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Mechanism Of VOC Release From Lumber Kilns

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Abstract

Hydrocarbon (Method 25A) emissions from drying softwood lumber have been measured in full-scale experiments. The mechanism proposed comprises three components: release of turpentine dissolved in the surface layer of water on the wood, water-mediated transport of turpentine from the interior of the wood to the surface, and evaporation during the falling rate period. The result allows the total Method 25A release to be estimated without knowledge of the airflow through the kiln. Full-scale Method 25A emissions from lumber can be predicted from laboratory work on sawdust, indicating that the mechanism is independent of the type of furnish.

Introduction

The measurement and control of VOC emissions are of current interest since regulatory compliance is expensive. To date, the source of VOCs and the factors that govern their release have been addressed empirically, *e.g.* through study of the relationship between VOCs and operational parameters such as temperature and wood geometry (Shmulsky 2000 a,b,c; Shmulsky and Ingram 2000). Also, seasonal factors significantly affect the amounts of monoterpenes (the predominant VOC component) present in living southern pine trees (Conners *et al.* 2001). In this paper we discuss the mechanism of VOC release from commercial drying of lumber and establish a quantitative link to emissions from other types of furnish such as particles.

Experimental

Southern pine lumber was dried in a relatively new commercial southern pine dry kiln in the Southeastern US. The wood was dried to a target MC of 14–14.5% through indirect heating with steam coils; the loads were mixed charges of 2 x 10's and 2 x 12's, with a volume of about 105,000 b.f. The dry bulb temperature was ramped up to 100°C in three hours and then gradually increased, reaching 115°C by the end of the run (about 17.5 hours). The vents were kept closed for the first four hours (*i.e.*, the warm-up period plus one additional hour), and then the exhaust vents were opened fully for the duration of the run. The intake vents were kept closed throughout; hence the data collected generally represent actual changes in the kiln atmosphere resulting from lumber drying with minimal influence of external air infiltration.

Hydrocarbons emissions were measured during July and November 2000 through Method 25A (Anon 1995) and are reported on an as-propane basis. The emissions were measured after diluting the kiln air sample with an equal amount of ambient air to minimize instrument problems caused by the high sample humidity. Air samples from within the kiln were also collected hourly in chilled methanol impingers, and the trapped α -pinene was determined by gas chromatography. The condensed water was weighed to calculate the water:analyte ratio.

A trailer was sited adjacent to the kiln to house instrumentation, and sampling probes were inserted at breast height through two gasketed holes in the kiln wall to determine whether the air flow and/or sampling location might affect the measurements. One was placed close to the kiln entrance; the second was positioned at the middle of the kiln. Each probe was a 70-cm long piece of 0.6 cm copper tubing (preheated to over 200°C) tipped with a fine mesh filter. Method 25A measurements were made continually at both locations; kiln air was sampled through heated lines to avoid condensation problems. The values from the two probes were almost identical, confirming that the kiln volume was well-mixed.

Results and Discussion

The concentration vs time profile for VOC release from wood is complex. There is an initial burst very early in the drying process and the VOCs then emerge in a near-constant amount until the wood is almost dry, at which point the emissions increase. The timing of the first signal depends on the amount of wood surface exposed to hot air; *e.g.* the peak for particle appears earlier than that for lumber. Additionally, the position of the first peak is independent of dryer temperature, suggesting that it originates from surface material while the wood warms up. Turpentine components can be rapidly lost from surficial water; we estimate that loss of α -pinene from a 1 mm water film at 25°C occur with a half-life of only 100 seconds (Banerjee 2001), a value that decreases at higher temperature. There is ample precedence for the loss of high-boiling compounds from water surfaces. For example, polychlorobiphenyls are lost from Lake Superior principally through volatilization (Jeremiason *et al.* 1994) because of their high Henry's Law coefficient (the air:water distribution coefficient).

Consider the emissions from southern pine sawdust measured in a tube furnace in the laboratory (Banerjee 2001) at furnace temperatures of 105° and 200°C as illustrated in Figures 1a and 1b. The differences between the water and α -pinene signals from sawdust at 105° and 200°C can be reconciled through the following argument. At 105°C, the evaporation of water is initially slow but α -pinene dissolved in the surface layer of water is rapidly lost. As the wood warms up, the rate of evaporation of water increases and the water signal rises.

