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C.J. Martino, H. Yan, S. Lim, S. Banerjee, L.P. Otwell, M.E. Hittmeier, N. Srivatsa

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Effect of Mat Uniformity on Formaldehyde and Methanol Release During Hot-Pressing

Christopher J. Martino, Hui Yan, Steven Lim, Sujit Banerjee Institute of Paper Science and Technology 500 Tenth Street NW Atlanta, GA 30318

> Lawrence P. Otwell, Michael E. Hittmeier Georgia-Pacific Corporation PO Box 105605 Atlanta, GA 30348

> > Narendra Srivatsa
> > International Paper Corporation
> > 1422 Long Meadow Road
> > Tuxedo, NY 10987

Abstract

Laboratory work shows that the steam released when resin-coated flakes are hot-pressed carries out the methanol and formaldehyde, whose concentrations in the emissions are linearly related. The scatter in the relationship increases considerably when the process is scaled up. However, for particle, the scatter is minimal even in full-scale work. These compounds mainly derive from the resin formulation, but are also produced in small quantities from the thermal degradation of wood. If the mat is non-uniform, then hot spots develop and the contribution from wood tissue degradation becomes irregular and leads to scatter. A simple heat transfer model suggests that variation in mat density is the probable cause of the scatter. Hence, if mat uniformity is controlled, then methanol and formaldehyde will be released principally with the steam, and it may be possible to treat air emissions from pressing *only* when steam is evolved.

Factors governing the release of methanol and formaldehyde have been studied recently in response to present and pending environmental regulations (Carlson et al., 1995). These compounds are considered to be hazardous air pollutants, or HAPs. Wolcott et al. (1996) measured the levels of methanol and formaldehyde released from pressing resin-coated particleboard and found them to be proportional to the amount of water evolved, which implied that these compounds were transported out of wood by the expressed water. This suggests that the volume of air subject to control devices such as regenerative thermal oxidizers (Matros et al. 1996) could be reduced if the press emissions were isolated and treated only during the release of steam. For a conventional press, the bulk of the steam escapes when the press opens. We have measured the profiles of these HAPs and other volatile components while pressing flakes or particle in laboratory, pilot, and full-scale settings and have identified some of the factors that influence the feasibility of treating a segregated air stream.

Experimental

The furnish used was pine throughout. Small laboratory-scale measurements were made at the Institute by placing about 15 g of flakes (collected from several facilities) in a foil bag constructed from 0.005-cm 309 high-chromium stainless steel and fitted with air intake and outflow tubes. GP145C48 core PF resin was added to the flakes at 2.2% of oven-dried wood mass. The bag was sealed and placed between the heated (250°C) top platen (diameter: 13 cm) and lower cold platen of an electrohydraulic press (MTS), and pressed at 1,500 kPa for three minutes. The final MC was less than 1%. Airflow of 0.5-1 lpm was maintained through the bag during pressing and for five minutes thereafter and the emissions were vented through 10 mL of chilled water. The trap water was then analyzed by gc. Breakthrough was measured by placing a second trap in series after the first. Carryover of formaldehyde and methanol into the second trap was <10% and <30%, respectively.

For experiments where multiple samples were taken during a run, green pine flakes were dried at 105°C to initial MCs of 15, 9, and 6.5%. Core resin (GP145C48) was added at 2.2% of oven-dried wood mass, and the flakes were pressed at 1,500 kPa for various intervals. The upper platen was kept at 200°C; the lower platen was at room temperature. Airflow of 0.3 lpm was maintained through the bag.

Larger-scale laboratory pressing was done at Georgia-Pacific's Decatur, GA, facility. Rotary-dried flakes (MC: 8.6%) were obtained from the Georgia-Pacific's Grenada, MS, mill. Conveyor-dried flakes (MC: 6.6%) were collected from Norboard in Tupelo, MS. Boards of 1.9 cm and 0.95 cm thickness were pressed (a) without resin, (b) with GP145C48 core resin (2.2%), and (c) with GP145C30 face resin (2.2%). Slack wax (1%) was added to the resin. Boards were pressed for five minutes at 1,700 kPa to a density of 640 kg/m³ under an airflow of 2 lpm. Time-dependent collections were made with chilled water impingers. An attempt was made to detect phenol by gc; none was found at a detection limit of 1 mg/kg.

