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Mechanisms of Terpene Release During Sawdust and Flake Drying

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Abstract

The water and α-pinene released during sawdust and flake drying were simultaneously measured. For sawdust, the drying profiles for water and pinene are very different at oven temperatures of 105°C, but are fairly similar at 200°C. There is an initial burst of pinene very early in the process, which is attributed to the loss of pinene dissolved in surface water. Later, the pinene and water are released in a near-constant ratio, which is ascribed to water mobilizing pinene from the interior of the wood matrix to the wet line. The surfactants present in wood are believed to solubilize pinene into water. The pinene:water ratio is similarly constant for drying flakes. Finally, when the wood is almost dry, pinene is lost through evaporation. Hence, at least three mechanisms are operative for the movement and release of α-pinene and other terpenes from wood.

Introduction

Volatile organic compounds (VOCs) released during softwood drying fall under environmental regulation, and there is much recent interest in defining the nature and mechanism of these emissions (Baumann *et al.* 1999; Cronn *et al.* 1983). Softwood VOCs are principally terpenes, of which α-pinene is the major constituent. Methanol, formaldehyde, and other products of wood tissue decomposition are also present (Barry and Corneau, 1999; Su *et al.* 1999). VOCs from hardwood consist of only these decomposition products. Two VOC signals emerge during softwood drying. There is a sharp initial spike, followed later by a second broad signal that begins when the wood is almost dry (Banerjee *et al.* 1995). The intensity of the second signal increases with increasing dryer temperature; it rises sharply at 165°C, the boiling point of α-pinene, indicating that it originates from simple evaporation of terpenes (Banerjee *et al.* 1998b). This paper evaluates the various mechanisms through which terpenes are released from softwood sawdust and flakes during drying, through study of α-pinene as a model compound.

Materials and Methods

Sawdust obtained from the Adel, GA, mill (owned at the time by Weyerhaeuser) was sieved through an 18-mesh screen. Flakes were obtained from the Georgia-Pacific OSB mill in Dudley, NC. The material was dried in a 1.5-inch diameter ceramic tube furnace whose midsection was electrically heated (Banerjee *et al.* 1998b). The furnish (<8 g) was placed in a ceramic boat in the heated zone. Air was metered to the tube inlet at 0.25 lpm, and the emissions collected in a trap containing 2 g of Tenax-GR. To establish recoveries, α-pinene (2 μL) was evaporated in a 130°C furnace for 3 minutes under an airflow of 0.25 lpm, and the emissions trapped. The trap was then desorbed with about 3-4 mL of methanol, which was analyzed by gc on an HP5 column. A recovery of 80 ± 10% (n=14) was obtained. Corresponding experiments where 0.5-1 g of deionized water were evaporated and trapped gave a recovery of 80 ± 16%, as measured by the weight gained in the trap. The traps were changed every three minutes when

emissions from wood were collected. α-Pinene constituted 65 and 40% of all the gc signals observed during drying at 105 and 200°C, respectively. All experiments were duplicated. Typical results are illustrated in Figures 1-4, with α-pinene and water emissions being expressed as ppb and ppm, respectively, per green-basis weight of wood. The dried sawdust was Soxhlet-extracted with methanol, which was analyzed by gc.

For the pressing experiments, green softwood flakes (4 pieces, 8-10 g) were pressed between blotters in an electrohydraulic press (Banerjee *et al.* 1998a) at a peak pressure of 2,000 psi delivered in a 40 ms pulse. Water and organics were expressed into the blotters, which were sonicated in methanol, and analyzed by gc.

Results and Discussion

Drying curves for α-pinene and water at various temperatures are illustrated in Figures 1-4. First, consider the 200°C profile in Figure 4 where the pinene and water signals closely track each other. Both components are removed through heat, and if they had behaved independently of each other, the profile for pinene would have lagged behind that of water on account of its higher boiling point. The similar profiles of the two components require a common mechanism to be responsible for their removal. Most likely, water transports the pinene through the wood matrix to the wet line.

