FT-IR characterization of biofilms formed on engineered biofiltration media treating volatile organic emissions for the forest products industry

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ABSTRACT

The gaseous emissions from hardboard mill presses at lumber plants contain both volatile and condensable organic compounds, as well as fine wood and other very small particulate material. Biological emissions control for these compounds present several challenges. The biofiltration media provides support and contact between the gas phase contaminants and active microbial cultures attached as biofilms on the media's surface. As the transformations in the biofilm and the media during optimal biofiltration operations are not well understood, the main aim of this project was to characterize the biofilm formed on the media during the biofiltration process using Fourier Transform Infrared Spectroscopy (FT-IR) and the FT-IR Microscope, and also examine the results along with the performance data of VOC biofiltration field and pilot scale tests. Some differences in the absorbance spectra were observed in the media and biofilm samples collected from the top and the bottom bed of the biofilters. This work suggests that while FT-IR spectral information can provide some useful insights to biofilm coverages and quality within media sections, more work and measurements will be needed to correlate the information to biofiltration performance and optimization.

1 INTRODUCTION

Industrial plants and processes use and emit various types of volatile organic compounds (VOCs), which are amenable to biological treatment. Biofiltration is an emerging and an attractive air pollution control technology for the removal of VOCs present at low concentration in the emissions from forest products plants. The filter media is one of the most critical elements of a biofiltration system as it provides contact between the gas phase contaminants and active microbial cultures either immobilized within and/or attached as a biofilm on the media's surface. Examination and characterization of the biofilms formed during bioloigcal treatment may provide some insight into process optimization and further enhancement of the technology.

An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Each different material is a unique combination of atoms, so no two compounds produce the exact same infrared spectrum. Fourier Transform Infrared Spectroscopy can thus result in positive identification (qualitative analysis) of different types of material. Additionally, the size of the peaks in the spectrum is a direct indication of the amount of material present. FT-IR can be very useful in determining the quality and consistency of multiple samples.

Other researchers have begun to examine the utility of FT-IR characterization in biological systems. Haberhauer *et al.* (1999) used FT-IR to characterize the decomposition processes of spruce litter in organic soil layers from several forest regions. The investigators found a broad intense band at 3400 cm^{-1} wavenumber due to stretching vibrations of bonded and nonbonded hydroxyl groups and another broad band at 1630 cm^{-1} due to C=O vibrations of carboxylates and aromatic vibrations. A peak at 1510 cm^{-1} was attributed to amide vibrations and aromatic C=C vibrations and the transmission FT-IR band at 1630 cm^{-1} showed significant correlation to soil organic C content. When biological activated carbon was used as a support medium for biofilters treating gas contaminants, FT-IR analysis was performed on the carbon samples collected after the process (Duan *et al.*, 2005). The fingerprint of the spectra showed peaks 1120 and 580 cm^{-1}, which represented the vibration from SO_4^{2-} indicating sulfuric acid as the dominant oxidation product of H_2S.

In this project, engineered biomedia samples from a field scale sequential biotrickling-biofiltration unit operated by BioReaction Industries LLC at the Stimson Lumber Plant in Gaston, Oregon, USA and samples from an experimental biofiltration experiment conducted in the laboratory at the Texas A&M University-Kingsville treating á-pinene emissions were evaluated with FT-IR techniques. An FT-IR fingerprint of the biofilms on the biofilter media located in different sections of the biofiltration process was obtained. Biofilm and media samples were collected from the top and the bottom bed of the biofilters. The FT-IR bench (Attenuated Total Reflectance) unit spectra and spectra from an FT-IR microscope (Transmission) were also compared and both found to be useful for certain evaluations.

The main aim of this project was: 1) to characterize the engineered VOC biofiltration media biofilm samples from a field scale operation at the Stimson Lumber Company application using ATR FT-IR analysis and the FT-IR Microscope; 2) to compare the biofilm samples from different sections of the biofiltration units; and 3) to compare of the quality of biofilm samples from different locations on the media surfaces.

2 MATERIALS AND METHODS

The Nicolet Nexus 470 FT-IR unit which has a relatively simple interferometer assembly was used in this study. The Fourier Transform aspect of the infrared response defines a relationship between a signal in the time domain and its representation in the frequency domain.

The main component of the FT-IR is the interferometer. It splits and recombines a beam of light such that the recombined beam produces a wavelength-dependent interference pattern called interferogram. The interferometer consists of 2 mirrors and a KBr beamsplitter positioned at an angle of 45° to the mirrors. Incident light strikes the beamsplitter so that half of the light is transmitted through the beamsplitter and half to the mirrors. The two components are then reflected back and recombined into the beamsplitter with half of the light passing on toward the sampling areas and half traveling back to the source (Thermo Nicolet, 1999).

