Volatile organic compounds emissions from radiata pine MDF as a function of pressing variables

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Abstract

This research was performed to investigate the effects of press temperature, press time, and resin content on the emissions of volatile organic compounds (VOCs) and formaldehyde during the pressing of radiata pine medium density fiberboard (MDF). To statistically quantify the amount of total VOCs (TVOCs) and formaldehyde according to pressing conditions, this experiment was designed using a central composite design. Detected VOCs were pentanal, hexanal, α-pinene, β-pinene, octanal, heptane, borneol, heptadecane, and octadecane. The most prominent factor affecting the emissions of TVOCs was pressing temperature, followed by pressing time. Resin content appeared to have no effect on TVOC emissions although it was the most important factor influencing formaldehyde emissions. The TVOC emissions appeared to proportionally increase with press temperature and press time. The TVOC emissions showed a linear response with the emission of any individual VOC. This technique offers a potential way to predict TVOC emissions from any individual VOC emission.

Medium density fiberboard (MDF) has been increasingly used in the manufacture of cabinets, furniture, and other finished wood products. In Korea, the 2001 production of MDF exceeded approximately 1,016,000 m^3 and the production appears to be continuously increasing (KFRI 2002). However, the industry has faced challenges as public attention has become focused on the emissions of volatile organic compounds (VOCs) from manufacturing facilities. Much of the concern is related to the potential health and environmental effects of VOCs emitted, because VOCs act as a source of air pollution and ozone precursor chemicals that react with sunlight to change the ozone balance (Larson et al. 1992, Knotts et al. 1995, Milota 2000, Bowyer et al. 2001). As a result of the increasing attention, wood panel industries have experienced increasing regulatory scrutiny over the last few years and have been encouraged to reduce the amount of VOCs emitted from the panel manufacturing processes as well as from the panel itself.

VOC emissions come primarily from volatile and semivolatile extractive compounds, chemical reaction products of the wood extractives, degradation products of the wood, and chemical reaction products of the wood adhesive. However, the types of VOC emissions are highly dependent on temperature (Mezerette and Girard 1991). Highly temperature-dependant VOC emissions indicate that hot-pressing during MDF production may be one of the most important sources of VOCs (Boswell and Hunt 1991, Boswell et al. 1995). Since the temperatures of interest during MDF production are limited to about 180°C, most VOCs mainly arise from volatile and semivolatile extractive compounds and wood adhesive in the MDF furnish.

Although VOC emissions vary widely depending on manufacturing conditions such as pressing time and temperature (Carlson et al. 1995, Ingram et al. 1995, Wolcott et al. 1996, Barry and Corneau 1999, Wang and Gardner 1999, Barry et

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Table 1. — Defiberizing conditions of wood chips.

Steaming temperature	Steaming pressure	Presteaming time	Defiberating time
(°C)	(kgf/cm^2)	----------------(min)----------------	
170	7	3	1

al. 2001), the amount and composition of VOCs emitted are highly species dependant since the sources of VOCs are volatile and semivolatile extractive compounds. In Korea, radiata pine (*Pinus radiata* D. Don) has been one of the most used raw materials for manufacturing MDF. However, little work has been done to obtain emission data for radiata pine, and to develop a model that predicts VOC emissions. In this research, the effects of press temperature, press time, and resin content on the emissions of VOCs during the pressing of radiata pine MDF were investigated and the possibility of predicting VOC emissions during the pressing process was examined.

Materials and methods

Radiata pine fibers and commercial urea-formaldehyde (UF) resin were commercially prepared by a major Korean MDF manufacturer: Dongwha Enterprise Co. Ltd. The average lengths and thicknesses of fibers were 4.33 ± 0.87 mm and 45.23 ± 6.55 μm, respectively, and the formaldehyde-to-urea ratio used to manufacture the boards was 1.35. The defiberizing conditions of wood chips are shown in **Table 1**.