Pilot-scale work was done with the press at the University of Minnesota, Duluth. The press temperature ranged from 182 to 216° C; the total press time was 4 minutes. The starting MCs of the 0.9×2.25 meter panels were 2-9%. Liquid resin from Neste was added at 4%, and wax from Borden was present at 1% of dry wood mass. The mat was formed by hand. Since measurement of board strength was not planned, no attempt was made to orient the flakes. The bottom platen was porous, and the emissions were collected and expressed from a single outlet. Collections were made from this outlet by drawing the emissions at 2 lpm through a chilled water impinger. Four 1-minute collections were made, with the impingers being changed between collections. Each impinger was weighed before and after sampling to determine the water condensed. The amount of water lost from the wood was known from the weight of the wood before and after pressing. The VOC:water ratio collected in the impinger was then applied to the water lost from the wood to obtain the VOC released on a dry-mat basis. In addition to the compounds listed, hexamethylene tetramine was found in about a quarter of the samples at up to 6 μ g/g.

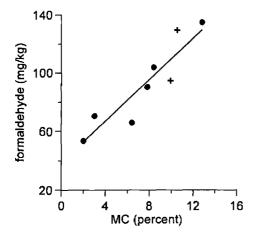
Full-scale measurements were made in a particleboard mill. UF resin was added at 10% of oven-dried fiber weight in the face and 8% in the core. The board (1.9 cm) was 40% face and 60% core. A heated 30-meter line was placed adjacent to the press. Hence, a mixture of press emissions and ambient air was collected. This was unavoidable, since a single collection point

was unavailable. The platens were kept at 156°C, and a pressure of about 3,500 kPa was applied to the board. The time for loss of daylight was 13 seconds and the press remained closed for three minutes. The emissions were drawn sequentially through three chilled water impingers. Collection was begun when the press just closed. The length of each sampling period was varied from 90-240 seconds to catch the emissions from different stages of pressing. The dead volume in the sampling tube corresponded to a clearance time of twelve seconds. The amount of water collected in the trap was immeasurably small because the press emissions were diluted with ambient air.

Results and Discussion

Results for flakes pressed in the small-scale MTS press are shown in Figure 1. The slopes are similar, suggesting that they originate from the same process. Hence, it appears that the methanol and formaldehyde in the resin formulation are driven out of the mat together by the steam released. Emissions in the absence of resin were much smaller; these arise from the thermal degradation of wood tissue (Su et al. 1999). Hence, as noted by Wolcott et al. (1996) for particle, most of these HAPs derive from the resin formulation, and only a small part comes from wood breakdown.

The above results were obtained under conditions where the furnish was pressed to almost complete dryness, *i.e.*, almost all of the water was expressed by the end of the run. In order to determine whether the HAPs were removed continually with the steam, flakes were pressed at various starting MC values and the HAPs collected at different levels of pressing. The results are illustrated in Figure 2. Note that the methanol and formaldehyde track each other closely. The total formaldehyde emission over the total three-minute period for all three conditions is 120 ± 20 mg/kg; the corresponding value for methanol is 100 ± 30 mg/kg. The slope of the line in the top panel (MC: 6.5%) in Figure 2 is steeper than those of the others. The lower-moisture flakes would reach a higher average temperature than the others since evaporative cooling by the escaping steam would be less pronounced. As a result, wood-tissue degradation would be more extensive and would increase the total quantity of HAPs released.



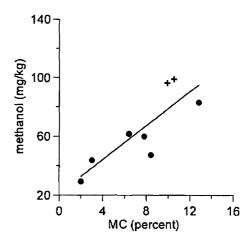


Figure 1: Formaldehyde and methanol from the pressing of pine (circles) and aspen (crosses) flakes with 2.2% core resin.

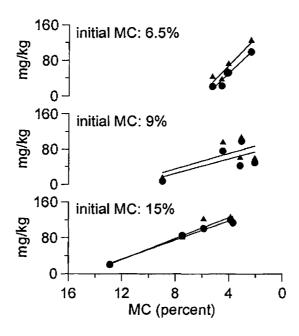


Figure 2: Relationship between HAPs emissions and MC from pressing pine. The circles and triangles represent methanol and formaldehyde, respectively.