Figure 1. FT-IR laboratory at TAMUK.

Figure 2. FT-IR bench with Smart Miracle Accessory

Several IR techniques are available for biological investigations. The analysis can be performed using Specular Reflectance, Diffused Reflectance and Transmission techniques. Different accessories are needed for each of these tests. The Thermo Nicolet Continuμm Microscope at TAMUK (Figure 1) provides both high performance infrared sampling and visible-light microscopy. It can be used in the Transmission or the Reflectance modes. It provides a continuous view of the sample while simultaneously collecting the data. The Reflex aperture provides redundant infrared masking, which reduces the effects of diffraction.

With polychromatic light (radiation with more than a single wavelength), the output signal is the sum of all signals at the detector which is the Fourier Transform of the spectrum also called interferogram (Thermo Nicolet, 1999). The interferogram contains basic information on frequencies and intensities characteristic of a spectrum, which is then converted into more familiar forms using Fourier Transform methods. The interferogram is a function of time domain and the spectrum is frequency domain. Band intensities can be expressed either as transmittance (T) or absorbance (A). Transmittance is a ratio of radiant power (I) transmitted by a sample to the radiant power incident on the sample. Absorbance is the algorithm, to the base 10, of the reciprocal of the transmittance. The Thermo Nicolet FT-IR bench unit at TAMUK uses an ATR (Attenuated Total Reflectance) Smart Miracle accessory for the analysis of the samples (Figure 2). ATR is a non-destructive surface analysis of strong IR absorbing materials. The depth of penetration ranges from 0.6 μm to 2.0 μm. The FT-IR ATR method offers the advantage of in-situ examination and also an ability to characterize chemical changes that occur due to the presence of moisture. The advantage with the ATR is that very little sample preparation is required.

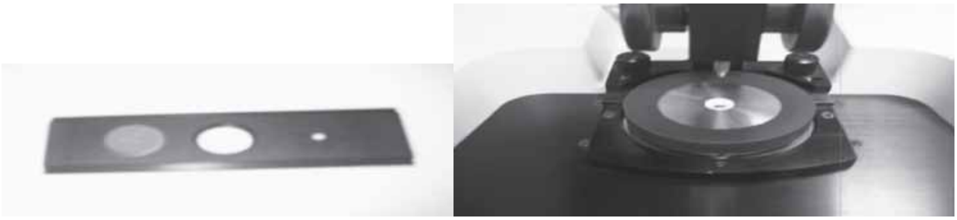
Sample Preparation:

Media samples were collected and preserved at 3°C until they were ready for measurement. Microtweezers and micro-sampling blades were used to lightly scrape the outer surface of the media and collect a small amount of wet sample for FT-IR analyses (usually less than 1 mg required).

<u>For the Continuum Microscope:</u> The axes were perfectly aligned and the detector cooled using liquid nitrogen. The background was collected by placing the gold mirror in the objective and observing it under the microscope (Figure 3a). Without changing the settings, small particles of the media sample were collected and placed on the gold mirror and the spectra was measured.

<u>For the FT-IR Bench:</u> A background spectrum was collected by collecting the raw media samples not used in the biofiltration process. The media samples from the field were observed visually and noted in terms of their color and dryness. The wet

layer (biofilm) on these media samples was collected and also analyzed. The sample was kept in direct contact between the halide crystals of the bench-scale FT-IR unit (Figure 3b), and the spectra was obtained and replicated at least twice. This fingerprint spectra of the sample was then subtracted from that of the background dry material, and the resultant composition of the wet sample was obtained.



(a) (b)

Figure 3. Sample compartment for the FT-IR showing (a) Microscope gold mirror slide, and (b) Bench (Smart Miracle sample compartment) for the ATR.

3 RESULTS AND DISCUSSION

The forest products industry encompasses a vast number of wood processes, which can utilize large amounts of energy during product manufacturing and sometimes in emissions control applications. The forest products sector includes logging, sawmills and planning mills, softwood veneer and plywood mills, hardboard veneer and plywood mills, particleboard, oriented strand board (OSB), other reconstituted wood products mills and pulp and paper mills. The operations can produce air emissions, including fugitive emissions, which may amount to several thousand tons of VOCs and HAPs per year potentially released into the atmosphere.

The Stimson Lumber Company is a private forest products and natural resource company with a plant located in the vicinity of the city of Gaston, Oregon, USA, which emits low concentrations of VOCs and HAPs into the atmosphere from the plant’s wet hardboard making process through the main ventilation system. In 2005 through mid 2006, a pilot scale biological treatment unit consisting of a biotrickling filtration section and a biofilter section in series was installed to treat a portion of the flow from the main press vent.

