FINAL PROJECT REPORT

Coupled Physical/Chemical and Biofiltration Technologies to Reduce Air Emissions from Forest Products Industries (DE-FC07-96ID13440)

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A-Project Objective:

The research is a laboratory and bench-scale investigation of a system to concentrate and destroy volatile organic compounds (VOCs), including hazardous air pollutants, formed from the drying of wood and the manufacture of wood board products (e.g., particle board and oriented strandboard). The approach that was investigated involved concentrating the dilute VOCs (<500 ppmv) with a physical/chemical adsorption unit, followed by the treatment of the concentrated VOC stream (2,000 to 2,500 ppmv) with a biofiltration unit. The research program lasted three years, and involved three research organizations. Michigan Technological University was the primary recipient of the financial assistance, the USDA Forest Products Laboratory (FPL) and Mississippi State University (MSU) were subcontractors to MTU. The ultimate objective of this research was to develop a pilot-scale demonstration of the technology with sufficient data to provide for the design of an industrial system. No commercialization activities were included in this project.

Background: The following tasks, milestones and schedule are given below for the project.

Task	Milestones and Schedule
1.1 - Design Considerations for the Adsoprtion/Desoprtion System (MTU)	Completed in First Year of Project.
1.2 - Adsorption Studies (MSU)	Completed in First Year of Project.
1.3 - Desorption Studies (MSU)	Completed in First Year of Project.
1.4 - Design Considerations for the Biofiltration System	Completed in First Year of Project.
1.5 - Isolation and Characterization of Microorganisms (MTU)	Completed in First Year of Project.
1.6 - Determination of the Rate if Model VOC Degradation (MTU)	Completed in First Year of Project.

1.7 - Determination of Toxicity and Mutagenicicty of Model Compounds and Degradation Products (MTU)	Completed in First Year of Project.
1.8 - Analysis of Biofilter Media (FPL)	Completed in First Year of Project.
1.9 - Management and Reporting	Completed in First Year of Project.
2.1 - Integrated Bench-Scale Biofiltration Unit	Completed in First Two Months of Year Two.
2.2 - Assembly of an Integrated Bench-Scale Biofiltration Unit (MTU)	Completed in Months 2-4 of Year Two.
2.3 - Testing of the Integrated Bench-Scale Biofiltration Unit (MTU)	Completed in Month 3 of Year Three.
2.4 - Analysis of the Biofilter Media (FPL)	Completed During Month 4 of Year Two.
2.5 - Management and Reporting.	Completed during Year Two of Project.
3.1 - Design of a Pilot-Scale System and Selection of Site for Demonstration (MTU)	Completed During Month Five of the Third Year.
3.2 -Assembly of the Pilot-Scale System at OSB Facility (MTU)	Completed During Month Eight of the Third Year.
3.3 - Testing of the Integrated Pilot-Scale Biofiltration Unit (MTU)	Ongoing Throughout the Fourth Year.
3.4 – Collaborative meeting with research staff from MTU, Industrial Partners, and Interested Vendors.	Completed During the Eleventh Month of Fourth Year
3.5 - Management, Reporting, and Presentation of Results	Ongoing Throughout the Fourth Year.

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III-RESULTS

The main part of this report comes from two papers presented at national conferences and published as proceedings. These results are based on the work of investigators who have been funded by the State of Michigan and or partially or completely funded by the Department of Energy. The initial paper describes the experimental techniques used in the study during both the laboratory phase and the pilot plant studies. It includes most of the analytical techniques used in the study. It was presented at the Air and Waste Management Association Annual Meeting in St. Louis, Missouri on June 21, 1999. The second paper was presented at a conference in Washington D.C. on October 1999. This report describes the results of the Pilot Plant trails. Most of the information for this report has come from the two papers; some of the results and conclusions were modified and expanded in this report because of new information that was obtained after the two papers were completed.