Flakes were pressed to 1.9 cm and 0.95 cm boards in larger-scale laboratory work. Emissions of methanol and formaldehyde from the 0.95 and 1.9 cm boards were similar, even though the 0.95 cm boards contained half as much total resin. This is likely related to the fact that very similar quantities of water were expressed from both boards, since the thinner board reached a higher overall temperature. These results are consistent with the premise that HAPs are released as a near-constant fraction of the steam evolved.

Results from pilot work are illustrated in Figure 3 for formaldehyde. There is a weak linear trend (r^2 =0.59) and the scatter is extensive. The scatter for the corresponding methanol plot (not shown) is even greater, and the relationship between methanol and formaldehyde (Figure 4) also shows high scatter. The mat was formed by hand and was not oriented, which must have led to significant density differences. This would give rise to uneven drying, and wood tissue degradation would be more extensive in some regions than in others. We believe that the observed scatter arises from these irregularities.

The relationship between formaldehyde and methanol is surprisingly linear in full-scale work with particle, as shown in Figure 5. Figure 6 illustrates the quantities of methanol and formaldehyde collected over various periods. The emissions seem to peak at the point at which the press opens. Steam evolution began midway into the press cycle, and the probe sampled this steam diluted with ambient air. Much more steam was released when the press opened but if the concentration of HAPs *in* the steam were unchanged, then the amount of HAPs collected would remain approximately the same, since the probe draws a constant volume of sample.

In sum, linear relationships were obtained in laboratory work with flakes, but extensive scatter occurred in pilot measurements. However, full-scale measurements with particle gave

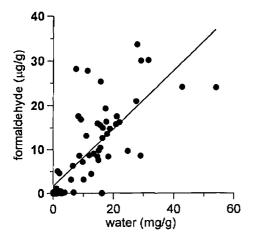


Figure 3: Relationship between formaldehyde and water emissions.

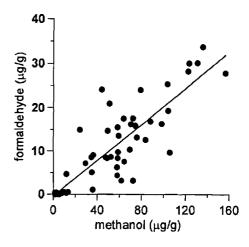


Figure 4: Relationship between methanol and formaldehyde emissions.

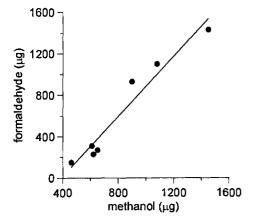


Figure 5: Relationship between formaldehyde and methanol emissions in the full-scale trial.

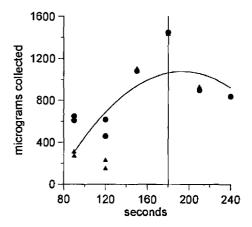


Figure 6: Methanol (circles) and formaldehyde (triangles) collected in the full-scale trial. The line represents the time at which the press opens.

good results. The difference is attributed to differences in uniformity. The methanol and formaldehyde in the resin formulation are principally driven off by the steam, and they would emerge with the steam if the contribution from wood degradation were small. Density differences would lead to uneven heat transfer, which would give rise to differences in the degree of tissue degradation. This would add variability to the total methanol and formaldehyde emissions, as observed in the pilot-scale results. Good results were obtained in full-scale measurements since particle is quite uniform in comparison to flakes.

The effect of pressing variables on mat temperature was studied with a simple heat transfer model. Our objective was to determine the point at which steam would begin to evolve from

the mat and the factors that could affect the timing of this release. For our objective of treating segregated HAPs emissions to be viable, the release would have to occur over a predictable period. We assumed that a constant-temperature platen would contact the mat, and that the mat temperature would be uniform throughout. We recognize that temperature differences exist across the width of the mat (Bolton 1989a, 1989b) and that mass transfer occurs (Kamke and Casey 1988) from the surface to the core during early pressing. However, these factors would not lead to significant steam evolution from the mat. Our only objective was to project when the mat temperature would reach 100° C as a function of operational parameters.

It has been shown (McCabe et al., 1985) that eq. (1)

$$T = T_s - \frac{8}{\pi^2} e^{-\left(\frac{\pi}{2}\right)^2 \frac{c d \tau}{s^2}} \left(T_s - T_a\right) \tag{1}$$

applies when a mat contacts a constant-temperature platen, where T_s is the constant average temperature of surface of the mat, T_a is the initial temperature of the mat (ambient temperature), T represents the average temperature of mat at time t_T , α is thermal diffusivity, t_T is the time of heating, and s is one-half of the mat thickness.

