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Low VOC Drying of Lumber and Wood Panel Products
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Hui Yan, Sujit Banerjee
Institute of Paper Science & Technology

Terry Conners, Leonard L. Ingram, Ashlie T. Dalton, M.C. Templeton, Susan V. Diehl

Mississippi State University

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Summary

- Results from a multi-year study show that a significant part of the extensive variability observed in OSB flake dryer emissions can be traced to physiological effects, and the rest can be attributed to handling and other factors.
- Low-headspace treatment of lumber was scaled up to the 50 kg level. The amount of turpentine collected was of the same magnitude as that released upon drying lumber. For the process to be economical, the wood must first be brought to about 95°C with steam, and then processed with RF.
- Attempts to remove VOCs from OSB through low-headspace by placing a curtain over the furnish failed because of leaks. A more rigid container will be required.
- RF-treatment does not alter the gas permeability of lumber.

Effect of seasonal variation in southern pine terpenes on dryer emissions

This study was begun in 1996 because a southern pine oriented strand board (OSB) mill reported wide variability in Method 25A VOC emissions measured in the field. Two measurements could not be reproduced even when taken on the same day; it was unknown whether this result was due to random variability in the raw material itself, systematic seasonal variations, or to handling. An additional issue was that the sporadic measurements typically made in the field may include unrecognized seasonal effects, atypical of average annual emissions. The mill was interested in alternative means of making measurements and sent samples of fresh flakes to the Institute of Paper Science and Technology for analysis. These samples were wrapped, stored cold, and dried in a 130°C tube furnace equipped to monitor total hydrocarbon emissions (Banerjee *et al.*, 1998). The results of laboratory analyses from the first two year's samples demonstrated that the VOC concentrations varied by as much as 500% (from ~ 300 μg/g to 1500 g/g on a wet basis), as shown in Figure 1.

Consistent with the mill's previous Method 25A measurements, significant variation was apparent even within single sampling dates. There appeared to be some degree of interactive relation with the ambient temperature and rainfall data (Figure 2), but (at least in part because of the data variability) it was not clear that there was a significant cause-and-effect relationship. It

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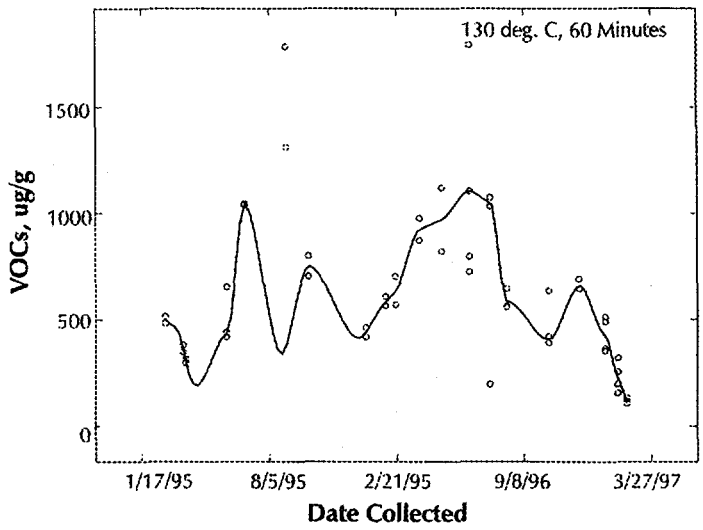

Figure 1: Results of laboratory analyses of southern pine flakes from a North Carolina OSB mill.

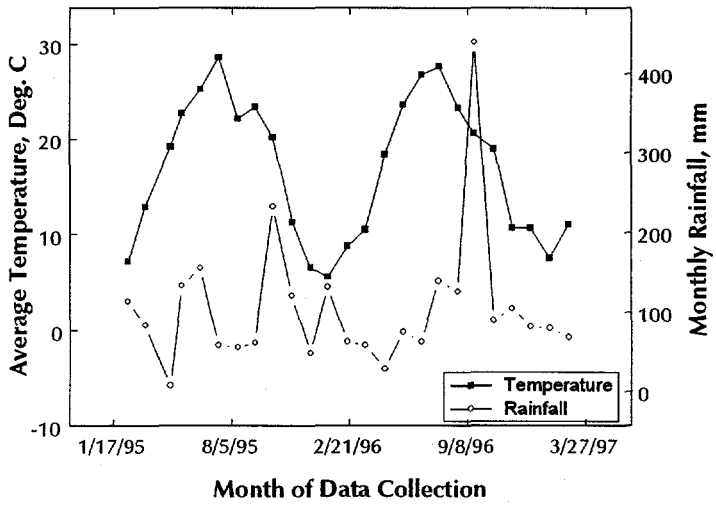

Figure 2: Rainfall and temperature data corresponding to North Carolina OSB mill location.

seemed likely that other factors such as handling, storage conditions, or sampling at the mill might be affecting the laboratory measurements. The company requested further work, including measurements of VOCs from standing trees, to verify the scatter in the flake VOC measurements and to determine, if possible, the reasons for the large variation in the measured VOC concentrations. This work is still in progress, but this report provides the information available at this time.