A. ABSTRACT

Biofiltration utilize microbial processes, which are immobilized in a water phase (biofilm) on a solid support. The contaminated air stream passes through the biofilter, and chemicals in the air equilibrate with the biofilm. The microorganisms in the biofilm convert the chemicals mainly into carbon dioxide and water. Biofilters traditionally have been utilized in processes where there is a high volume of air containing low levels of compounds. There are several operational limitations for biofilters. The low efficiencies of the biofilters, which require large systems, microbial breakdown of the solid support, problems of cycling of compounds onto the biofilters in most commercial processes (uneven amounts of compounds in the air), and the very large variations in the rate of biological breakdown of difference chemical This project was undertaken to determine the feasibility of using physical/chemical methods to adsorb and then desorb analytes in order to convert a dilute, high volume air stream to a more concentrated low volume air stream. The chemical/physical (adsorption/desorption) system will also serve to provide a relatively consistent air stream to the biofiltration units in order to alleviate the perturbations to the system as a result of uneven analyte concentrations. The ability to concentrate a dilute air stream and provide a constant stream of VOCs to the biofiltration unit will allow for smaller, more efficient, and more economical biofilters. Two years of laboratory studies and pilot-scale trials on these coupled systems have shown that they are indeed able to efficiently concentrate dilute streams, and the coupled biofilters are able to remove 90%+ of the VOCs from the adsorption/desorption unit.

B. INTRODUCTION

Air emissions from all industrial sectors in the U.S. are becoming more strictly regulated due to increased public and environmental concerns. Public pressure in the 1970s led to the initial passage of the Clean Air Act in 1976, followed by the Clean Air Amendments in 1990. These new regulations, especially the amendments, have had major effects on the forest product industries in the United States.

The U.S. Environmental Protection Agency (USEPA) has collected information of general interest regarding environmental issues associated with specific industrial sectors [1]. The total amount of air toxics by the lumber and wood products industry was 41,423 short tons per year according to EPA's toxic release inventory (TRI) [1]. The majority of these emissions are at low pollutant concentrations and high volumetric flow rates found in the area of energy input or production, such as steam generation from burning wood residue, and processes such as wood drying, resin blending, board pressing and product storage. Major emission gases are nitrogen oxides (NO_x), sulfur oxides, carbon monoxides, odor, volatile organic compounds (VOCs), and other toxic species which lead to smog/ozone problems [2]. The areas receiving the most environmental scrutiny are the dryers and presses in panel plants. Drying or pressing of solid wood or wood flakes/fibers at high temperatures facilitates the release of various components in the form of particulates and gases [3].

In order to meet current and future regulations and to handle a gas stream with these characteristics, expensive technologies such as regenerative catalytic oxidation (RCO), regenerative thermal oxidation (RTO), chemical scrubbing, recuperative oxidation via recirculation, and biological processes such as biofiltration will have to be used [4].

Biofiltration is one alternate control technology that has the potential for a cost-effective control of both VOC and Hazardous Air Pollutant (HAP) emissions, providing a method to comply with the Clean Air Act Amendments and still be globally pre-competitive [4-6]. These processes biochemically oxidize organic contaminants, such as VOCs/HAPs, into environmentally benign end products, usually carbon dioxide and water. The cost effectiveness of a biological process is due to the use of microbial metabolism instead of destruction via chemical or thermal means [7,8].

The VOCs/HAPs released by the forest products industry include tars and resins, organic acids, fatty acids, terpenes, and alcohols, plus some low molecular weight volatile organics, such as benzene and toluene [4,5,9]. The levels of VOCs released during wood drying or pressing can vary significantly during mill operation [6,10]. Wide variations in the physical and chemical properties of these compounds as well as fluctuations in VOC concentrations, particularly in high levels, can pose difficult challenges in biological processes [11,12]. For example, some of these VOCs are readily biodegradable at faster rates, have low molecular weight, and do not bioaccumalate or persist in the environment, but are major toxic releases [e.g., methanol, which is in the top ten on the Toxic Release Inventory (TRI) [1,13]. Other major VOCs, although not regarded as toxic releases and not regulated, can react in the atmosphere to deplete ozone and also need to be controlled. These latter compounds have been reported to biodegrade with low degradation rates, and have high boiling points, molecular weights, and octanol-water partition coefficients (e.g., monoterpenes)[14-17]. These types of VOCs pose the most serious problem to biofilters by producing toxic metabolic intermediates [18,19]. Biofiltration technology has been proven successful for the degradation of VOCs such as methane, propane, hydrocarbons, gasoline, cyanide gas, iso-pentane, toluene, methylene chloride, trichloroethylene, ethyl benzene, chlorobenzene, perchloroethylene and terpenes [5,9,20-28].