The α -pinene and water signals track each other well at 200°C. Both components are removed through heat, but at 200°C the profile for α -pinene (with its higher boiling point of 156°C) would have lagged behind that of water if they were volatilized independently of each other. The similar profiles for the two components indicate that a common mechanism is responsible for their removal. One possibility is that water dissolves the α -pinene and moves it out to the wet line, whereupon they both evaporate. However, the α -pinene:water ratio in Figure 1b is 0.001, whereas the solubility of α -pinene in water is estimated to be only 25 ppm at 95°C (Banerjee, 2001). The difference can be closed if the effect of surfactants such as oleic acid is considered. These compounds are present in wood at 25-50 kg/tonne (Smook 1989) and can greatly elevate the solubility of organics in water (Edwards *et al.* 1991; Liu and Chang 1997). Most of the turpentine released is located in resin canals which also hold the resin and fatty acids. Hence, when the resin canals burst during drying, the mixture of turpentine and surfactant would spill into the wood matrix and the surfactants would solubilize the turpentine into water.

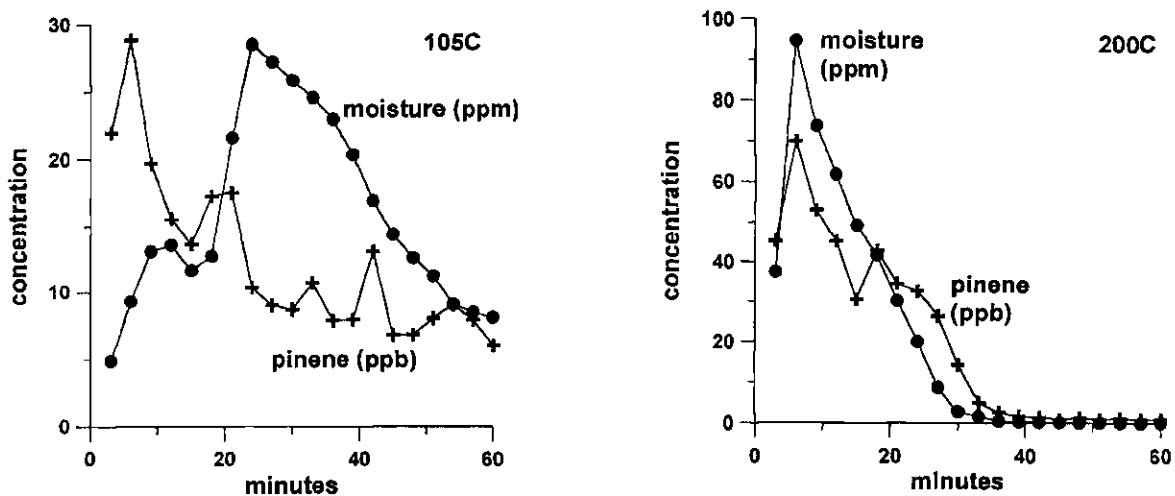


Figure 1. (a) α -Pinene emissions versus water released at 105°C; (b) Pinene emissions versus water released at 200°C.

α -Pinene and water emissions collected during the drying of southern pine sawdust at various temperatures are plotted as α -pinene:water ratios in Figure 3 (Banerjee, 2001). The α -pinene:water ratio in the central region (where the temperature remains steady at about 95°C because of evaporative cooling) is fairly constant at about 0.1% at all temperatures. Remarkably, the 0.1% value cited above also holds approximately for tamarack, spruce and fir (Yan and Banerjee, 2001).

Late in the drying process α -pinene is lost through simple evaporation from hot, dry wood. The increase in VOC emissions during late drying in Figure 3 reflects increasing α -pinene evaporation as the wood temperature climbs after the evaporative cooling effect of water is lost. Hence, there seem 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 ascribed to the loss of α -pinene dissolved in surface water. α -Pinene and water are then released in a near-constant ratio, and this is attributed to water and surfactant mobilizing α -pinene from the interior of the wood matrix to the surface. Finally, when the wood is nearly dry, α -pinene is lost through evaporation. As shown below, VOCs are released from lumber in exactly the same manner.

Representative emissions profiles for the July and November commercial dry kiln runs are illustrated in Figure 4. All runs were replicated, and the replicates within each sampling event agree very well. The November emissions are somewhat higher than those in July, possibly because of seasonal factors (Conners *et al.* 2001). Profiles of α -pinene and water are illustrated in Figure 5; there is a remarkable mirror-image relationship. As discussed earlier, the high initial α -pinene signal is believed to reflect loss of surficial material. α -Pinene is then lost along with