Before further processing, the fibers were dried to a final moisture content of 7 percent. The UF adhesive contained 10 percent ammonium chloride as a hardener, and it was sprayed onto the fiber furnish in a drum blender by using a compressed air spray head. After blending, the furnish was hand felted into a 250- by 250-mm deckle box. The mat was then pressed in the hot press, which was maintained at various pressing conditions. There were 15 different MDFs manufactured according to a 2^3 central composite design (**Table 2**). Each variable was coded by the following methods to ease calculation:

$$C = \{R - [\max(R) + \min(R)]/2\} \;/\; \{[\max(R - \min(R)]/3\}$$

where C = a coded value; R = the actual value.

The experimental design essentially consists of eight equally spaced points on a circle of radius $\sqrt{2}$, one run in the design center and six points on a circle of radius 1.5. Although the point with radius $\sqrt{2}$ offers more precise results for modeling, the value of 1.5 instead of $\sqrt{2}$ was chosen to easily control the pressing variables in this experiment (Myers and Montgomery 1995).

To collect hot-press emissions during MDF manufacturing, a system similar to the one described by Barry et al. (2001) was constructed (**Fig. 1**). The size of the caul plate was 250 by 250 by 15 mm thick and the diameters of the air-inlet and air-outlet ports were 5 mm. When the top platen of the press contacted the mat, ambient air was pulled into the caul air-inlet ports at a rate of 1.5 L per minute. Then exhaust gases were passed through the caul outlet port to the gas collection system consisting of a series of three scrubbers; one scrubber consisted of a 1000-mL vacuum flask in dry ice baths, filled with 500 mL of water to catch formaldehyde, and the others were filled with 500 mL of methylene chloride to catch VOCs.

The samples collected in the first trap were quantified for formaldehyde using the acetylacetone method according to Korean Industrial Standard F 3200 (KSA 1997). The samples

Table 2. — Central composite design for the pressing conditions.

Actual factor values			Coded variables		
Press temperature	Press time	Resin content	Press temperature	Press time	Resin content
(°C)	(sec)	(%)			
160	240	10.0	−1	−1	−1
180	240	10.0	+1	−1	−1
160	360	10.0	−1	+1	−1
180	360	10.0	+1	+1	−1
160	240	16.0	−1	−1	+1
180	240	16.0	+1	−1	+1
160	360	16.0	−1	+1	+1
180	360	16.0	+1	+1	+1
170	300	13.0	0	0	0
170	300	8.5	0	0	−1.5
170	300	17.5	0	0	+1.5
170	210	13.0	0	−1.5	0
170	390	13.0	0	+1.5	0
155	300	13.0	−1.5	0	0
185	300	13.0	+1.5	0	0

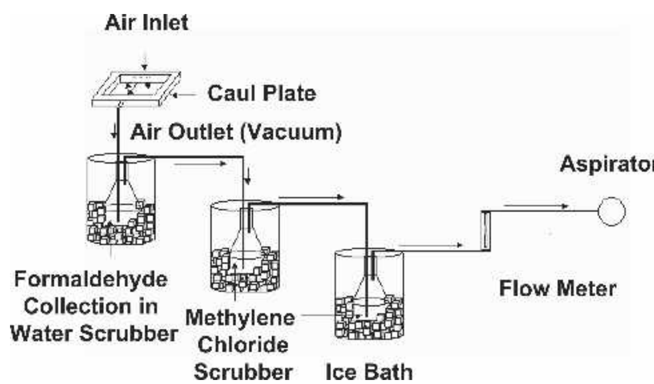

Figure 1. — Caul plate collection system used to collect press emissions.

collected in each trap were analyzed by gas chromatography/mass spectrometry (GC/MS) for the identification and quantification of VOCs. The GC oven was programmed for 4 minutes at 40°C, followed by heating to 280°C at 10°C/min, and held for 8 minutes. The mass scan ranged from 40 to 500 atomic mass unit (amu). Methanol and low molecular VOCs were not analyzed in this study.