Biofiltration systems are particularly effective when used with systems that generate large quantities of air containing low concentrations of biodegradable VOCs (<100 ppmv). Most of the above referenced applications were able to achieve 95 to 100 percent removals after optimizing the system. To our knowledge, no reports have been found regarding the use of a concentrated stream of VOCs as a feed for a combined biofiltration system (combined chemical/physical and biological).

Studies have been conducted using activated carbon adsorbent as a buffer to minimize the fluctuations into the biofilter units by providing a consistent concentration [29]. Other studies have used activated carbon absorbents to minimize fluctuations and provide a relatively constant VOC stream to the biofiltration unit [30]. A mixed bed of compost material and activated carbon has been used in biofilters to increase the residence time and to enhance the biological breakdown of certain VOCs [29,31]. Pretreatment units to trap VOCs from the panel industry have also been proposed [6]. These studies illustrated the necessity of finding an improved method of VOC delivery to the biofiltration system so that microbial activity could be maximized (i.e., best removal efficiency). The more optimized the microbial activity is in the system, the

better the removal of the VOCs, the lower the operating cost, and less maintenance is required by the system.

For successful application of biological process to reduce the air emissions from the forest products industry, a process needs to i) biologically degrade all types of VOCs (including HAPs), ii) be flexible enough to handle the fluctuations in VOC (and HAP) concentrations in the air stream; and iii) reduce the high volumetric flow rates to be treated, thereby reducing the size of the treatment unit as well as the operating cost.

One of the ways to reduce both the fluctuations in feed concentration and high volumetric air flows is by concentrating the emitted VOCs by adsorption, using a physical/chemical pretreatment unit [29,32]. Adsorbents, such as activated carbon, have been used for removal of VOCs, as well as for buffers to minimize fluctuations to the biofiltration units [29,30,32]. Still, other researchers have used activated carbon to eliminate, or at least reduce, the lack of VOCs due to down time of operational units [30]. Upon saturation, these pretreatment units can be desorbed using water and steam wash, or thermal desorbed alone or in combination with other treatments, to release high concentrations of VOCs to the biological units. Overall, almost any process with a combined biological component would have significant cost advantages over a chemical/physical treatment alone [4].

The advantages of these combined processes include the following: i) obtaining a controlled, consistent, constant concentration of VOCs/HAPs and air flow in the feed stream to the biological treatment unit, thus reducing the air volume as well as avoiding the fluctuations which otherwise may alter the degradation rates, ii) significantly reducing the air volume to be treated, resulting in smaller biofiltration units and significant savings in equipment, space and maintenance, and iii) obtain overall better removals of poorly biodegraded compounds. Currently, there is no published literature on this type of "second generation treatment process" and very limited information of the first generation biofiltration process used in the forest products industries.

C-MATERIALS AND METHODS

1. Laboratory Coupled System: The adsorption unit consists of an adsorption cell filled with 100 grams of 40-mesh activated carbon in line with a bark-based biofilter. Dowex and Tenex were also evaluated as adsorbents (MTU unpublished data), but carbon was selected, due to its cost and overall effectiveness. Each adsorption cell is constructed from a 280 cm^3 galvanized steel pipe (10cm x 6cm) with threaded end caps for easy removal. Tapped into each end of the adsorption cell is a stainless steel quick-connect fitting (Badger Valve and Fitting; Neenah, WI) with ¼" O.D. tube connections. All air lines are plumbed using ¼" O.D. Teflon line. An air stream containing methanol (90 ppmv) and alpha-pinene (10 ppmv) as the surrogate VOCs, flows into the adsorption unit at a rate of up to 4000 ml/min. The air stream passes through the adsorption cell and flows into a set of two biofilters (initially one biofilter module) in series. This unit is referred to as the adsorption biofilters. The air stream is produced via an air compressor with the introduction of methanol and alpha-pinene by way of in-line syringe pumps (KD Scientific, Wooster, MA). The flow rates of both the air line and concentration of the VOCs are regulated using micrometering valves (Badger Valve and Fitting, Neenah, WI). The air stream is passed through the adsorption cell and methanol and alpha-pinene are collected for three days and then the cell is rotated into the desorption unit. After collection of the VOCs, the concentrated adsorption cell is placed into an oven controlled at 50?C for thermal desorption. Clean air passes through the three desorption cells at 120 ml/min, and thermally desorbs the contaminants for nine days (with each of the three desorption cells at a different stage of desorption). The desorption of the concentrated cells is intended to produce higher concentrations of methanol and alpha-pinene than introduced into the adsorption system. The waste stream from the desorption unit is then sent to a set of three biofilters in series. This unit is referred to as the desorption biofilters. After complete desorption, one of the "stripped" desorption columns is sent back to the adsorption set-up for collection of VOCs. This process produces a constant rotation of the adsorption/desorption cells. At any one time, there are always three cells being thermally desorbed and one