One possibility is that pinene dissolves in water and then moves with it. In order to determine whether the water in wood is saturated with α-pinene, water was pressed out of green wood and its α-pinene content measured. A value of 15 ppm was obtained, which is higher than the reported water solubility of 5 ppm at 25°C (Fichan *et al.* 1999). The higher value in wood moisture is probably due to the presence of surfactants such as oleic acid, which would increase solubility. The solubility of α-pinene at higher temperatures is unknown, but a value of 25 ppm at 95°C was estimated through the UNIFAC method (Banerjee 1996). Pinene:water ratios (taken from values in Figures 1-4) are plotted in Figure 5. The ratio in the central region (where the temperature remains steady at about 95°C because of evaporative cooling) is fairly constant at about 1,000 ppm, which is much higher than the estimated solubility. However, as discussed above, the surfactants in wood will increase pinene solubility, and more surfactant will dissolve at the higher temperature. Surfactants are known to be able to induce order-of-magnitude increases in the water solubility of hydrophobic organics (Edwards *et al.* 1991; Kile and Chiou, 1989; Liu and Chang, 1997). At 25-50 kg/tonne, there is certainly a sufficient quantity of resin and fatty acids in wood to induce solubilization (Smook 1989), although only a small fraction of this will dissolve. Hence, the simplest mechanism that accommodates the similar pinene and water profiles in Figure 4 is that pinene is solubilized into water by the surfactants present, and is then moved to the wet line. It should be noted that the pinene must be actually solubilized and not just moved as droplets, since otherwise the VOC profiles would be much noisier than is observed.

Corresponding profiles for flakes are illustrated in Figures 6-8; the pinene and water signals match well. A plot reported earlier for flakes (with total VOCs measured instead of just α-pinene) is reproduced in Figure 9, and the VOC:water ratio in the central region is 500-1,000 ppm, which is similar to the value observed in Figure 5. This confirms the validity of using α-pinene as a model compound for softwood VOCs. Hence, the pinene:water ratio in this region of

the drying curve is insensitive to both the type of furnish and the dryer temperature, which would occur if the water in wood was pinene-saturated. Differences in dryer temperature do not influence the solubility, since the wood tissue temperature remains at just below the boiling point of water on account of evaporative cooling, regardless of the dryer set temperature (Banerjee *et al.* 1998b).

The position of the early pinene peak is temperature-independent and remains constant at 3 minutes, which suggests that it originates from the surface. Although the boiling point of α-pinene is higher than that of water, it peaks <u>earlier</u> than does water at the lower temperatures. Consider the effect of heating a piece of green wood in air. Since the Henry's Law coefficient (the air:water distribution) of α-pinene is high at 14,300 Pa m^3/mol (Fichan et al. 1999), the compound will tend to transfer from surface water to air. Using a standard two resistance air:water model Mackay has shown that the half-life of a compound with a Henry's Law coefficient of > 250 Pa m^3/mol in a 1 m^2 water film is 0.69 L/K$_w$, where L is the film thickness in meters, and K$_w$, the water mass transfer coefficient, is 1 x 10^{-5} m/s at 25°C (Mackay 1985). This leads to a half-life of 100 seconds from a depth of 1 mm, and much less at higher temperatures. Although the depth of the surface water film in wood is unknown, it is clear that α-pinene can be rapidly lost from surficial water even when the wood is relatively cool. Hence, the transfer of dissolved pinene to air must be a component of the initial signal. As a result, the initial dip in Figure 5, which reflects the proportionately higher loss of pinene over water from sawdust is absent in Figure 9, which applies to flakes.

The differences between the water and pinene signals from sawdust at 105 and 200°C can now be reconciled through the following argument. At 105°C, the evaporation of water is initially slow, and pinene is lost from the surface with a proportionately small loss of water. At the higher oven temperature, the wood heats up faster, the interior water with its dissolved pinene load moves to the surface more quickly, and both constituents are released together.

Finally, pinene can be lost through simple evaporation late in the drying process. It has been shown previously (Banerjee *et al.* 1998b) that the loss of VOCs from dry wood is vapor pressure driven. For example, the VOC-dryer temperature curve breaks upwards at about 160°C, the boiling point of α-pinene. The increase in VOC emissions during late drying in Figures 5 and 9 reflects increasing pinene evaporation as the wood temperature climbs after the evaporative cooling effect of water is lost.

It is apparent from Figures 1-4 that the amount of α-pinene released increases with increasing temperature. In an attempt to establish a mass balance, the dried wood was solvent-extracted to determine the residual α-pinene. The results, shown in Table 1, indicate that the total pinene (released during drying and remaining in the dried wood) apparently increases with increasing temperature. The reasons are not known. One possibility is that there are occluded regions in wood that are difficult for the solvent to access, but from which pinene can be removed through heat.

In summary, there seems to be (at least) three mechanisms for the movement and release of α-pinene and other terpenes from wood. A burst occurs very early in the process, and this is attributed to the loss of pinene dissolved in surface water. Pinene and water then tend to be re-

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leased in a near-constant ratio, and this is attributed to water mobilizing pinene from the interior of the wood matrix to the surface. It is believed that the surfactants present in wood solubilize pinene into water. Finally, when the wood is nearly dry, pinene is lost through evaporation. These mechanisms can be used to predict VOC emissions under different drying conditions, and to identify strategies that favor isolation of low-volume VOC-rich streams that lend themselves to incineration.

