	2,4-Dimethylstyrene
	Bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene
Aldehydes	Benzaldehyde
	Nonanal
Aromatics	p-Xylene
	1,2,4-trimethyl-Benzene
	4-ethyl-1,2-dimethyl- Benzene
	1-methyl-4-(1-methylpropyl)-Benzene
	Naphthalene
	2-methyl-Naphthalene
	Ethylbenzene
Alcohols	2-butoxy-Ethanol
	1-butoxy-2-Propanol
	Benzyl Alcohol
Ketones	Acetophenone
Alkanes	Tetradecane
	Pentadecane

* The word “main” implies that the concentration was more than 0.1μg/m^3, and it was detected more than 35 times.

The ester compounds were mainly acetic acid butyl ester. This was possibly derived from the UF resin (Wang and Gardner 1999). Although the concentrations of ester increased obviously, the total amount was just 3 to 5%. The terpenes were derived from wood elements, especially pine (Baumann *et al*. 1999, 2000); thus, the increasing terpene content was due to the addition of wood particles. Regarding aldehydes, these compounds

are the main components of particleboard (Baumann *et al*. 1999; Hodgson *et al*. 2002; Costa *et al*. 2014). Hexanal, benzaldehyde, and nonanal were detected in all of the boards. The hexanal was considered from the wood elements (Hodgson *et al*. 2002), and benzaldehyde and nonanal was most possibly due to the curing or pyrolysis of UF resin (and Gardner 1999). The higher density, thickness, and resin content of particleboards caused more terpenes and aldehydes emission, and this was considered a primary reason for the increase in TVOC. However, the greatest proportion of TVOC were aromatics. The increase in aromatics was due to increasing of wood amount (Jensen *et al*. 2001).

CONCLUSIONS

1. The TVOC and VOCs emissions of the particleboard manufactured under different conditions were investigated in this research. As the exposure time was extended, the TVOC emission from each manufacture conditions of particleboards (density, thickness, resin content) were decreased. The higher density, thickness, and resin content of particleboard at each time of measurement caused a higher concentration of TVOC emission and exhibited a negative correlation on the TVOC emission level.
2. Based on the results of chemical composition analysis of TVOC derived from 60 exposure days, it could be found that the increasing of density, thickness and resin content caused an increment of the kinds of chemical substances, in addition, the aromatics were confirmed as the most compounds of TVOC.
3. The increasing level of esters, aldehydes, and ketones were most sensitive to the change of manufacture conditions. However, terpenes exhibited a positive increment by adding the density and thickness but a negative influence by increasing resin content. This result indicated that terpenes compounds in the TVOC were mostly derived from wood particles.

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