

Continuous Monitoring of Volatile Organic Compounds During Kiln Drying with MEMS Chemical Sensors Based Mini-GC

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The Forest Products industry has been a significant source of environmental pollutants in both urban environments and otherwise pristine natural environments. Seacoast Science, Inc is working with AMEC (Forest Industries Division) and Mississippi State University (MSU) to demonstrate the feasibility of an inexpensive, lightweight detector using MEMS-based microcapacitor sensors for chemical pollutants associated with wood processing. Success was demonstrated through the design, development and assembly of chemical detectors taken for field-testing at MSU's experimental wood drying kiln¹. This issue is of significant interest to national, state and local government regulatory agencies as hazardous air pollutants (HAP) must be monitored², and use of an integrated, low cost, real time detector is crucial to accomplishing this task³.

The newly developed monitor and the associated experiments presented herein detail trials conducted at MSU's experimental wood drying kiln in Starkville, MS. A significant issue for the forest products industry is the lack of complete data on VOC emissions from manufacturing processes. The information that is available from laboratory and field trials was obtained by taking periodic samples of vapor exhaust from kilns for laboratory analysis, a costly and time consuming process. The available data covers only a few common lumber species, a limited range of feed stock characteristics, and limited process variables. This uncertainty and limited information has led to ill-founded public concern, and conservative and inflexible regulatory requirements that threaten to overly burden the industry⁴.

Ultimately, Seacoast Science proposes to develop a detector system that is selective and sensitive to chemicals emitted by the forest products industry in a small, low-power system designed for portable operation. The strength of this system is from the integration of the preconcentrator, chromatography column and the chemoselective MEMS sensor array. By taking advantage of these specific chemical interactions and by comparing the responses of several capacitors, each filled with a different polymer; it is possible to distinguish different volatile chemicals from each other. The ability to gather multiple bits of information on a particular chemical means that any pattern recognition algorithm used will have a better chance of identifying that chemical species. Identifying the chemical species is the first step in control of the pollution associated with the forest product industry⁵.

Seacoast Sensors

Seacoast Science employs a MEMS-sensor based on micromachined elevated interdigitated electrode capacitors⁶ (**Figure set 1**). These interdigital transducers (IDT) are approximately 400 μ m long and 3.5 μ m wide and have 25 alternating sense and drive electrode pairs (each beam separated by 3.5 μ m) in parallel supported by 2 μ m tall insulating posts above the lower substrate. The electrode fingers are coated with a polymer using an ink-jet⁷. The head, which is mounted on a translation stage, has a 30 or 80 μ m diameter nozzle that expels droplets of a polymer solution. Each drop is typically

a few tens of picoliters in volume and 30-100 μm in diameter. The interaction between target analyte and polymer modifies the dielectric properties of the polymer resulting in a change in capacitance. Seacoast's MEMS detector array operates well in ambient air at ambient pressures and temperatures, thus requires no special carrier gas.

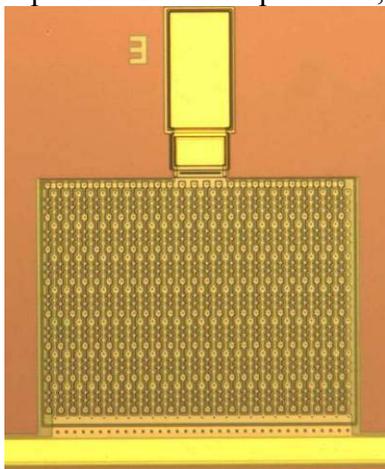


Figure 1a. Micrograph of a Seacoast Science interdigitated electrode sensor element.