cell being adsorbed. Based upon earlier studies conducted at MTU, this will provide a relatively constant desorption concentration of the surrogate VOCs.

A coupled bench-scale biofiltration unit (including adsorption/desorption unit) was set up as illustrated by Figure 1. All of the biofiltration experiments are conducted at ambient temperatures (22?C±3?C). Each biofiltration column was filled with approximately 350 grams of dry Douglas fir bark chips sieved to a uniform #10 size (a bed height of 15.24 cm). Each biofilter has an approximate empty bed volume of 2500 cm^3. Each biofilter module is constructed from six-inch (O.D.) acrylic pipe (7.27cm I.D.) with threaded PVC end caps. Tapped into each end cap are ¼" O.D. stainless steel Swagelock fittings. The system is frequently checked for gas leaks to assure that it is completely sealed. Two biofiltration modules are in line with the adsorption unit (adsorption biofilters), while the remaining three modules are in line with the thermal desorption unit (desorption biofilters). The two biofilter modules in line with the adsorption unit are used to degrade any of the VOCs that pass through the adsorption cell. Sampling of the influent and effluent streams is done at various points throughout the system (to determine the concentrations of the contaminants) using on-line gas chromatography (GC) equipped with a flame ionization detector. For two cycles of the four adsorption/desorption cells the influent flow rate was 600 ml/min. On 4/14/98 the flow rate was increased to 1L/min and then further increased to 2L/min on 6/4/98, then 3L/min on 7/14/98, and then 4L/min on 12/3/98. The unit was shut down on 9/2/98 and was restarted on 10/2/98 to evaluate the effect of a prolonged shut down on the overall system. Step-wise increases were utilized to evaluate the performance of the adsorption/desorption process with various flow rates. Bacteria were added to the media before each biofilter module was assembled, and nutrients were added based on dry media weight. At start-up, Nitrogen and Phosphorus, in the form of NH_4NO_3 and $NH_4H_2PO_4$ was added by weight of media at an amount of 1% and 0.1%, respectively. On a monthly basis, 50 grams of "wet" media was removed from each biofilter to determine a variety of chemical and biological factors (data not presented here). On these sampling dates, nutrients were added to each biofilter based on its new media weight.

2.Pilot-Scale Biofilter Set-up: The pilot-scale demonstration was conducted at an OSB mill in Michigan. The adsorption unit consists of an adsorption cell filled with 1000 grams (1kg) of 40-mesh activated carbon in line with two bark-based biofilters. Each adsorption cell is constructed from a 2000 cm^3 galvanized steel pipe (25.5cm x 10cm) with threaded end caps for easy removal. Tapped into each end of the adsorption cell is a stainless steel "quick-connect" fitting (Badger Valve and Fitting; Neenah, WI) with 1" O.D. tube connections. All air lines are plumbed using 1" O.D. stainless steel line. A waste stream from the mill's presses, containing VOCs, flows into the adsorption unit at a rate of 40 L/min. The waste stream passes through the adsorption cell and flows into a set of two biofilter modules in series. The flow rates of the waste stream are regulated using metering valves (Badger Valve and Fitting, Neenah, WI). The adsorption unit collects the VOCs for a period of one week and then the cell is rotated into the desorption unit. After a week of collection, the concentrated adsorption cell is placed into an oven controlled at 50?C for thermal desorption. Clean air passes through the three desorption cells at 1.2 L/min, and thermally desorbs the contaminants over a three weeks period (with each of the 3 desorption cells at a different stage of desorption). The desorption of the concentrated cells is intended to produce higher concentrations of methanol and alpha-pinene than introduced into the adsorption system. The waste stream from the desorption unit is then sent to a set of three biofilters in series. After complete desorption, one of the stripped desorption columns is sent back to the adsorption set-up for collection of VOCs. This process produces a continuous rotation of the adsorption/desorption cells.