The biofilter media beds were comprised of engineered media of organic substrate formed around inorganic support material (manufactured by BioReaction Industries as BioAIRSpheres®) and connected in series. The uniform-shape engineered media were 2.54 x 10^{-2} m hollow polyethylene spherical structures packed with organic, nutrient-providing, compost-based media. Both units, the BTF and BF, shared a water sump with volume of nearly 5.66 m^3. The biological system operated at approximately 0.71 m^3/s of inlet air, and provided an EBCT (empty bed contact time) of 45 seconds for the entire bio-oxidation system. In spite of the fluctuation of the press vent emissions from the wet-process hardboard plant of from 12-20 ppm VOCs in the inlet stream, the pilot scale biofiltration system successfully dampened the irregularities and kept the Total VOC emissions below the objective of 5 ppm throughout the project period (Santos *et al.*, 2007). Most of the VOCs encountered were characterized by GC-MS as aldehydes, ketones and α-pinene emissions. Solid samples collected from several locations within the media beds were preserved at 3°C and shipped to Texas A&M Kingsville for FT-IR analyses.

Several functional groups which might be encountered in the organic samples were targeted for FT-IR examination. Table 1 shows some potential wavenumbers and functional groups chosen for examination.

Table 1.
Functional groups of compounds potentially encountered in the biofiltration media treating α-pinene and formaldehyde.

Functional Class	Range (cm-1)	Assigned Groups
Alcohols and Phenols	3580-3650	sharp O-H
	3200-3550	O-H (H-bonded)
	970-1250	strong C-O
Aldehydes	2690-2840	C-H
	1720-1740	C=O (saturated aldehyde)
Carboxylic Acid	2500-3300	broad O-H
	1705-1720	C=O (H bonded)
	1210-1320	strong O-C
Alpha-pinene	700-900	

Table 2 shows the unique identification and sample collection locations for the different samples used for analysis using the ATR FT-IR bench and the FT-IR Microscope.

Table 2.
Samples analyzed using the FT-IR ATR and the FT-IR Microscope.

Samples Analyzed	
Sample IDs	**Location and analyses**
I-030107	Right surface of media collected on 3-1-07
II-030107	Left surface of media collected on 3-1-07
III-030107	Bottom surface of media collected on 3-1-07
IV-031207	Bottom of media collected on 3-12-07
V-020806	Bottom of media collected on 2-8-06
VI-031207	Microscopic analysis of media collected on 3-12-07

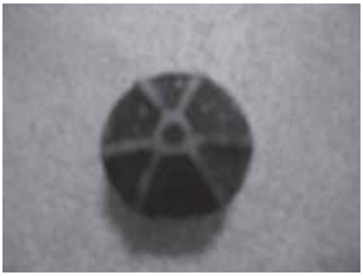


Figure 4. Photograph of typical Bioairsphere® media prior to wet film sampling.

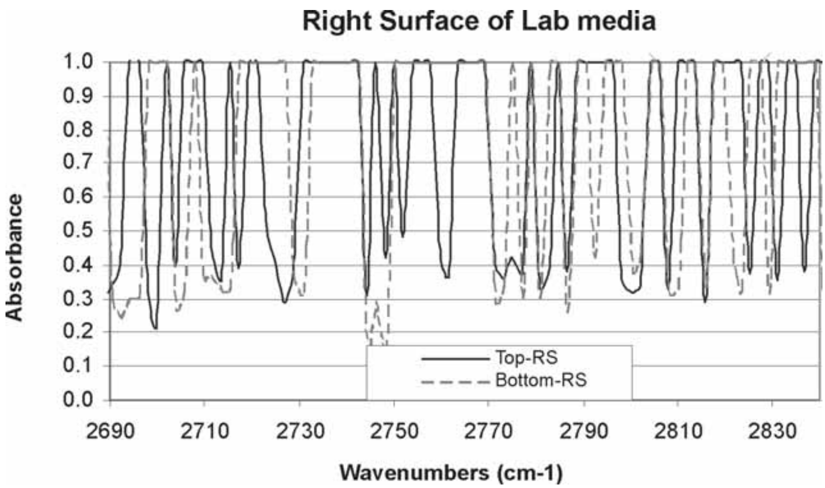


Figure 5. Bench data of samples I-030107 collected on the 3-1-07 for wavenumbers 2690-2830 cm^{-1}, representative of aldehydes and carboxylic acid groups, showing a comparison of the spectra of the right surface of the top and the bottom media of the biofilter.

Figure 4 shows a typical media sphere collected from the biofiltration units. Small scrapings of biofilms were collected from different locations on the media and examined.

Figure 5 shows a comparison of the right surface of top and the bottom section media samples.