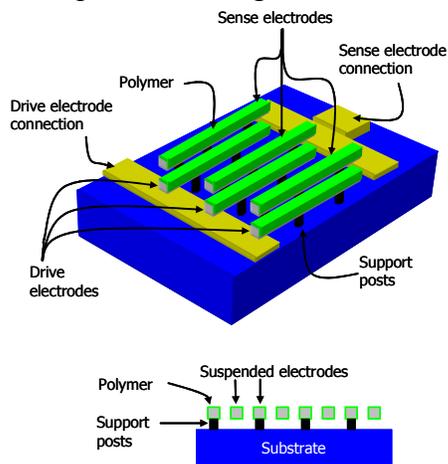


Figure 1b. Cross-sectional diagrams of a Seacoast Science sensor element.

SeaPort MiniGC:

Seacoast's basic Mini-GC (**Figure Set 2**) concept involves the same components as in most conventional gas chromatographs: 1) an inlet, 2) a preconcentration stage, 3) a chromatographic column, and 4) a detector. However recent advances at Seacoast have allowed us to develop a much smaller, portable system based on our proprietary chemicapacitors. Working backwards, the multidimensional detector array optimized in Task 1 replaces conventional detectors. This frees the system from the need of a carrier gas and reduces power requirements compared to the common detectors and relaxes the need for high chromatographic resolution since the multi sensor array will respond differently to the various chemicals.



Figure 2a. (above). Closed Mini-GC with cell phone. **Figure 2b.** (right). Mini GC with integrated touch screen computer.

Both the column and preconcentrator are filled or coated with proprietary polymers or conventional GC column packing materials. This makes the system modular and tunable to a specific application when needed.

The Mini-GC has the following features:

- Direct Injection or Vapor Sampling
- Sample Pump with Flow Control
- Chemicapacitive Sensor Array
- Preconcentrator – Controlled Collection Times/Temperatures
- Chromatography – Programmable Thermal Profiles
- First Generation
 - Weight - 7lbs
 - Size – 416 in³
- Separates and Detects Complex Mixtures
- Designed to be compatible with many detectors - MEMS, MOS, IMS, SAW
- No Carrier Gas Required

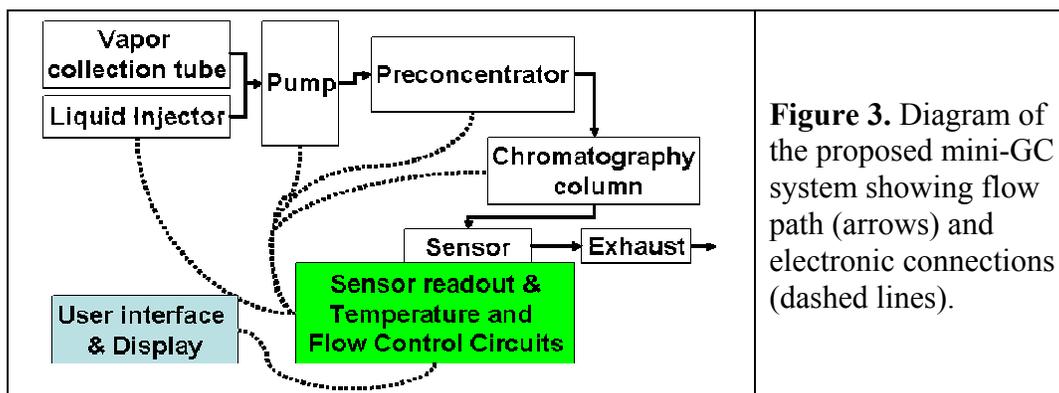


Figure 3. Diagram of the proposed mini-GC system showing flow path (arrows) and electronic connections (dashed lines).

Sensor Testing: Initial testing was performed on individual chemicals of interest. Chemicals were produced utilizing four different methods and three different detector assemblies. See **Table 1** for a matrix of completed testing. The chemical delivery methods include 1) Utilization of our modified vapor delivery system to deliver known chemicals at controlled concentrations, humidities and temperatures to evaluate sensor and precon performance; 2) Spiking these same chemicals into an environmental chamber to evaluate our chemical sampling/collection system; 3) Heating of pine needles, cones, wood and bark in a laboratory environment (**Figure 4**) and sampling off of the Mississippi State University experimental kiln. The limits of detection from the vapor delivery system for the bare sensors and preconcentrator can be found in **Table 2** while the other data will be discussed below.