The coupled pilot-scale biofiltration unit (including adsorption/desorption unit) was set up as illustrated by Figure 2. All of the biofiltration experiments are conducted at ambient temperatures (22?C?5?C). Each biofilter module is constructed from stainless steel and is 17.5"x17.5"x17.5" in size. Tapped into each end of the biofilters are 1" O.D. stainless steel Swagelock fittings. The system is checked frequently to prevent gas leaks and to make sure that it is completely sealed. Two biofiltration modules are in line with the adsorption unit (adsorption biofilters), while the remaining three modules are in line with the thermal

desorption unit (desorption biofilters). The two biofilters in line with the adsorption unit are used to degrade any of the VOCs that pass through the adsorption cell. Sampling of the influent and effluent streams is done at various points throughout the system (to determine the concentrations of the contaminants) using on-line gas chromatography (GC) equipped with a flame ionization detector. Each biofiltration column was filled with approximately 50 lb of dry Douglas Fir bark chips sieved to a 1" to 1-1/2" size. Each biofilter module has an approximate empty bed volume of 5300 cm^3. Bacteria were added to the media before each biofilter module was assembled, and nutrients were added based on dry media weight. Again at start-up, Nitrogen and Phosphorus, in the form of NH_4NO_3 and $NH_4H_2PO_4$ was added by weight of media at an amount of 1% and 0.1%, respectively.

3.Chemical Analysis of VOC stream: All biofilter and adsorption/desorption influent and effluent lines were connected directly to an electronically actuated 16 port switching valve (Valco, Inc., Houston, TX) for online VOC analysis. The switching valve was controlled by the manufacturers software and was synchronized with the GC sampling sequence for fully automated analysis. GC analysis was performed on a HP 6890 GC (Hewlett Packard; Palo Alto, CA) equipped with a six port gas sampling valve, a 30 meter by 0.45 mm i.d. DB-5 capillary column with a 0.25 ?m film thickness (J&W Scientific; Folsom, CA), and a flame ionization detector (FID). Samples were delivered via on column injection using a 1.0 ml sample loop heated to 120?C. The column oven was held isothermally at 180?C for three minutes and the FID was operated at 250?C. A ten-minute equilibration period was programmed into the GC sequence after the switching valve selected a new sample, to insure all sample lines had been thoroughly flushed.
Total hydrocarbon analyzer (THC) analysis was performed with a J.U.M. Engineering Model 3-200 FID analyzer in accordance with EPA Method 25A. Calibration was performed with hydrocarbon free air (Praxair Technology, Inc.; Chicago, IL) for zero calibration and 90 ppm certified standard propane in air (Praxair Technology, Inc.) for high-end span calibration. The sample was introduced to the FID analyzer from the emission source via a Teflon transfer line heated to 400?F.

4.Chemical Analysis and Moisture Content of the Biofilter Media: Media samples from the dismantled biofiltration columns (5.0 grams wet wt.) were placed in two respective 40 ml VOA vials containing 10.00 ml of distilled water for the extraction of methanol, and 15.00 ml HPLC grade hexane (Fisher Scientific, Chicago, IL) for the extraction of alpha-pinene. After the samples were agitated at room temperature for 30 minutes for the extraction of methanol, and 10 minutes for the extraction of alpha-pinene, they were allowed to sit for 18 hours at 4?C before analysis. Analysis was performed on a HP 5890 GC (Hewlett Packard) equipped with a 30 m by 0.25 mm i.d. DB-5 capillary column with a 0.25 film thickness (J&W Scientific; Folsom, CA) and a FID. The column temperature was held isothermally at 50?C and 60?C for the analysis of methanol and a-pinene, respectively. The injection port was operated at 250?C and the FID at 280?C. A split ratio of 50:1 was used for the analysis of methanol, and splitless injection was used for the analysis of alpha-pinene.
Moisture content of each media sample was determined gravimetrically by weighing 3-5 grams of the media before and after it was heated in an oven at 106?C for 24 hours.