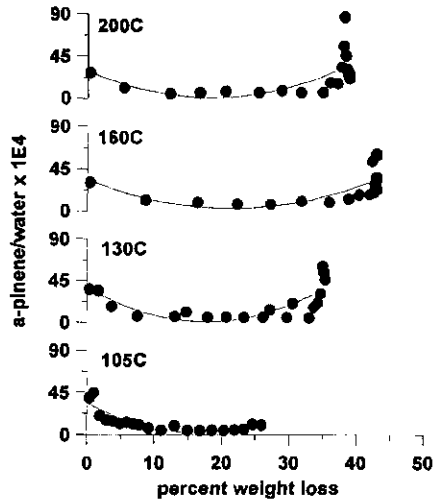


Figure 3. α -Pinene/water ratios for southern pine sawdust.

water at an approximately constant ratio from 5–13 hours. Finally, local overdrying occurs (on surfaces) and the VOCs rise as the water emissions taper off during the falling rate period. Note that the pinene:water ratio (in Figure 5) after the vents are opened after four hours is approximately 0.1%, the same value observed in Figure 3. If this value is applied to the water lost from drying lumber from a moisture content of 100 to 15%, then 2.1 lbs/Mbf of α -pinene would be released. This result does not consider the final uptick in Figure 4 that increased the emissions from these particular runs by about 35% compared to what they would have been had the VOC emission rate been constant until the run was completed. α -Pinene represents about two-thirds of the total turpentine emissions from southern pine, and therefore a value of 4.4 lbs/Mbf is calculated for Method 25A emissions (*i.e.*, after the vents were opened).

Emissions for the first four hours can be estimated through the following analysis. The emissions will principally occur through leaks as the air within the kiln expands from an ambient temperature to 100°C. The VOC concentration in the commercial kiln averages about 2,000 ppm during the first four hours, and the kiln volume less the volume of the wood is approximately 52,000 cu ft. Heating this volume from ambient temperature (say 30°C) to 100°C expands it by 23%. The amount of VOC contained in this volume is 0.5 lbs/MBf. If this is added to the emissions estimated for the remainder of the kiln cycle, then an overall value of 4.9 lbs/MbF or 3.9 lbs/dry ton results, which compares well with results from a recent multi-facility study on lumber drying (Otwell, 2001). Importantly, the calculation does not consider airflow at all. Except for the initial spike, the emissions are normalized with respect to the water lost. Hence, the contribution of leaks is relatively unimportant, since the calculation does not consider *how* the emissions leave the kiln, only that it does so. Key features of the approach are that the VOCs and the water in the headspace are uniformly distributed, and that pinene is released as a constant fraction of water for most of the drying cycle. There are two major sources of variability. The 0.6 lbs/Mbf value for the initial closed-vent period is load-specific. It, and the 35% adjustment for the final uptick will depend on factors such the kiln layout, drying conditions and final moisture content.

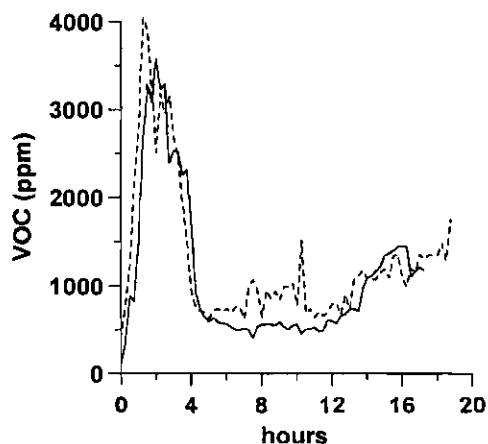


Figure 4: Method 25A profiles collected from a commercial southern pine dry kiln in July 2000 (bold) and November 2000 (dashed).

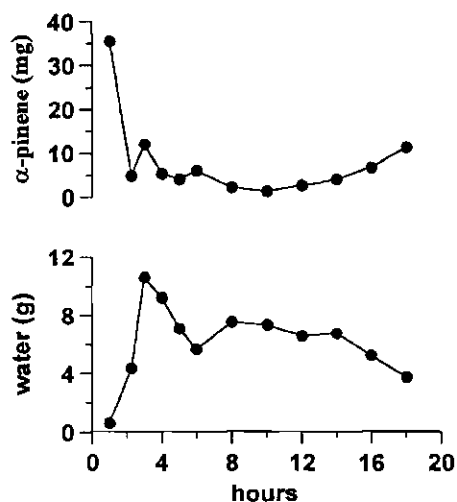


Figure 5: α -Pinene and water profiles collected from the commercial dry kiln run in July 2000.

It is important to remember that the basis of the calculation, the α -pinene:water ratio of 0.1% was derived from laboratory work with sawdust and can also be applied to emissions from drying OSB furnish (Banerjee 2001). Hence, the mechanism of VOC emissions from wood seems to be similar across furnish types.

Acknowledgements

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