Results and discussion

The emission of VOCs and formaldehyde varied widely depending on the pressing conditions; however, the emissions tended to proportionally increase with pressing time and temperature (**Table 3**). VOC emissions were in the range between 50.23 mg/L ovendry (OD) board to 285.16 mg/L OD board, and formaldehyde emissions were between 65.28 mg/L OD board to 203.98 mg/L OD board. Detected VOCs were pentanal, hexanal, octanal, α-pinene, β-pinene, borneol, heptane, heptadecane, and octadecane. Of the amount of VOCs detected, aldehyde accounted for 36 percent (hexanal > pentanal > octanal), terpene for 40 percent (α-pinene > β-pinene > bor-

Table 3 — Formaldehyde and TVOC emissions during the hot-pressing of MDF at various pressing conditions and resin contents.[a]

Press temperature	Press time	Resin content	Formaldehyde	TVOC
(°C)	(sec)	(%)	--------(mg/L OD board)--------	
160	240	10.0	65.28 (2.61)	48.78 (2.19)
180	240	10.0	106.12 (2.86)	80.19 (2.30)
160	360	10.0	94.94 (1.60)	71.22 (0.54)
180	360	10.0	138.79 (3.43)	124.00 (4.62)
160	240	16.0	83.17 (2.62)	56.22 (1.63)
180	240	16.0	133.07 (3.84)	93.69 (2.95)
160	360	16.0	175.23 (1.92)	96.47 (1.17)
180	360	16.0	191.77 (1.99)	195.82 (3.23)
170	300	13.0	155.17 (7.40)	155.73 (7.25)
170	300	8.5	110.43 (3.39)	90.97 (3.01)
170	300	17.5	168.64 (1.90)	161.79 (2.14)
170	210	13.0	71.08 (1.41)	88.80 (1.14)
170	390	13.0	203.97 (3.05)	183.77 (2.92)
155	300	13.0	94.04 (2.62)	40.18 (0.77)
185	300	13.0	160.27 (3.05)	228.12 (3.28)

[a]Values represent the means of five replicates, and values in parentheses are standard deviations.

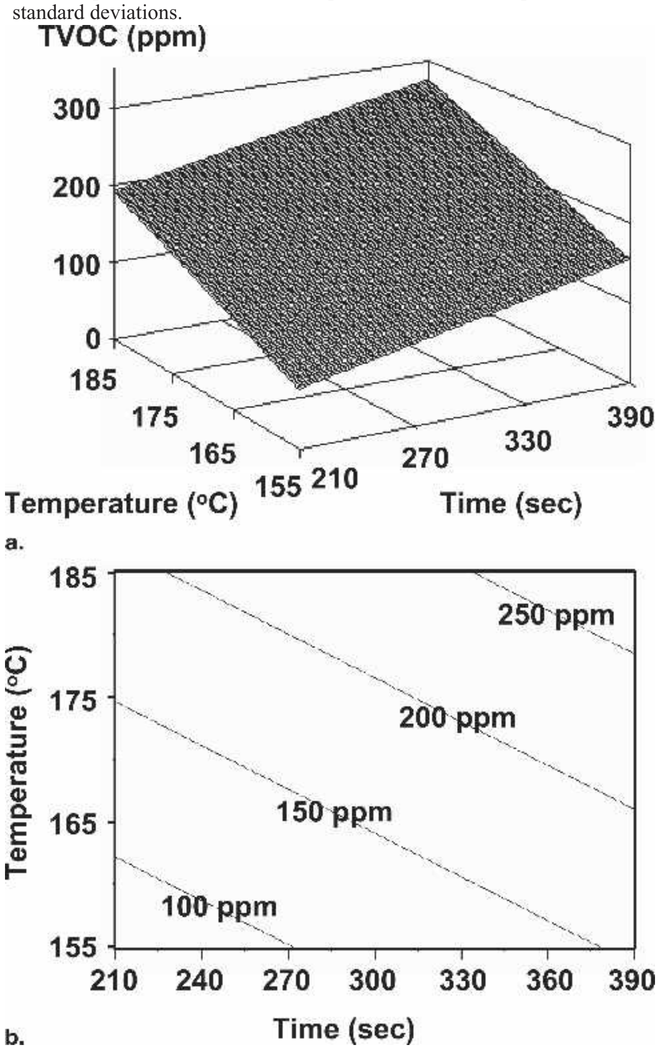

Figure 2. — TVOC emissions (mg/L OD Board) as a function of press temperature and press tim; a. three-dimensional response surface; b. contour plot.