D-RESULTS

1.Adsorption of Model Compounds: The adsorption of methanol in the pretreatment system is shown in Figure 3. During the study discussed in this paper, there was an average of influent methanol concentration of 91.5 ppmv (S.D. ±24.1). There was very little adsorption of methanol in the pretreatment system with an average of 57.7 ppmv (S.D. ±40.8) of methanol leaving the pretreatment system. However, methanol, which passed through the pretreatment system, was degraded to less than 7 ppmv in the modular biofilters

attached to the pretreatment unit. The exception to this removal efficiency was on approximately 6/1/98 when methanol was shown to be breaking through the system. At this point, another biofilter module was placed on the pretreatment system and removal immediately dropped to below 2 ppmv (95+%) and stayed at that level until immediately after the shutdown period of 9/2/98. The temporary decrease in efficiency was due to an increase in system flow rate. After the shutdown, methanol removal has been gradually increasing. This is most likely due to the fact that there was no methanol entering the system during the shutdown, and microbial methanol degradative abilities had been "shut down". It was assumed that the removal efficiency would eventually reach "preshutdown" levels, as it did in the beginning of the study (i.e., an acclimation period).

The adsorption of alpha-pinene in the pretreatment system is shown in Figure 4. Alpha-pinene adsorbed onto the activated carbon in the pretreatment system with and average influent concentration of 16.1 ppmv (S.D. ±4.1), and left the pretreatment system at a concentration of 2.5 ppmv (S.D. ±0.7). The 2.5 ppmv passing through the pretreatment system was subsequently degraded to an average of 1.1 ppmv (S.D. ±O.6) in the modular biofilters attached to the pretreatment system. As was expected, throughout the shutdown of 9/2/98 there was a continually decreasing amount of alpha-pinene being desorbed from the desorption cells.

2. Desorption and Biofilter Destruction of Model Compounds: As indicated in the above section the adsorption and subsequent desorption of methanol was highly variable. Again the average influent methanol concentration of the entire system was 91.5 ppmv, and the amount being desorbed was 57.7 ppmv (S.D. ±40.8). The very high standard deviation for this value reflects the lack of any real concentrating effect with the methanol. This lack of adsorption is due to the type of adsorbent being used and the chemical properties of methanol. Different adsorbents would be better suited for methanol. However, the highly variable concentrations of methanol leaving the desorption cells were degraded to an average of 4.1 ppmv (S.D. ±4.1) in the modular biofilters attached to the desorption system (Figure 5).

As discussed earlier, the adsorption and subsequent desorption of alpha-pinene was very effective. Again the average influent alpha-pinene concentration of the entire system was 16.1 ppmv, and the amount being desorbed from the desorption cells was 68.1 ppmv (S.D. ±4.0). From the flow rate increase of 5/5/98 to the end of the study, the concentration of pinene leaving the desorption system was 90.1 ppmv (S.D. ±10.5). As can be seen from Figure 6, the concentration of alpha-pinene was relatively constant throughout the study. Figure 6 further demonstrates (with the exception of immediately after the 10/2/98 start-up) the high degree of degradation taking place within the modular biofilters attached to the desorption system, to an average of 0.5 ppmv (S.D. ±1.1). Thus, the overall average removal of alpha-pinene from the desorption system (i.e., degradation of the concentrated stream) was 98+%.

The overall performance of the coupled biofilter system in removing methanol, is shown in Figure 7. Again, the overall average influent concentration of methanol was 91.5 ppmv, and the combined effluent (from the modular biofilter attached to both the adsorption system and the desorption system) of methanol was 6.1 ppmv. This results in an overall system removal efficiency of 93+%. Analogously, as illustrated in Figure 8, the overall average influent concentration of alpha-pinene to the coupled biofilter system was 16.1 ppmv, and the combined effluent (from the modular biofilter attached to both the adsorption system and the desorption system) of alpha-pinene was 1.6 ppmv. This is an overall removal efficiency of 90%. In addition, the coupled system limited average alpha-pinene emissions from the system to approximately 1 ppmv or less.