Table 1. Testing matrix performed during Phase I program.

Detector Assembly	Vapor Delivery System	Spiked Glass Chamber Mixture	Pine material in lab*	Pine in Kiln
Sensors	X			
Precon + Sensors	X	X	X	
Precon + Column + Sensor	X	X	X	X

* This testing was done for system optimization only.

Table 2. Limits of detection for the bare sensors and preconcentrator.

Chemical	Bare Sensor (ppm)	Preconcentrator (ppm)	Polymer
Ethanol	4.8	0.05	Adiol
Methanol	7.0	0.55	Adiol
Toluene	26.0	1.40	PECH
a - pinene	11.11	0.43	Adiol
b - pinene		0.2	Adiol
Limonene	4.6	0.78	Au:C12 sh12
Myrcene	4.25	0.024	Adiol
Pentanal	14.5		Adiol
Acrolein	4		SC F-108
Benzene	2.1		Adiol
Formaldehyde	1.02		OV-275
Pentanone	1.35	0.008	Adiol
Hexanone	0.12	0.19 μ g	Adiol

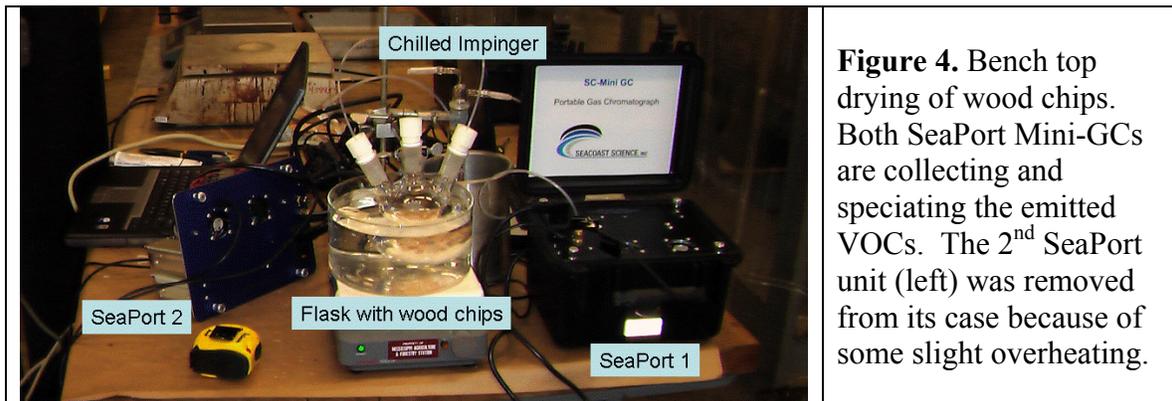


Figure 4. Bench top drying of wood chips. Both SeaPort Mini-GCs are collecting and speciating the emitted VOCs. The 2nd SeaPort unit (left) was removed from its case because of some slight overheating.

Monitoring VOCs emitted from the bench top drying of wood chips:

1. Approximately 500 ml of southern pine wood chips were cut and collected from the same wet wood samples.
2. Approximately 50 g of these chips were loaded into a 500 ml round bottom flask.
3. Both SeaPort GC units were set up to sample the exhaust from the chip-filled flask. The exhaust was passed through a cold impinger to remove liquid water from the exhaust before reaching the Seacoast systems.
4. The flask was heated slowly with a water bath to 180°F over the three hour experiment (**Figure 4, above**).

Field Tests – Mississippi State Experimental Kiln: Seacoast took two prototype detector systems for testing of the chemicals emitted from Mississippi State University’s pilot-scale kiln. It was considered a successful trip, as the results far exceeded expectations. Testing was performed over two days at Mississippi State University facilities. On Day

1, freshly sawn lumber was prepared for the pilot-scale kiln. Additionally, wood chips were collected for bench top drying and analysis with the Mini-GCs. On Day 2, the pilot-scale kiln was operated and the exhaust was analyzed using the Mini-GCs and Mississippi State University's total hydrocarbon analyzer.