As part of this investigation the available literature was reviewed to determine if variability in total VOC (monoterpene) content had been studied before. There are numerous articles describing the variation of VOCs from resinous conifers, but most of the available information has been collected from studies of needles, seedlings and twigs. No information was found that described the variation of VOCs in the trunks of standing trees. A number of studies were found that describe the changes in monoterpene composition on a seasonal basis for various species, but most of these were conducted over periods of one year or less. For example, Zafra and Garcia-Peregrin (1976) surveyed the composition of essential oil distilled from *Pinus halepensis* twigs for part of one year (from October through June) and found that the principal components were sabinene and α-pinene. In this study, there was approximately twice as much sabinene as α-pinene; the α-pinene proportion seemed to decrease slightly during the cooler months (by about 10%), while the sabinene proportion increased commensurately. The small month-to-month differences noted for the concentrations of terpenes in the twigs were seen in needles as well. An investigation of *Pinus elliottii* by Bin *et al.* (1992) found that the amount of "turpentine" steam-distilled from resin from tapped trees increased from July to November, and that the major constituents were α-pinene and β-pinene. α-Pinene constituted about two-thirds of this mixture, although the proportion of β-pinene was somewhat greater during the cooler months. Lerdau and Stilts (1992) found "seasonal declines" in monoterpene concentration but constant emissions from foliage; Lerdau *et al.* (1995) later reported a strong effect of temperature and seasonality on emissions. He-Ping (1995) reported that the relative contents of some volatile terpene compounds collected from the foliage of *Pinus tabulaeformis* varied between the summer and the winter months; for example, the α-pinene and β-pinene concentrations both increased by about 25% during the summer months compared to the January samples. There are evidently important genetic and physiological aspects of terpene biosynthesis that affect tree-to-tree variations. Raffa (1991) has also reported that the monoterpene concentration in grand fir (*Abies grandis*) increased nearly four-fold after insect attack. All of this information did little to answer our immediate question.

Experimental

An experiment was planned in early 1997 to compare VOC emissions from fresh southern pine flakes with samples obtained from standing trees. In a continuation of the initial study, samples of southern pine flakes were requested on a periodic basis from the North Carolina OSB mill for laboratory VOC analysis, and plans were made to monitor the monoterpene concentrations in a longitudinal study using twelve straight, well-formed loblolly pine trees (*Pinus taeda*) (each approximately 39 cm (15 inches) in diameter and forty years old) in the Mississippi State University's John W. Starr Memorial Forest. These trees were naturally reseeded, not from a plantation, and all of the trees should have a somewhat similar genetic provenance because they were located in the same area. From March, 1997, until September of that year one 0.5 cm (0.2 inch) diameter increment core was taken from each tree per month for analysis of the monoterpene and resin acid content according to the analytical procedure described at the end of this paper. The first core from each tree was taken at breast height, and successive cores were offset by several inches both horizontally and vertically/upwards (Figure 3). To prevent infection, each hole was plugged with a maple dowel immediately after the core was taken. Each core was been divided into three portions prior to analysis (inner third, center third and outer third) to enable us to study the intra-tree monoterpene distributions should this prove useful at a later date.

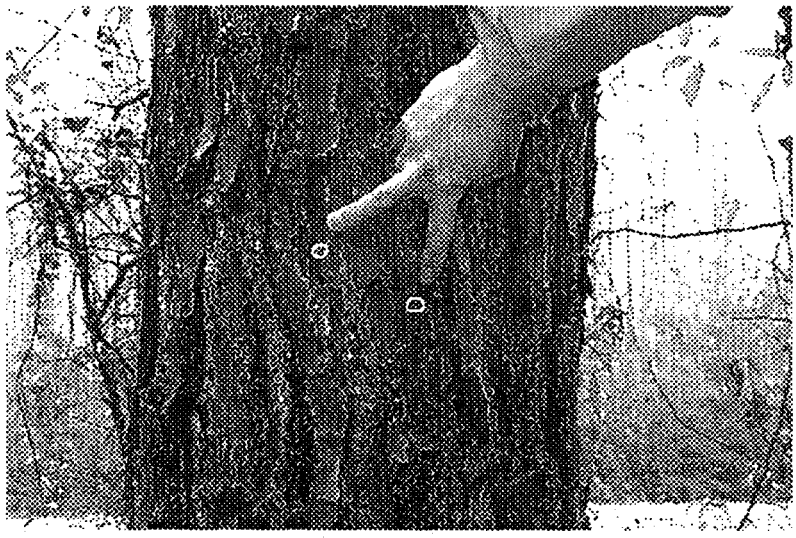

Figure 3: One of the sampled trees with two increment-cored locations marked.