In addition to removal efficiencies, the solid support was sampled five times throughout the study to evaluate the microbial effects on the structure of the solid support (data not reported here). After each sampling event, the removed media was not replaced with new media. Thus, the amount of media added to each system at start-up was approximately 550 g per module or 2,200 g for the total system. After each sampling event, 50 g of sample was removed from each module for the various analysis. The beginning volume of the solid support was 2550 cm^3, and at the end of the study the volume was 1487cm^3. Thus, over the course of the study the amount of the target analytes removed per g of media, or per unit volume of media, continually increased. For example, after the first sample day approximately 5 ng/hr/g (solid

support) of alpha-pinene was degraded, while after the last sampling time the removal was over 400 ng/hr/g. Similarly, methanol removal was approximately 40 ng/hr/g at the beginning of the study, while at the end of the study the system was removing over 2,750 ng/hr/g. There was little degradation of the solid support over the course of this study.

The fact that the removal efficiency, in terms of analyte removed per gram of solid support, increased throughout the study may suggest that the system has the capability to remove much higher levels than were tested in this study. Should this be the case, the size of a unit could be decreased and in practical application save significant space and cost at an industrial site.

3. Pilot-Scale Evaluation of Technology: The Pilot plant ran for approximately two years. The design of the pilot plant unit is shown in the diagrams and pictures below:

One of the main features of this technology is the fact that it will eliminate the fluctuations in VOC concentration observed in industrial press streams. At the pilot-scale site, the air emissions (VOC) data was collected and characterized using both a Total Hydrocarbon Analyzer (THC) and an on-line Gas-Chromatography using a flame ionization detector (GC-FID). The THC data, shown in Figure 9, illustrates the characteristic fluctuations in VOC concentration during the press cycle. It is the target of this project to eliminate these fluctuations by the use of the adsorption system. These cycles cause significant and detrimental problems to the microbial community within the biofilter. The fluctuations in VOC loadings caused by this cycling result in decreased overall efficiencies of the units. Further evaluation of the THC data using on-line GC/FID (Figure 10) confirmed the variability of VOCs in the air stream. The on-line GC-FID data illustrated that the effluent stream from the presses contained a relatively simple mixture of compounds. As Figure 10 illustrates, the major components in the air stream are methanol and alpha-pinene, and several compounds formed or released from the resin used in the board production. It should be noted that the chromatogram represents the major constituents of the air stream. Other studies, using solid support cartridges, which collect both the major and minor components, indicate that the air stream also contains a large number of minor components. They include terpenes, fatty acids, resin acids, lignin fragments and substituted phenols.
Variation during the press cycle, for in the five major components, is shown in Figure 11. Methanol is the major component in the air stream. The concentrations of four components do not change during the press cycle. The only compound that appears to be temperature dependent is alpha-pinene.
Data from the pilot-scale demonstration show that the adsorption system is effective in adsorbing and destroying the VOCs in air stream (Figures 12 and 13). Small amounts of methanol and resin compounds are breaking through the adsorbent (as was expected), but these are easily degraded in the adsorption biofilters. The pilot-scale unit has demonstrated promise in concentrating terpenes in the air stream, as was demonstrated in the laboratory phase of this project. The alpha –pinene has been concentrated to around 10ppmv and when it exits the final biofiltration unit the concentration in the air is between 0 to 1 ppmv. Methanol is not being concentrated in the system but it easily destroyed in the adsorption biofilters. Well over 90% of the air emissions are being degraded in the two biofilters.

E. CONCLUSIONS

This projects objective was to determine the feasibility of using physical/chemical methods to adsorb and then desorb analytes in order to convert a dilute, high volume air stream to a more concentrated low volume air stream. Another advantage of the chemical/physical (adsorption/desorption) system is to provide a relatively consistent air stream to the biofiltration units in order to alleviate the perturbations to the system as a result of uneven analyte concentrations.
Laboratory and pilot plant studies have shown that this approach does work and will provide improved destruction of VOCs from the Forest Products industry. The combination of a solid support has the potential to be a real benefit to the forest products and allied industries, and to move biofiltration technology to another level when compared to other air treatment systems. In particular, this technology would allow for smaller units to be built, saving space and capital investment. This size reduction would be accomplished by having a unit which was much more efficient than traditional biofilters. These systems would also provide for better overall destruction and removal of problematic compounds such as terpenes. Analogously, by decreasing the variation in the influent streams, it may make biofiltration a more applicable technology to industries that experience frequent and often longer down times. In addition, by maintaining basal levels of analyte during down times, it will reduce the acclimation time required once production starts-up again, and thus maximum removal is reached more quickly. In summary, this technology will provide a new approach for handling the VOCs produced during manufacturing of board products.