Preparing samples for the pilot-scale kiln:

1. Approximately 100 board feet of freshly sawn southern pine lumber was acquired by Mississippi State, and then refrigerated.
2. The wood was graded by Sita Warren, who gave the lot an A for quality (**Figure 5**).
3. The lumber was cut into twelve 2 x 6 x 25 inch boards, for a total of 25 board feet (**Figure 6**).
4. A one-inch piece was cut from each end of every board (**Figure 7**); the pieces were dried to determine the initial moisture content of the wood.
5. The cut lumber for kiln drying was stored overnight in the refrigerator.



Figure 5. Sita Warren and Ruben Shmulsky grade wet Southern Pine boards.



Figure 6. Wood is cut into twelve 2 x 6 x 25 inch boards.

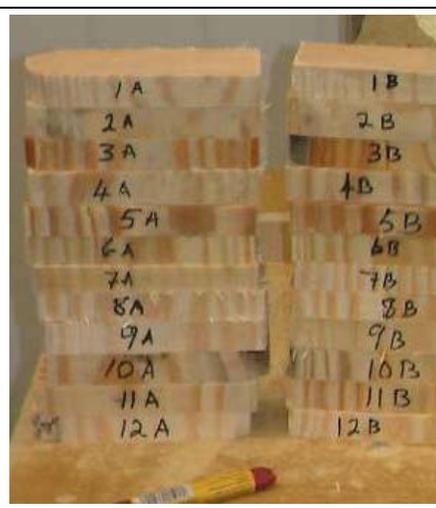


Figure 7. Collection of one-inch sections cut from both ends of each board. Pieces were quickly dried to determine moisture content

Day 1 Chip Drying Data

The Mini-GC units were set up to collect, speciate, and detect the chemicals emitted by the wood chips within a five-minute cycle. The beginning of each cycle is triggered by the rapid heating of the preconcentrator. **Figure 8** shows two five-minute cycles and **Figure 9** shows a two-hour window that indicates an increase in sensor response correlated with an increase in the release of terpenes from the wood. Following this experiment, it was determined that the chips were not completely dried.

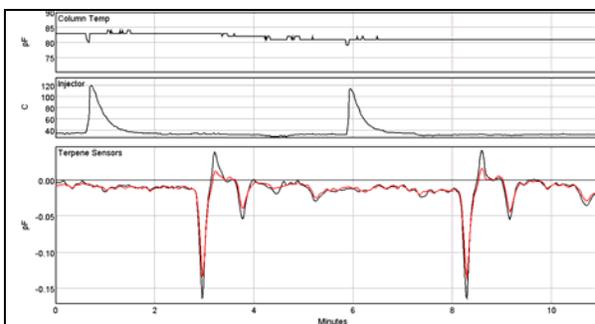


Figure 8. Data from two five-minute cycles taken during wood chip drying. The column temperature was held constant at 82°C. The preconcentrator injector was thermally cycled to 120°C every five minutes. The sensor spikes indicate terpene detection

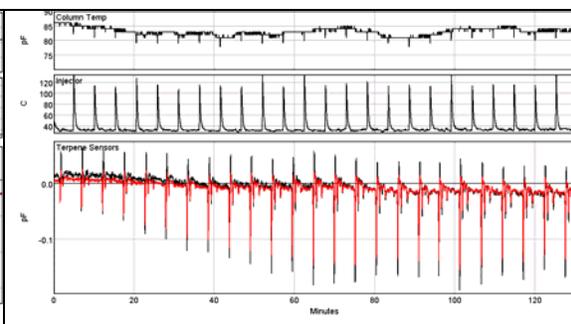


Figure 9. Over 2 hours of five-minute cycles. Note that the magnitude of the response on the terpene detector increases during the first 60 minutes before stabilizing. The pine chips then maintained this high level of terpene release until the wood chip temperature was decreased.