In September of 1997 the sample trees (although clearly marked) were cut by an overzealous logging equipment demonstrator, and after a one-month hiatus the experiment was continued with another twelve trees in a nearby location. These trees are of similar age and size to the original sample trees. Like the original sample, the second group was naturally reseeded and was not part of a plantation planting. One of the twelve trees was cut and dissected during the month of December, 1998, to determine whether the repeated sampling and plugging caused injury-induced resin to bleed internally and bias the data, but no evidence was seen to indicate that this was a problem.

The potential for handling and storage conditions to affect VOC measurements was recently addressed by the Mississippi State University Forest Products Laboratory. In a series of controlled experiments, southern pine chips from freshly-cut 16- to 18-year old trees were taken directly from a paper mill chipper. Samples of these chips were analyzed immediately (using five replications) for both α-pinene and β-pinene (which together comprise most of the monoterpenes in loblolly pine); additional samples, sterilized using sodium azide and maintained at room temperature, were measured every two or three days for two weeks. Approximately one-third of the α-pinene was lost during the first week, after which no further losses were noted. β-Pinene concentrations did not appear to be affected. Based on these results it is concluded that the handling and storage history of the flakes sent from the mill might affect the monoterpene concentrations of some samples.

Figure 4 shows the monoterpene concentration data collected and analyzed through August, 1998; a locally-weighted (loess) regression line (span=0.5) has been drawn through the data to help illustrate the overall trend in the face of such evident variability. Figure 4 shows that there are slight differences from one year to the next (no doubt partly caused by sampling different trees), but most of the change in concentration appears to be due to season or some associated climatological component. Based on these data it appears that loblolly pine trees have a greater

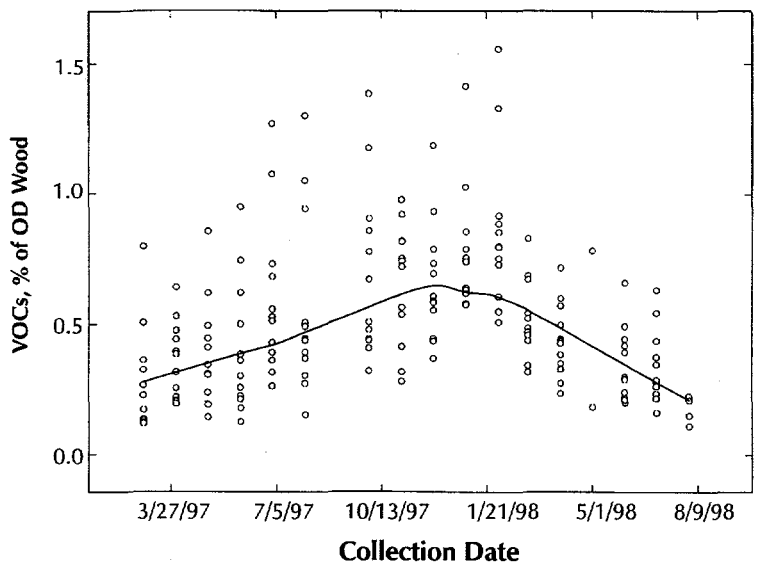

Figure 4: Total VOCs as a percent of ovendry (OD) wood from the longitudinal study of 12 loblolly pine trees (loess regression line shown overlaid on data, span = 0.5).

monoterpene content during the cooler months of the year. In Mississippi this also means that loblolly pine trees have a greater monoterpene content during the rainiest months of the year.

Because of reports which describe the variation of monoterpenes in needles of various conifers as functions of temperature, sunlight or moisture (*e.g.*, Lincoln and Langenheim (1978), Zafra and Garcia-Peregrin (1976)), climatological data were obtained from the USDA Agriculture Research Center at Mississippi State University (ftp://marlin.csrumsu.ars.ag.gov) and the average monoterpene concentrations were plotted as functions of these influences (Figures 5-7). Obviously the solar radiation and temperature data are highly correlated, so it is not surprising that these plots are similar. During the first year of sampling, the average monoterpene concentration increased as temperature increased then continued to climb to its highest point during the cooler months; this trend did not repeat during the second year of sampling. As can be observed from the graphs, during the second year the monoterpene concentrations actually decreased to the lowest levels observed during this experiment. Possibly this indicates an interactive effect with rainfall, as the summer of 1998 was considerably drier than the summer of 1997. It is also worthwhile to note here that samples containing the highest monoterpene concentration in a given month may have ranked much lower in other months. The climatological data will be statistically examined for correlative influences on the monoterpene concentrations after additional data have been collected.