IV. ACKNOWLEDGMENTS

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V. REFERENCES

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VI. PAPERS PRESENTED AND PUBLISHED

1999. Characterization of Alpha-Pinene-Degrading Microorganisms and Application to a Bench-Scale Biofiltration System. (*Archives of Environmental Contamination and Toxicology*, In Press.)
1999. Development of a "Second Generation"Biofiltration System. Air and Waste Management Association Annual Meeting. St. Louis, MO, June 21-24. (Abstract and manuscript accepted, In Press.)
1999. Development of a Novel On-Line GC Sampling Method for Industrial Effluents. Air and Waste Management Association Annual Meeting. St. Louis, MO, June 21-24. (Abstract and manuscript accepted, In Press.)
1999. Pollution Prevention Technology for the Forest Products Industry. Air and Waste Management Association Annual Meeting. St. Louis, MO, June 21-24. (Abstract and manuscript accepted, In Press.)
1999. Development of a Coupled Physical/Chemical and Biofiltration System. TAPPI Environmental Conference. Nashville, TN. (Abstract and manuscript accepted, In Press.)
1999. Reducing Volatile Organic Compound (VOC) Press Emissions from Oriented Strand Board (OSB) Manufacturing. TAPPI Environmental Conference. Nashville, TN. (Abstract and manuscript accepted, In Press.)
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1999. Developing of a " Second Generation Bifiltration System" , International Congress of Environmental Microbiology. Bogotá Columbia, June 1999 (Invited Speaker)
1999. A Treatment Train Approach for Handling Air Emission for the Treatment of Volatile Organic Compounds From Wood Processing, Forest Products Society, June 1999 (Invited Speaker)
1999. Controlling Air Emissions From Composite Mills Using Chemical Additives, Forest Products Society, June 9 (Invited Speaker)
1999. The Use of Biofilters for the Controlling Air Emissions, Forest Products Environmental Conference, March (Invited Speaker)
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1999. Biofiltration, AW&PA and DOE, Invited speaker on funded project, October 1998
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1998 Controlling Air Emissions in the Forest Products Industry, AW&PA, Invited speaker on funded project
1998, Recycling in the United States, Invited speaker by the Taiwanese Government
1998, Environmental Movement in the United States, Invited speaker by the Taiwanese Government, June 1998
1998, Bioremediation, a treatment for air, soil and water, a series of presentations for industrial and government groups in Argentina, February 1998
1998. Development of an on-line Gas Chromatographic Analysis for Volatile Organic Compounds in the Forest Products Industry, Proceedings from the Society for Industrial Microbiology, Bioremediation for Industry Meeting, West Bend, IN March 8-11,1998
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Figure 1. Schematic of Laboratory Coupled System.

Figure 2. Schematic of Pilot-Scale Coupled System.

Figure 3. Adsorption of Methanol in the adsorption/desorption system.

Figure 4. Adsorption of alpha-pinene in the adsorption/desorption system.

Figure 5. Methanol desorption and subsequent degradation in the "desorption" biofilter.

Figure 6. Alpha-pinene desorption and degradation in the biofilter.

Figure 7. Total methanol concentration entering and exiting the system (Overall system performance).

Figure 8. Total alpha-pinene concentration entering and exiting the system (Overall system performance).

Figure 9. Total hydrocarbon data from pilot-plant operation

Figure 10. Gas Chromatographs of the air stream. ("Top of the press cycle" refers to the highest concentration of the VOC concentration and "Bottom of the press cycle" refers to the lowest VOC concentrations in the air stream (see Figure 9)

Figure 11. Major Compounds detected by online analysis of five positions during the press cycle.

Figure 12. Alpha Pinene System Totals

Figure 13. Methanol System Totals