On the second day of testing, the Mississippi State University kiln was charged with the twelve pieces of cut wood (**Figure 10**). Two SeaPort Mini-GCs (**Figure 11**) and two total VOC analyzers sampled the exhaust to analyze the volatile chemicals emitted.



Figure 10. 23 board feet of wet southern pine loaded into the pilot-scale kiln.

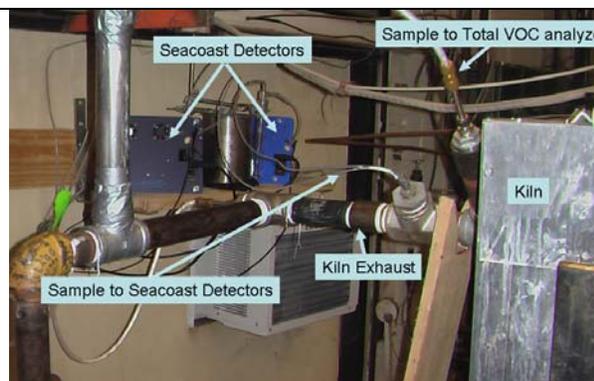


Figure 11. Seacoast Detector set up for Day 2 testing.

Day 2 Board Drying Data

Day 2 results were similar to Day 1, in that, as the temperature of the wood increased, the number and quantity of VOCs emitted increased (**Figure 12**). As the wood drying progressed, additional species of volatile chemicals were emitted until ultimately six separate species were detected and tentatively identified as α -pinene, β -pinene, β -myrcene, limonene, α -terpinol/estragola and diphenylmethane (**Figure 13**). These chemicals were emitted at various times during the drying process. Each 5-minute cycle was analyzed and the presence and relative amount of each of these six chemicals was determined (**Figure 14**). The relative “Total VOC” content was determined, plotted and compared to the results from the MSU total VOC analyzer (**Figure 15**).

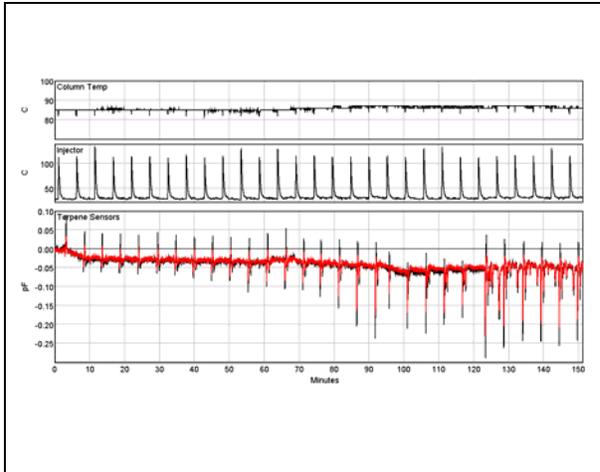


Figure 12. The first 2 ½ hours of Day 2 testing. The kiln temperature rose during this time, resulting in an increase in VOCs released and a corresponding increase in terpene sensor response.

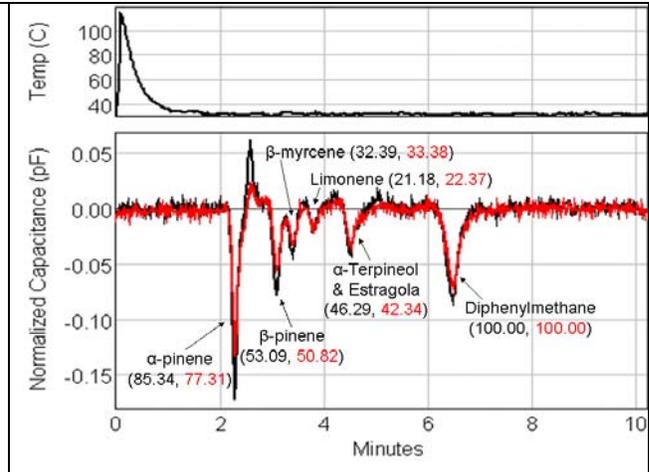


Figure 13. A ten-minute window showing six separate chemicals on two terpene sensors. The numbers indicate normalized peak integration values for each sensor.