Peaks of C-H bands were observed in both the bottom media and top media in the range of 2690-2830 cm^{-1}, representative of aldehydes. This could suggest a slight build up of aldehydes in the top bed as the biofilm may be less active at this point.

Samples V-020806 were collected on 2-8-06, from the top and the bottom of the field biofilter bed at Stimson Lumber. Physical examination of these samples showed slight variations in the biofilm coverage of the top and the bottom media of the biofilter. The media from the bottom biofilter was found to have a thicker coverage. It was more slimy and solid in color. The top media sample was drier due to moisture utilization in the biofilter. Figure 6 shows high absorption peaks representing C-H bands of aldehydes in the range of 2690-2790 cm^{-1} for both top and bottom media samples.

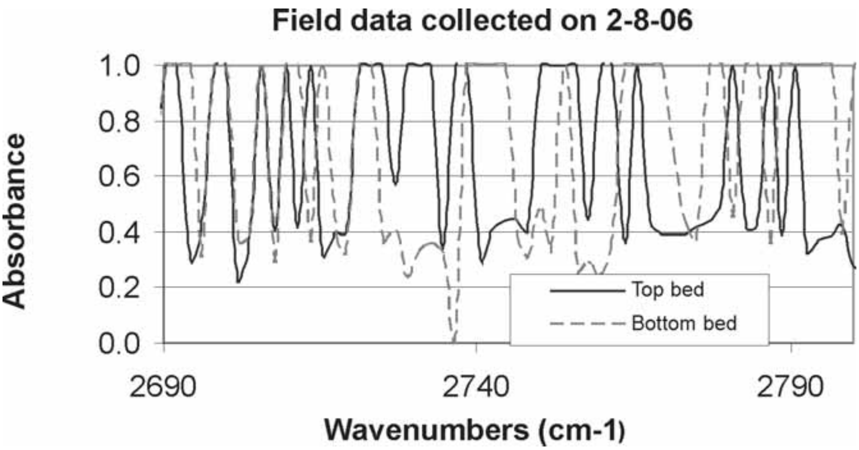


Figure 6. FT-IR bench data of samples V-020806 collected on 2-8-06, showing a comparison of spectra of the top and the bottom media of the Field VOC biofilter.

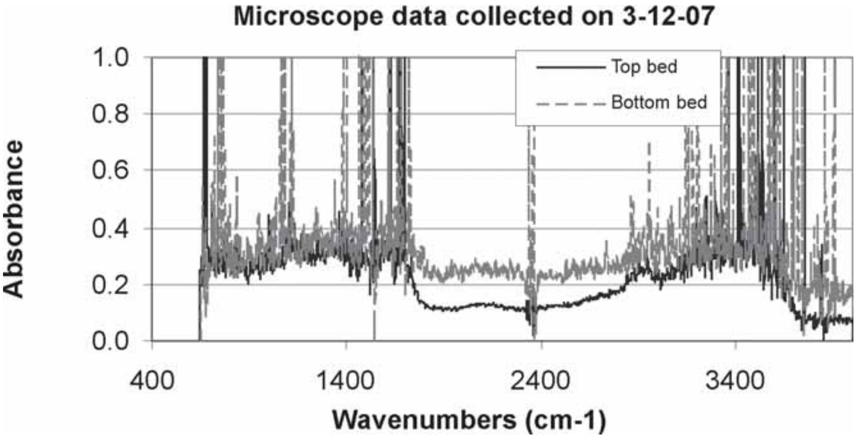


Figure 7. Microscope derived FT-IR data of sample VI-031207 collected on 3-12-07, showing a comparison of the top and the bottom media of the Lab biofilter over the entire range of wavenumbers.

FT-IR measurements were also performed using the FT-IR Microscope on samples collected from the top and the bottom bed of a lab biofilter treating α-pinene. The spectra is shown in Figure 7.

The broad bands in the bottom media in the range from 1800-3000 cm^{-1} are reflective of the higher water content and O-H stretch for the increased moisture in that range.

A comparison of the two FT-IR techniques is possible which shows the increased sensitivity of the Continuum reflectance resolution, but more qualitative value of relative measurements and comparisons for the solid sample ATR.

4 CONCLUSIONS

The FT-IR spectra obtained by examining the biofiltration media using the bench ATR unit and the Continuum FT-IR microscope showed biofilm differences at various wave numbers throughout the spectral ranges examined for these samples. Some significant differences in the absorbance spectra were observed in the media and biofilm samples collected from the top and the bottom bed of the biofilters. This work suggests that while FT-IR spectral information can provide some useful insights to biofilm coverages and quality within media sections, more work and measurements will be needed to correlate the information to biofiltration performance and optimization.

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