Equation (1) was applied to a 1.6 cm mat initially at 25° C pressed between 200° C platens. The thermal diffusivity was assigned a value of 1.889×10^{-3} cm²/sec (Kollmann and Côté 1968). The absolute value is not critical since the plot is relatively insensitive to thermal diffusivity and, in turn, to small changes in MC, which affects thermal diffusivity. Figure 7 shows that the time to reach 100° C is sensitive to mat thickness. In contrast, the mat temperature is relatively insensitive to small changes in platen temperature, as shown in Figure 8. Hence, mat thickness is the most important factor that affects the time of steam evolution. Since the flakes were not oriented during the pilot trial there were probably large differences in mat thickness, which probably led to the scatter observed. The scatter is lower for the full-scale trial because a mat comprised of particle is much more uniform than one prepared with flakes.

In summary, our laboratory and full-scale results confirm that methanol and formaldehyde are driven out with the steam released. This opens the possibility of treating emissions released only during this period if the steam and the HAPs emerge over a short predictable period. This requires the mat to be uniform, since otherwise some regions of the wood would overheat and release HAPs over a wider interval. Hence, mat uniformity is a key consideration if HAPs are to be treated only during steam evolution.

Acknowledgement

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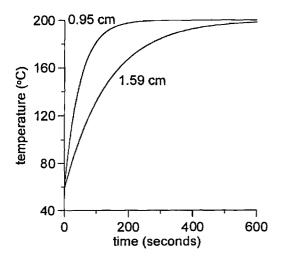


Figure 7: Effect of mat thickness on temperature profile (platen temperature: 200°C).

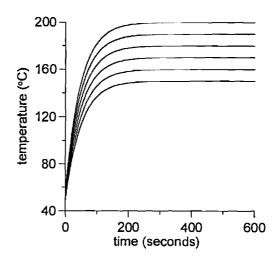


Figure 8: Temperature profiles of a 0.95-cm mat at platen temperatures of 150-200°C in 10°C intervals.

References

Bolton, A. J., P. E. Humphrey, and P. K. Kavvouras. 1989a. The hot pressing of dry-formed wood-based composites. Part III. Predicted vapor pressure and temperature variation with time, compared with experimental data for laboratory boards. Holzforschung. 43, 265-274.

Bolton, A. J., P. E. Humphrey, and P. K. Kavvouras. 1989b. The hot pressing of dry-formed wood-based composites. Part IV. Predicted variation of mat moisture content with time. Holzforschung. 43, 345-349.

Carlson, F. E., E. K. Phillips, S. C. Tenhaeff, and W. D. Detlefsen. 1995. A study of formaldehyde and other organic emissions from pressing of laboratory oriented strandboard. Forest Prod. J., 45(3), 71-77.

Kamke, F. A., and L. J. Casey. 1988. Fundamentals of flakeboard manufacture: internal-mat conditions. Forest Prod. J., 38(6), 38-44.

Kollmann, F. F. P., and W. A. Côté Jr. 1968. Principles of Wood Science and Technology. I. Solid Wood. p. 251. Springer-Verlag.

Matros, Y.S., G.A Bunimovich, S.E. Patterson, and S.F. Meyer. 1996. Is it economically feasible to use heterogeneous catalysts for VOC control in regenerative oxidizers? Catalysis Today, 2, 307-313.

McCabe, W.L., J. C. Smith, and P. Harriott. 1985. Unit Operations of Chemical Engineering, McGraw-Hill.

Su, W., H. Yan, S. Banerjee, L. P. Otwell, and M. E. Hittmeier. 1999. Field-proven strategies for reducing volatile organic carbons from hardwood drying. Environ. Sci. Technol., 33, 1056-1059.

Wolcott, J. J., W. K. Motter, N. K. Daisy, S. C. Tenhaeff, and W. D. Detlefsen. 1996. Investigation of variables affecting hot-press formaldehyde and methanol emissions during laboratory production of urea-formaldehyde-bonded particleboard. Forest Prod. J., 46(9), 62-68.