The Mississippi data (analyzed on an ovendry wood basis) were compared with the Institute of Paper Science and Technology data for the North Carolina OSB flakes (analyzed on a green weight basis). Figure 8 shows two loess regression lines (span = 0.5) based on averaged data for each sampling date; considering the differences in both analytical techniques and in the geographical origins of the specimens, the Figure 8 curves are remarkably similar.

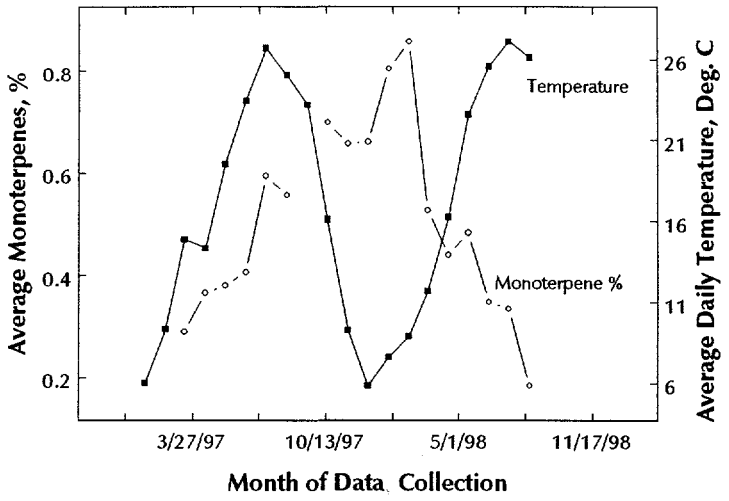

Figure 5: Average daily temperatures in Starkville, Mississippi *vs* monoterpene contents in sampled trees (percent of ovendry wood).

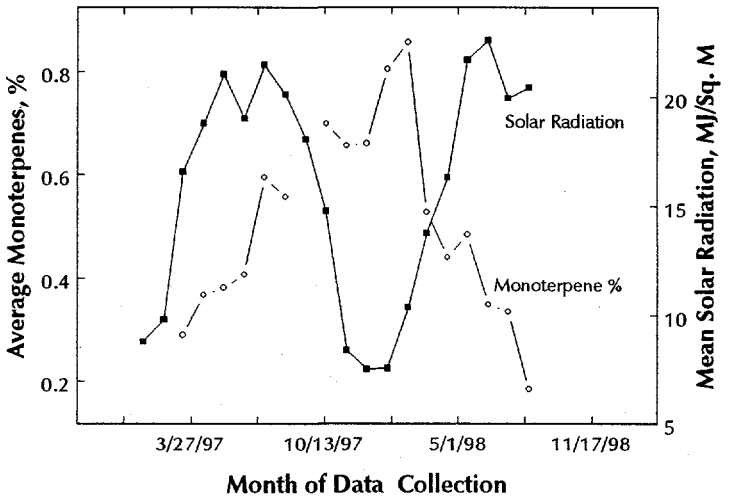

Figure 6: Average daily solar radiation in Starkville, Mississippi *vs* monoterpene contents in sampled trees (percent of ovendry wood).

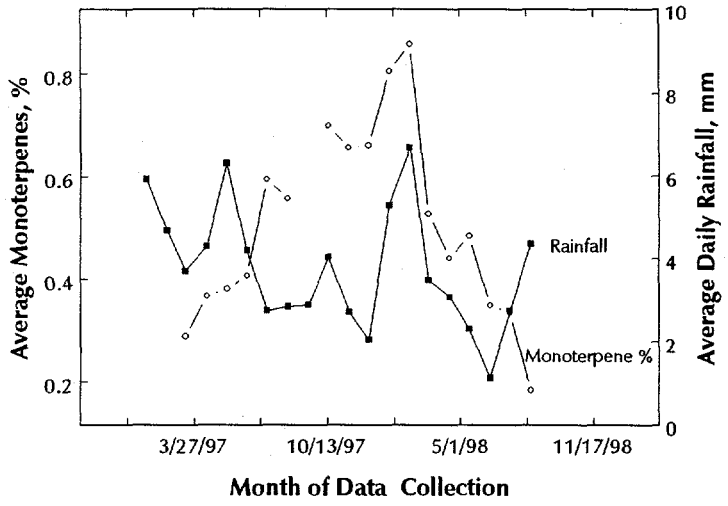

Figure 7: Average daily rainfall in Starkville, Mississippi *vs* monoterpene contents in sampled trees (percent of ovendry wood).