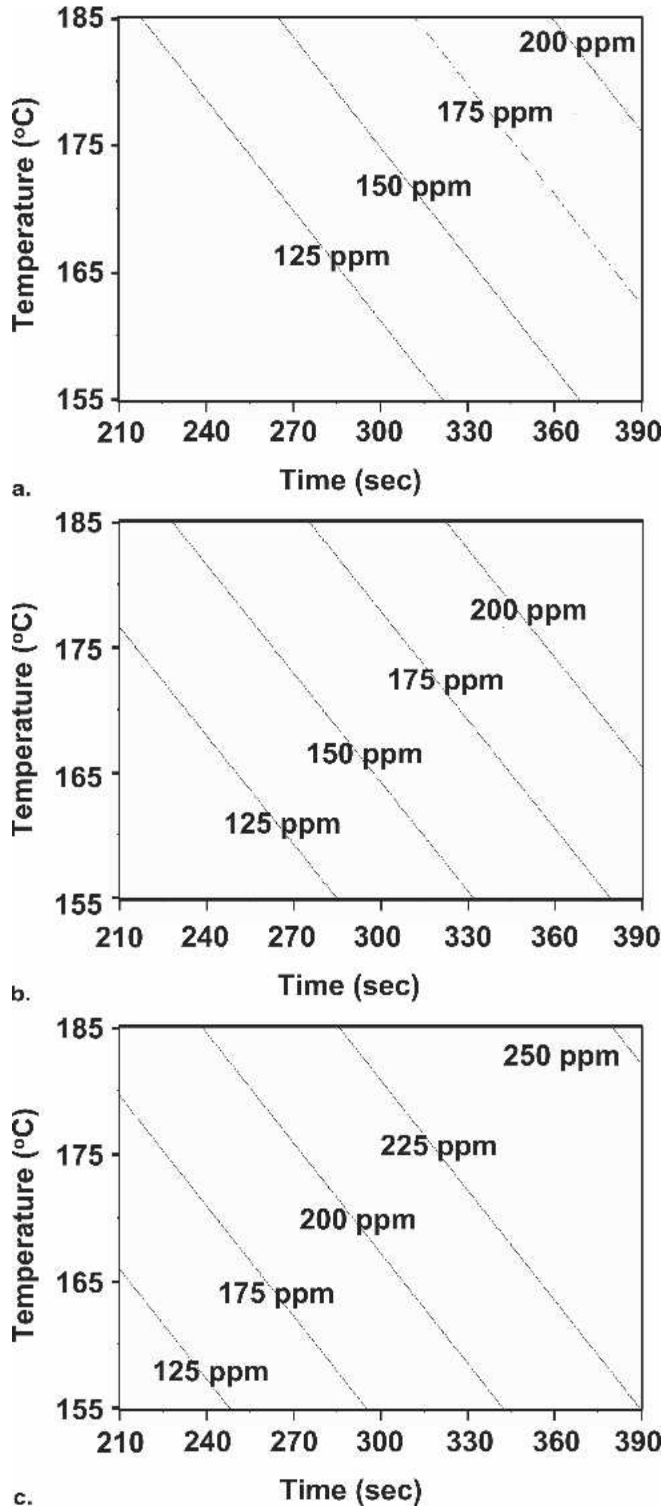

Figure 3. — Formaldehyde emissions (mg/L OD Board) as a function of press temperature and press time under the conditions of various resin contents; a. 10 percent; b. 13 percent; c. 16 percent.

neol), and alkane for 24 percent (heptane > heptadecane > octadecane)

The quadratic models were fitted as a function of press time, press temperature, and resin content using a 2^3 central composite design. The fitted quadratic equations in terms of the coded factors are as follows:

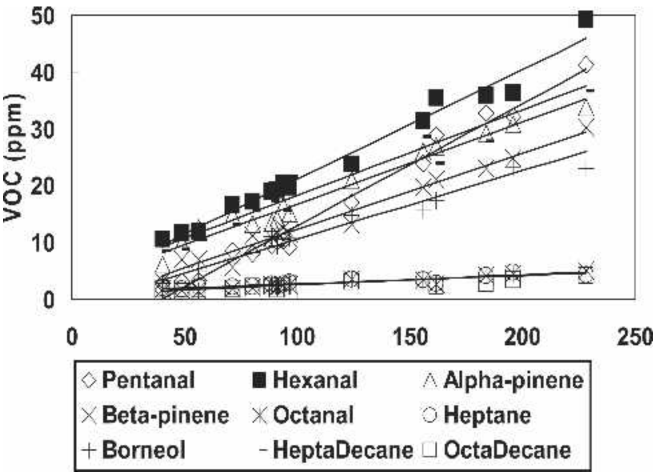

Figure 4. — Relationships between TVOC and individual VOC emissions.