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Table 1. α-Pinene released during drying and retained in sawdust.			
temperature (°C)	released during drying (μg/g)[1]	residual in wood (μg/g)[1]	total (μg/g)[1]
green furnish		250 ± 50	250
105	248 ± 1	102 ± 0	350
130	373 ± 2	27 ± 2	400
160	350 ± 10	6 ± 0	356
200	480 ± 60	3 ± 0	483
[1]average of 2 values, green basis			
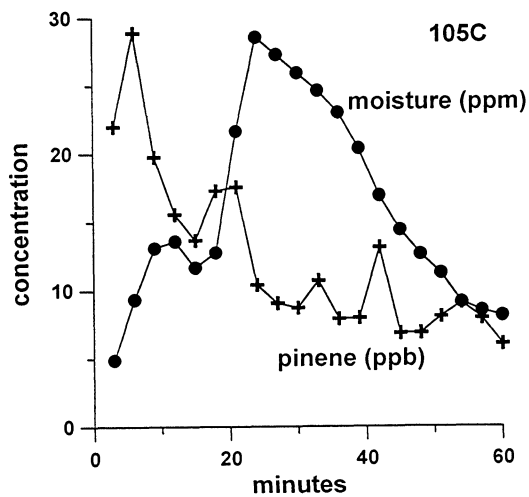
Fig. 1. Emissions from sawdust at 105°C.
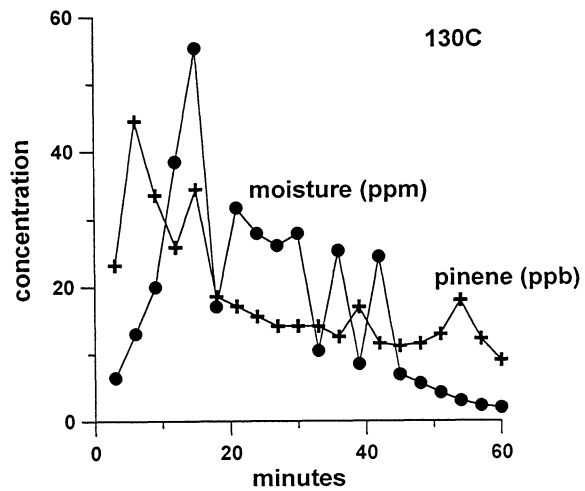
Fig. 2. Emissions from sawdust at 130°C.
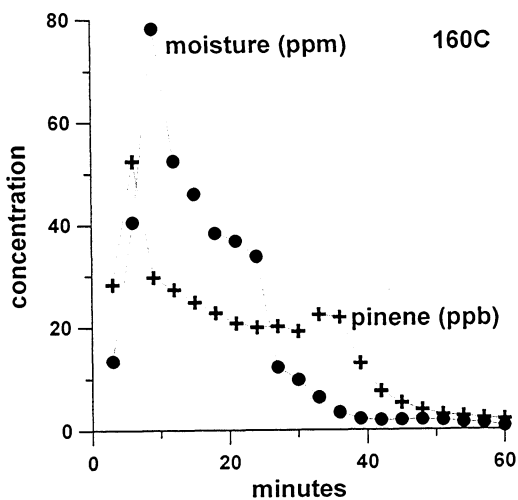

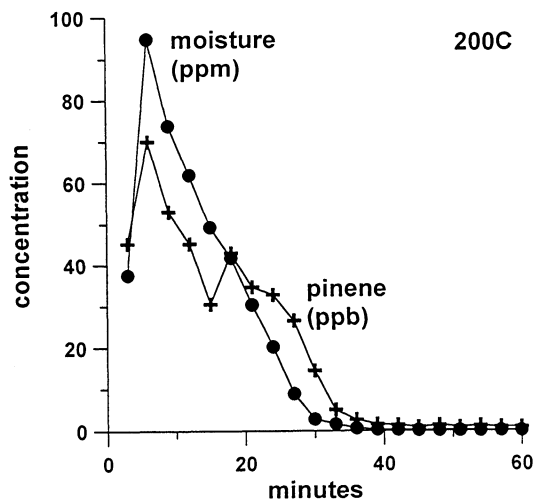**Fig. 3.** Emissions from sawdust at 160°C.