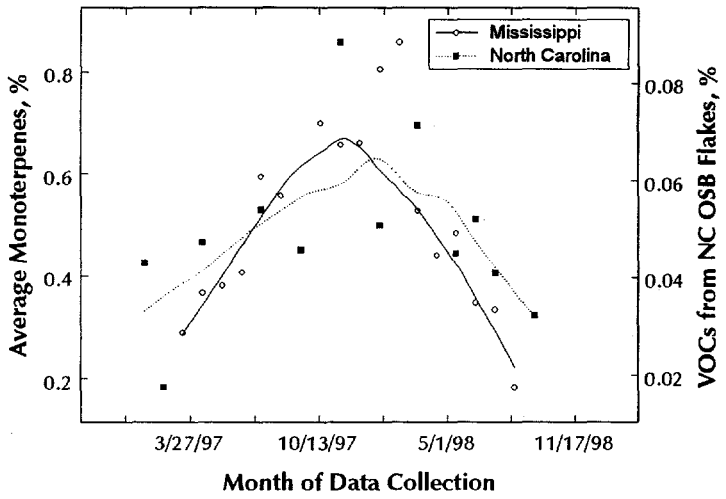

Figure 8: Comparison of the amounts of monoterpenes from Mississippi tree analyses with VOCs from North Carolina OSB flakes.

Significance of findings

There is a great deal of variability from sample to sample during any given analysis period, and consequently our findings may not be typical of the population of loblolly pine trees. In the trees we sampled, however, we found that the typical monoterpene concentrations in standing trees might vary by as much as 200% to 300% during the course of a year (depending on how the "typical" data measure is chosen). Between the lowest and the highest monoterpene concentrations recorded to date in the longitudinal study there is a difference of more than 700% over time. There is no reason to believe that the variability might be less for trees sampled from other

locations. The Mississippi and North Carolina data patterns are similar, suggesting that the data presented here are indicative of real trends and that they are not artifacts of analytical techniques. Seasonal influences appear to affect the monoterpene concentration in the stemwood of these loblolly pines, but even though there are specific short-term correlations with temperature and sunlight intensity it seems likely that there is an interactive effect with rainfall or some other unidentified influence. A more detailed study of possible interrelationships among climatological factors and monoterpene concentrations in trees is underway. It seems likely that a significant part of the variability in OSB flake dryer emissions can be traced to physiological effects, and the rest can be attributed to handling and other factors.

Method of analysis

One 0.5 cm (0.2 inch) increment core was taken from each of the selected loblolly pine trees per month. The cores were placed in pre-weighed test tubes, stored at 0°C and returned to the laboratory for analysis. Specimens were processed by adding 10 mL of methylene chloride and 1 mL of 1000 g/mL 1,4-dichlorobenzene, and a known standard concentration was placed in a clean test tube and stored with the samples until the analysis was completed. Samples were sonicated for one hour and concentrated in a hot water bath. One mL of 1000 g/mL diphenylmethane in methylene chloride was added as an internal standard. One mL was taken from the concentrate and 0.1 mL of diazomethane was added prior to analysis on a Varian 3600 gas chromatograph equipped with a J&W DB-5 30 meter capillary column and flame ionization detector. Target monoterpenes included: α-pinene, β-pinene, camphene, myrcene, limonene, fenchyl alcohol, borneol, methyl eugenol and 4-allylanisole. Increment cores were dried in an oven overnight at 103° C to obtain the dry weight of the wood.

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Scale-up of RF-induced VOC extraction from pine lumber

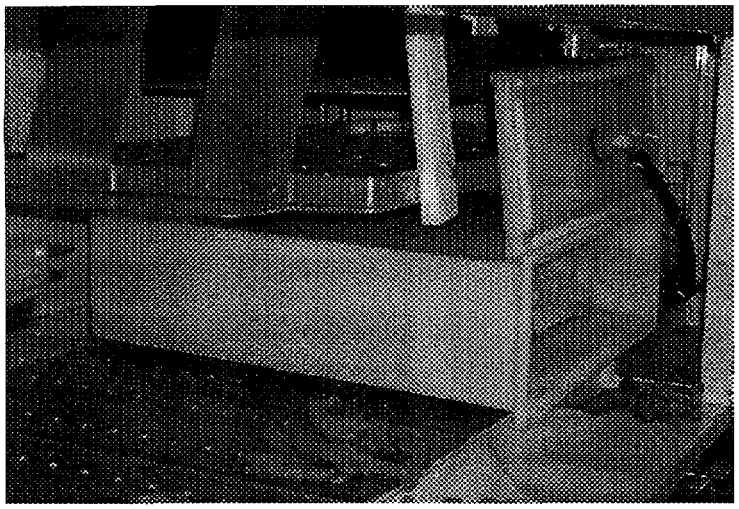

Figure 9: Illustration of the low-headspace positioned inside the Strayfield RF unit