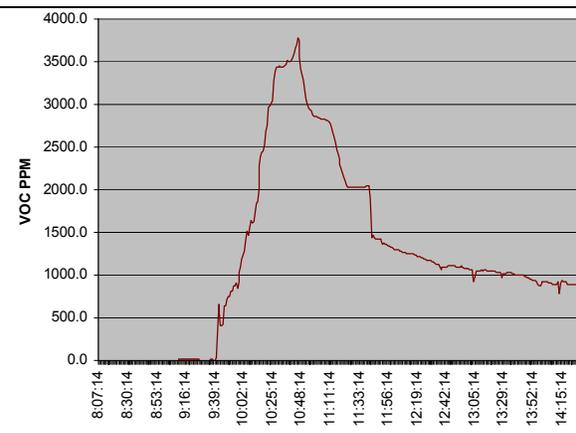
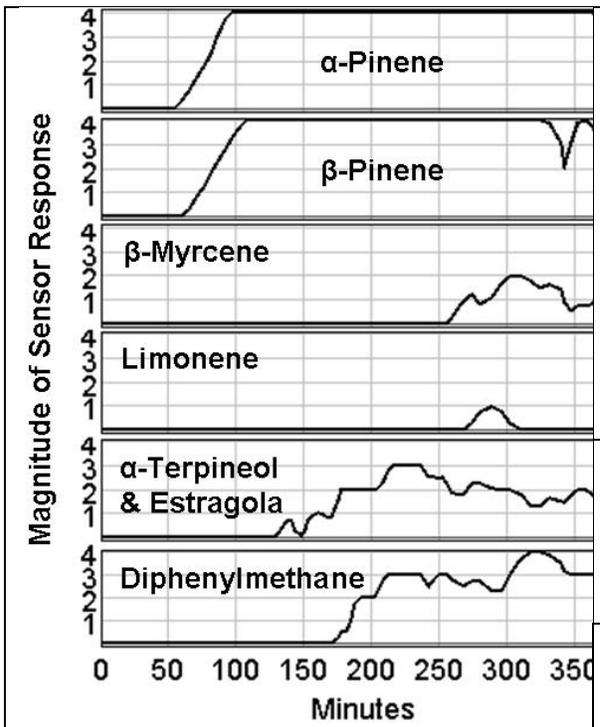


Figure 14 (left) Relative intensity of the six chemicals emitted during the 6 hour drying process. Chemical assignments are based on comparisons of retention time data from the laboratory and literature⁸.

Figure 15 (above) Results from the Total VOC analyzer.

The data represented in **Figure 14** displays a portion of the wealth of information possible from an on-line detector system. Here it is demonstrated that the sensor device can track the concentration of the individual chemicals emitted from the drying process. This information is required to optimize the management of HAP emissions. To achieve such optimization, the sensor will be tied to the wood drying control system. Active feedback-type controls will receive information from the sensor and make decisions regarding heating, venting, air velocity, etc., based on information from the sensor. In this manner, during the drying process as emissions decline, more aggressive drying can be used. During periods of greater emissions, drying rates or venting can be cut back. This

closed-loop control system effectively balances maximum production with minimum emissions.

Moisture Content (MC) of the Wood Boards

The initial moisture content for each of the twelve sample boards was estimated as the average initial moisture of the one-inch sections cut off the ends of each board. The green-weight and oven dry-weight were recorded to evaluate the moisture content of each one-inch sample. It appears that the moisture gradient along the boards was low in most cases, so the average is expected to be representative of the moisture throughout the board. The standard deviation of the moisture content is typical of the natural variation of lumber.