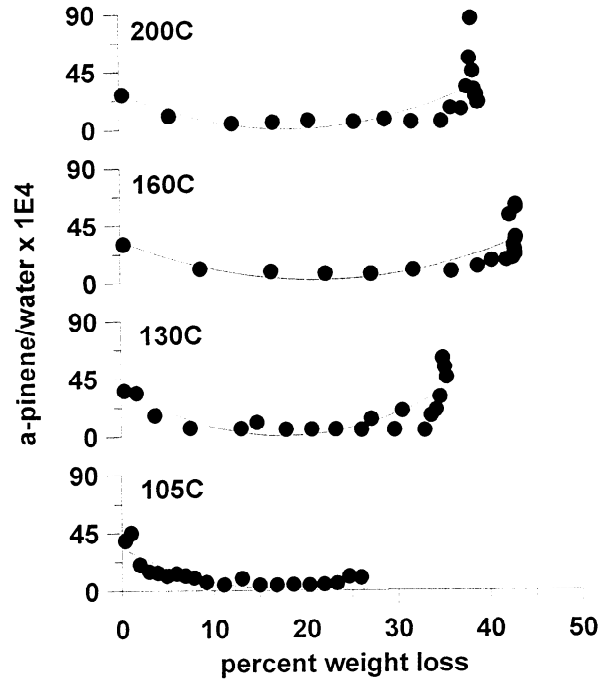**Fig. 4.** Emissions from sawdust at 200°C.

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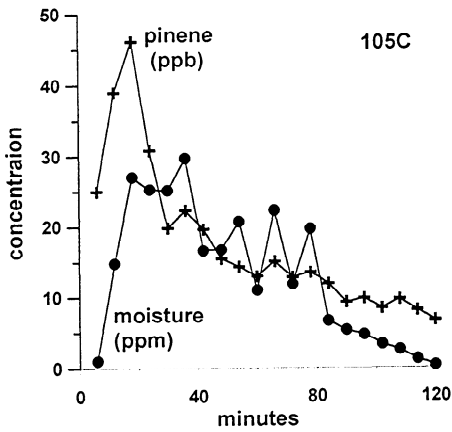**Fig. 5.** VOC/water ratios for sawdust.

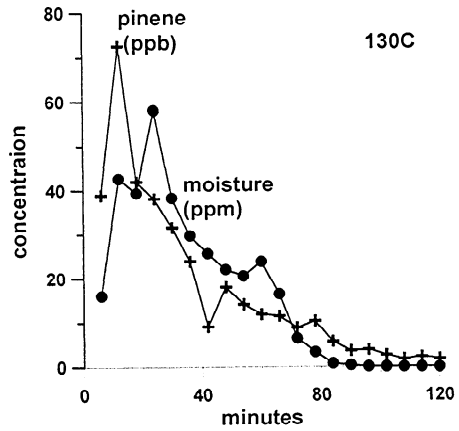**Fig. 6.** Emissions from flakes at 105°C.

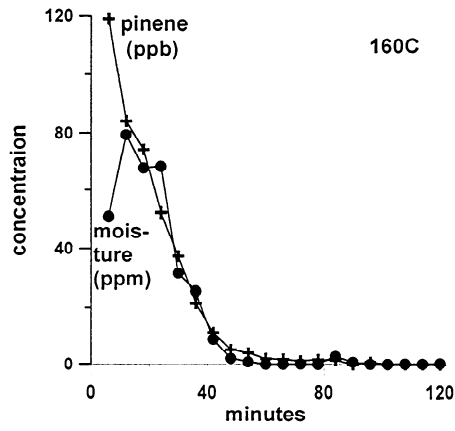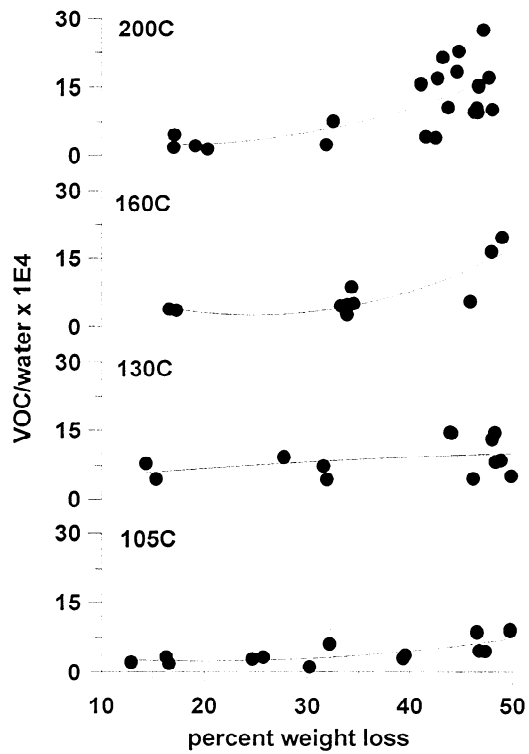**Fig. 7.** Emissions from flakes at 130°C.

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Fig. 8. Emissions from flakes at 160°C.

Fig. 9. VOC/water ratios for flakes (Banerjee *et al.* 1998).