Southern Pine lumber (2" x 4" and 2" x 6") was collected from Georgia-Pacific's Warrenton saw mill on October 19, 1998. The eight feet long pieces were cut into two feet lengths to fit inside our low-headspace reactor, which is a 24" x 8" x 30" polyethylene tank. Figure 9 illustrates the tank positioned inside Georgia Power's Strayfield RF unit. The steam from the sealed tank is guided to a water-cooled glass condenser. The pinene carried out with the steam was collected by skimming it from the surface of the condensed water. The condensate was analyzed by gc, and the bottle used to collect the condensate was washed with methanol and also analyzed by gc. The condensate contained a negligible quantity of turpentine. The methanol wash contained 5-10% of the total amount collected. The turpentine consisted principally of α- and β-pinene, respectively, in a 2:1 ratio. The results, shown in Table 1 demonstrate that 0.7 lbs per ton of turpentine was collected in the best case. This compares favorably with the value of roughly 1 lb/ton released during drying of lumber. We have previously shown that the turpentine collected reduces emissions by a corresponding amount.

The power used was compared to theoretical expectations as follows. Consider the second entry in Table 1, where 54.176 kg of lumber was irradiated. The total measured power consumption of 27.85 kwh included a stand-by component of 14.63 kwh (53 min x 0.276 kwh). The specific heat of oven-dry wood is

$$C_w = 0.271 + 0.095\ T \ (\text{in } ^\circ C)$$

At 60°C, this translates to 0.328 kcal/kg,°C . The temperature of 60°C was chosen to be mid-point between 20°C(ambient) and 100°C, the extreme temperatures experienced by the lumber. Heating 1kg of green wood from 20°C to 100°C requires

$$0.5 \times 1 \times (100-20) + 0.5 \times 0.328 \times (100-20) = 53.12 \text{ kcal}$$

If 1% of water is lost through evaporation, the heat required is

$$540 \times 0.01 = 5.4 \text{ Kcal.}$$

Hence the total amount of energy needed to heat wood from 20°C to 100°C and evaporate 1% of its weight by water is 58.52 Kcal/kg. This leads to 3,170 Kcal for the 54.176 kg used above, or

Table 1: RF treatment of pine lumber						
ID	**weight (kg)**	**RF time (min)[1]**	**percent weight loss**	**turpentine collected (g)**	**water collected (g)**	**power used (kwh)[2]**
10-21-1	27.264	79 (46)	2.66	8.90	725.7	33.82
10-22-2	54.176	53 (35)	1.30	9.41	706.7	27.85
10-28-3	50.162	52 (34)	0.82	7.23	409.8	26.62
[1]the bracketed value indicates the time at which steam emission is observed; [2]includes stand-by power of 0.276 kwh/min.						

Table 2: Turpentine recovery (μg/g, green basis) from irradiating pine veneer and lumber						
ID	**green wt. (kg)**	**irrad time (min.)**	**wt. loss (%)**	**turpentine recovered**	**methanol in condensate[1]**	**total VOC in condensate[2]**
veneer						
98-12-7	7.372	37	1.9	-	9.6	26.3
lumber						
98-12-10A	44.032	50	1.4	308	2.0	13.8
98-12-10B	44.448	52	1.2	267		
98-12-14A	45.327	50	1.4	278		
[1]by gc; [2]includes additional terpene-related gc signals						

3.7 kwh. Thus, 28% of the total power (excluding the standby component) was utilized. This compares favorably with a typical efficiency of 50%, given that ancillary power losses (e.g. heating of the reactor) were not considered.

The power cost of about 500 kwh per tonne is far to high to be economical, since it translates to about $12.5 per tonne. However, most of this cost is for heating the wood from ambient temperatures to about 95°C. Since the VOC is principally lost *after* this period, the economics dictate that the wood first be heated to 95°C with steam, and then processed by RF. Under this scenario, the power cost would drop substantially.

The above experiments were repeated with fresh (2 x 4 x 48") pine lumber obtained from from Pickens, SC, on 12.8.98. One set of measurements were also made with veneer was from Georgia-Pacific's Madison facility. Both furnishes were utilized within 6 days of cutting. The lumber was cut into 2-ft pieces and irradiated in our low-headspace unit. Most of the turpentine was recovered from the surface of the condensed water. For the second lumber entry in Table 2 (98-12-10B), the power consumption was 23.12 KWH. The turpentine recovered was almost pure pinene with an α:β distribution of 3:2. The pinene recovered corresponds to 0.7 lbs/ton which compares favorably with the value obtained above.