$$\textit{TVOC emission} = 173.67 + 40.23\,x_1 + 28.09\,x_2\ (r^2 = 0.86)$$

$$\textit{Aldehyde emission} = 69.15 + 16.55\,x_1\ (r^2 = 0.83)$$

$$\textit{Terpene emission} = 67.99 + 16.30\,x_1 + 10.90\,x_2\ (r^2 = 0.89)$$

$$\textit{Alkane emission} = 36.53 + 7.38\,x_1 + 5.61\,x_2\ (r^2 = 0.92)$$

$$\textit{Formaldehyde emission} = 159.35 + 18.31\,x_1 + 31.53\,x_2 + 19.50\,x_3\ (r^2 = 0.93)$$

where x_1 = a coded press temperature; x_2 = a coded press time; x_3 = a coded resin content.

TVOC emissions represent the total amount of aldehyde, terpene, and alkane emitted during hot-pressing. The coefficients of determination (r^2) are above 0.80, meaning that the models were highly accurate in reflecting the nature of the VOCs and formaldehyde emissions. The variable most significantly affecting the emissions of TVOCs was pressing temperature, followed by pressing time. However, no interaction among press time, press temperature, and resin content on the VOC emissions were found at a 95 percent confidence level ($\alpha = 0.05$). Resin content appeared to have no effect on TVOC emissions although it was the most important factor impacting the formaldehyde emissions. For practical applications, the fitted models were changed in terms of real variables as follows:

$$\textit{TVOC emission}\ \text{(mg/L OD board)} = -650.73 + 4.02T + 0.47t$$

$$\textit{Aldehyde emission}\ \text{(mg/L OD board)} = -212.23 + 1.66T$$

$$\textit{Terpene emission}\ \text{(mg/L OD board)} = -263.61 + 1.63T + 0.18t$$

$$\textit{Alkane emission}\ \text{(mg/L OD board)} = -117.05 + 0.74T + 0.99t$$

$$\textit{Formaldehyde emission}\ \text{(mg/L OD board)} = -394.00 + 1.83T + 0.53t + 6.50R$$

where T = press temperature (°C); t = press time (sec); and R = resin content (%).

Figures 2 and **3** show three-dimensional response and contour plots of the emissions of TVOC and contour plots of the emissions of formaldehyde, respectively. TVOC emissions continuously increased with the increase of press temperature and press time.

The most influential factor affecting the emissions of formaldehyde was the resin content, followed by pressing temperature and pressing time. The molar ratio of formaldehyde to urea used in this research was 1.35, which resulted in relatively high formaldehyde emissions. According to Carlson et al. (1995), one of the sources of formaldehyde emissions is the amount of free formaldehyde existing in liquid resin, which accounts for approximately 10 percent.

The relationships between TVOC and any individual VOC emissions detected are shown in **Figure 4**. The values of coefficients of determination are above 0.90, indicating that any individual VOC detected can be useful to predict the amount of TVOC emissions. Since pentanal showed the most sensitive response (the steepest slopes) with change of TVOC emissions, it may be used for the prediction of TVOC emissions for practical purposes.

Conclusion

The central composite design used for determining the relationships among pressing variables and the emissions of VOCs or formaldehyde was accurate and provided successful evaluation of the effects of pressing conditions on VOCs and formaldehyde emissions. Although formaldehyde emissions were affected by pressing temperature, pressing time, and resin content, no effect of resin content on TVOC emissions and no interaction among the variables were observed. Since pentanal showed the most sensitive response with the change of TVOC emissions, it may be used for the prediction of TVOC emissions for practical purposes. Further research is necessary to determine the optimum pressing conditions based on the relationships between VOC emissions and the mechanical properties of composite panels.

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