- Average Final MC% of Charge = 64%
- Average VOCs Released / 1000 Board Feet = 2.18 lbs. / 1000 Board feet
- Board Feet in Kiln = 23 Bd. Ft
- Dry Bulb Temperature = 240°F

Conclusions

In summation, the new SeaPort Mini-GC analyzer was tested at the bench-top and pilot-scale kiln levels. Small-scale kilns have been shown to be an acceptable method for estimating emissions from commercial operations. Seacoast Science's SeaPort Mini-GC performed above expectations. It responded to gross emission levels and provided chemical speciation. Additional testing and refinement of the Mini-GC system is underway. The results we have seen to date show excellent progress toward commercial testing and prototyping, and have led us to begin marketing the SeaPort Mini-GC as a prototype-level research tool.

In the tests drawing vapor samples from the kiln exhaust, the Mini-GC tracked the total VOC emission profile, the number and amount of VOCs, as they increased rapidly with heating, and then dropped off as the lumber dried. The data on the phased emission of different VOC species during this evolution is remarkable and provides a level of detail seldom achieved due to the difficulty and cost of taking vapor samples for laboratory speciation. This data can be crucial in accurately assessing the environmental impact and defining optimal mitigation approaches.

Note on Commercialization

Seacoast's Phase I teammates, Ms. Sita Warren (AMEC) and Dr. Rubin Shmulsky (MSU) have helped Seacoast approach potential industrial partners for support for further field trials, eliciting strong interest from several firms and mills. The level of interest results from the desire to have a robust and practical solution, to monitoring actual emissions levels and compositions in real time. It is known that wood species, moisture content and drying schedules greatly affect the actual emissions.

Currently, permitting and public reviews are based on conservative estimates based on limited laboratory data. The variation over the drying schedule seen here is ignored, as currently fielded technologies would require expensive analyses, of dozens of samples, to provide the level of information demonstrated here. There is no practical and economical means available to monitor, in real-time, the total VOC emissions from low concentration sources, let alone assessing the VOC composition - a critical influence on environmental impacts.

The industry consensus is that real-time measurements will enable cost effective VOC emissions management, avoiding excessively-expensive add-on equipment that increases energy consumption. This capability will also enable the industry to reassure the public and government regulators with ongoing VOC emissions monitoring.

Acknowledgements

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¹ Bartekova, A., C. Lungu, R. Shmulsky, P. Huelman, J.Y. Park. 2006. Laboratory evaluation of volatile organic compounds emissions from coated and uncoated oriented strandboard. *Forest Products Journal* 56(2):85-90.

² "Forest Products Portfolio Strategy: Industrial Technologies Program," US Department of Energy, 4/5/06

³ "Total World MEMS Sensors Market: Industry Challenges and Market Dynamics: Industry Challenges: Facing the Pricing Pressure; Packaging of MEMS Sensors" Frost & Sullivan, December 2006

⁴ "Hazardous Air Pollutant Emissions from Lumber Drying," *Forest Products Journal*, 7/1/06

⁵ "Total World MEMS Sensors Market: Industry Challenges and Market Dynamics: Industry Challenges: Facing the Pricing Pressure; Packaging of MEMS Sensors" Frost & Sullivan, December 2006

⁶ T.E. Mlsna, S. Cemalovic, M. Warburton, S. T. Hobson, D. A. Mlsna, and S.V. Patel, "Chemicapacitive Microsensors for Chemical Warfare Agent and Toxic Industrial Chemical Detection," *Sensors and Actuators B, Chemical*, 116(1-2) (2006) pp 192-201.

⁷ S.V. Patel, T.E. Mlsna, B. Fruhberger, E. Klaassen, S. Cemalovic, D.R. Baselt, "Chemicapacitive microsensors for volatile organic compound detection," *Sensors and Actuators B*, 96(3) (2003) 541-553.

⁸ A.L. Thompson, 'Volatile Organic Compounds Emitted During the Drying of Southern Pine Lumber' Master Thesis, Mississippi State University, December 1996.