Table 3: FID analysis of RF treated pine					
flake age (days)	RF time (min.)	percent wt loss during RF	VOC (μg/g, dry basis) 30 min	60 min	n
2	control	-	2,500±200	5,700±800	2
2	16	5.1	840±10	2,480±40	2
9	control		1,600±100	4,000±500	4
9	15	1.2	820±10	2,340±40	4
9[1]	10	6.5	1,100±400	3,000±1,000	6
22	control		1,400±300	4,500±500	4
avg.	6	2.8	1,200±500	3,000±1,000	2
[1]gc analysis: MeOH: 17.5 μg/g, total VOC: 54 μg/g, both on a dry basis					

Low-headspace RF irradiation of OSB

Our low-headspace polyethylene vessel was filled with 2-4 kg of pine flakes from Norbord's Mississippi facility, and then irradiated with Georgia Power's Strayfield unit. The steam that appeared after the interior temperature reached about 100°C was condensed. Also, the RF power was cycled at this point to minimize the amount of steam evolved. The internal temperature was maintained at 105-115°C. Since the vessel could only accommodate a maximum of 4 kg of flakes, not enough turpentine could be separated from the condensed emissions. The flakes were dried at 130°C under 3.5 lpm of air with FIA monitoring before and after irradiation to check the efficacy of RF treatment. In one case, the condensate was also analyzed by GC. The results listed in Table 3 show that low-headspace RF irradiation decreases VOC emissions. As before, the first part of the VOC signal in the control was removed upon irradiation.

Low-headspace RF treatment of OSB

In an attempt to extend the above results to a moving bed of flakes, a hood was designed with skirting so that the flakes would experience low-headspace conditions while under the hood. In this first experiment, the flakes were not moved; our intent was to establish the degree of VOC capture that could be achieved. The hood was fitted with plastic skirting to create the low-headspace environment, and an outlet port at the top was connected via plastic tubing to a condenser for VOC entrapment and containment. A trial was conducted in November, 1998 using green southern pine oriented strand board (OSB) flakes obtained from Norbord Industries, Guntown, Mississippi. However, this design proved to be unworkable; while it was probably adequate to collect VOCs, the skirting could not be sealed tightly enough around the flakes. Flakes became noticeably drier during the experimental trials, and only a small amount of VOCs was collected. To verify that there was a problem with the design (not the material), another trial was conducted using a sealable polyethylene box that had been previously used for lumber treatment trials. A significant amount of pinene was collected, and the material remained moist at the end of several minutes of RF treatment. Hence, treatment of flakes in a moving process will be difficult; a batch-continuos treatment will be necessary.

Effect of RF on wood permeability

The gas permeability testing apparatus used is illustrated in Figures 10 and 11. To test whether gas permeability was affected by RF treatment, sample stock was randomly selected from clear green southern pine 2" x 4" boards from a Mississippi sawmill. The boards were cut into 23" samples, and one-half of these were sent to IPST for RF treatment. After treatment these samples were returned to MSU, and all sample boards were dried at 100°C for 24 hours. The boards were then cut into halves, and two 5/8" x 2" cores were removed in the longitudinal direction from each sample with a core bit. To prevent air leakage perpendicular to the grain, each core was then dipped in a liquid rubber compound and cured for 24 hours at ambient conditions. Samples were cut using a table saw to approximately 26 mm in length, and the ends were then shaved with a razor blade to achieve the final surface with a minimum of obstructions. The samples were then re-dried at 100°C until a constant weight was achieved and stored in a desiccator over Drierite. The final dimensions of each specimen were measured immediately prior to test.

For testing, the specimens were placed in the sample holder where vacuum was applied for one minute to ensure stable conditions throughout the testing apparatus. Ambient air was used as the gas after it had passed over P_2O_5 and Drierite to minimize moisture in the system. Measurements were taken and the barometric pressure, the negative side vacuum, the pressure differential across the sample, and the air flow were recorded. Data were reported as m^3/m Pa-s to yield the superficial gas permeability. A total of 89 specimens were tested: forty-four untreated specimens and forty-five RF-treated specimens.

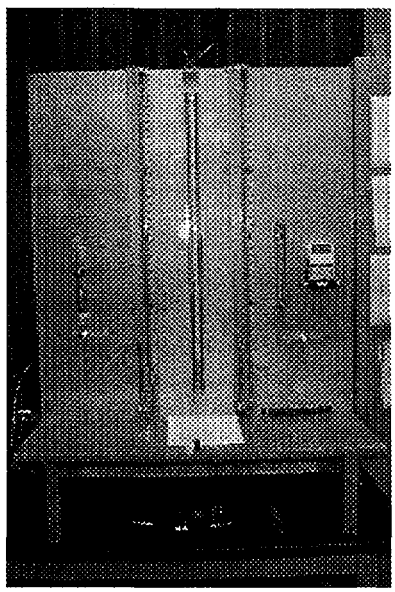

Figure 10: Gas permeability testing apparatus designed and constructed at Mississippi State University.

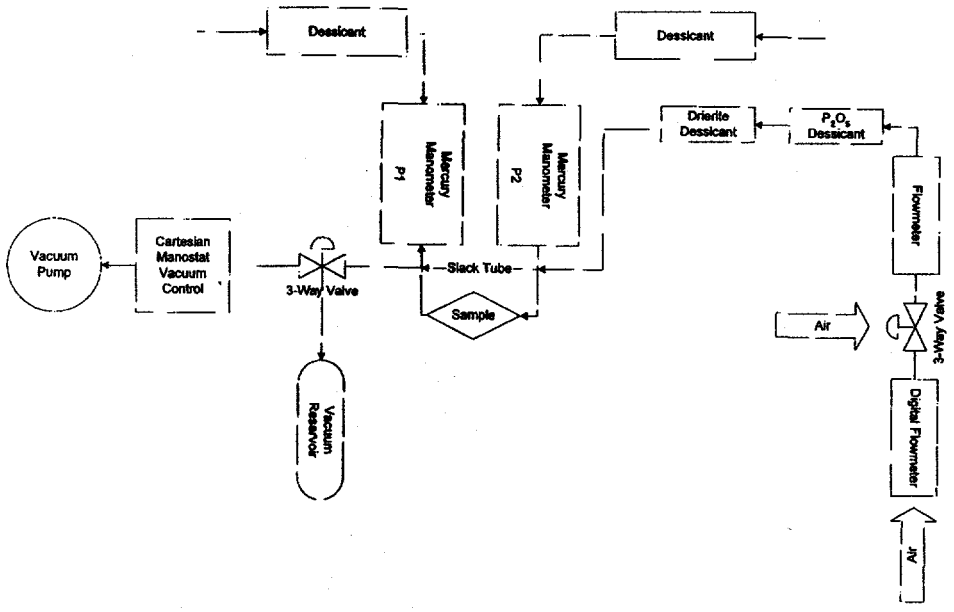

Figure 11: Schematic for gas permeability testing apparatus.

Because of the positive skewness of the samples it was evident that these sample groups might be best analyzed using nonparametric statistics. A few outliers appear to be present, but it was not possible to exclude them from analyses based on obvious experimental problems. Based on Shapiro-Wilk tests the hypothesis that these groups followed the normal distribution was rejected, so the two-sample Mann Whitney rank sum test (two-sided) was used to test for differences between these two groups. No significant evidence was found for different median values at α=0.05. Median values were found to be approximately 4.9×10^{-12} m^3/m Pa-s for the untreated specimens, and 5.7×10^{-12} m^3/m Pa-s for the RF-treated specimens. A box-and-whisker plot of the superficial gas permeability, K_g, for the two data sets is presented in Figure 12.

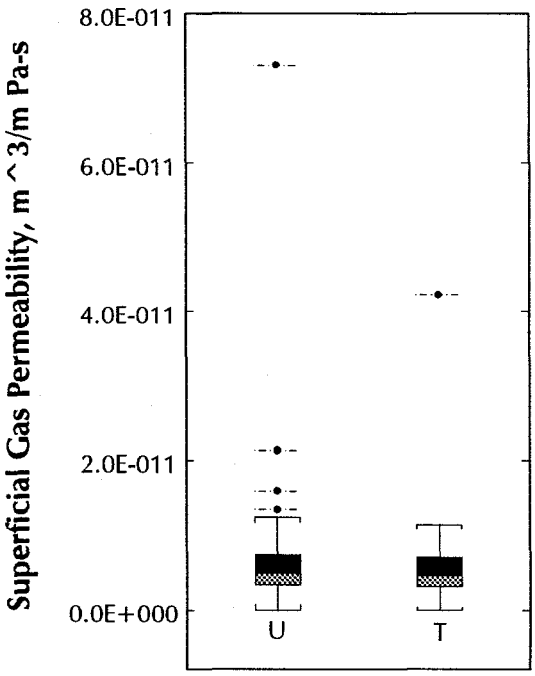

Figure 12: Gas permeability data for RF-treated (T) and untreated (U) specimens.