Speciated Volatile Organic Compound Emissions from a Medium Density Fiberboard Process in North Carolina

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Abstract

Bird, John. Master of Environmental Assessment. Speciated Volatile Organic Compound Emissions from a Medium Density Fiberboard Process in North Carolina**.**

Medium density fiberboard is a wood product manufactured from wood chips utilizing a thermomechanical pulping process. The thermomechanical pulping process imparts high pressure and energy to the wood in order to reduce the chips to a fibrous physical state. The fiber is then released in to a large heated dryer allowing steam and other volatile organic compounds to be released from the wood. A medium density fiberboard facility in Moncure, North Carolina was source tested to document all of the individual species of volatile organic compounds released from this process and these compounds' mass emission rates. The only publicly available emission factors for this process type are from the US EPA's AP-42 and the AP-42 is focused on criteria pollutants and the federal hazardous air pollutants list. Alpha-pinene, methanol, formaldehyde, acetic acid, formic acid, beta-pinene, p-xylene, and furfural were detected in the emissions. Understanding of speciated process emissions is important for any permitted facility in order to properly mitigate offsite impacts related to process emissions and the regulatory risks related to misreporting of process emissions. Acetic acid, for example, was emitted from the process in measurable quantities and this compound is a regulated North Carolina air toxic pollutant while not a US EPA hazardous air pollutant making it subject to State requirements but not necessarily Federal NESHAP requirements. Also, during the study total hydrocarbons were measured from a flame ionization detector and the device underestimated total VOC emissions when compared to the speciated VOC results. Speciated VOC sampling may provide a better accounting of all potential offsite and regulatory impacts from a facility based on this study's findings.

Contents

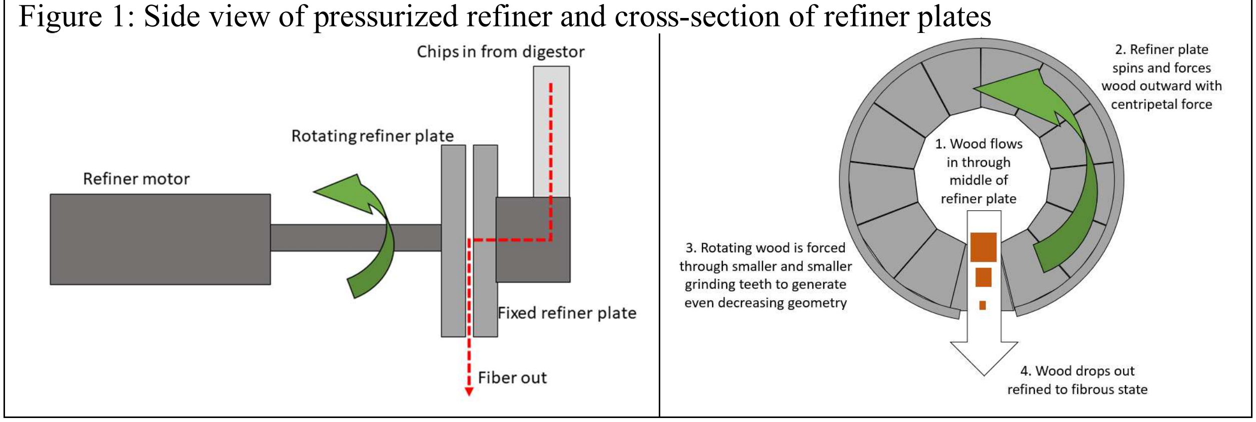
I. Introduction

Fiberboard is a mass produced wood product manufactured across the world. Fiberboard is used in flooring, furniture, and other household products that require easily etched or shaped pieces of structural members (Maloney, Introduction, 1993b). Fiberboard provides wood products manufacturers with an engineered, uniform product that can be cut into very intricate shapes via routing or machining. Examples of intricately etched fiberboard end products include crown molding in homes and custom doors (Maloney, Introduction, 1993b).

The fiberboard process requires whole logs to be chipped into pieces called "chips" that are small enough for mechanical or pneumatic conveyance systems (Maloney, Particle Generation, Conveying, and Storage, 1993c). Wood chips are then conveyed to the first key industrial process for fiberboard manufacturing called the digestor. In the digestor, steam and pressure are applied to soften the individual chips. The digestor process degrades the lignin and cellulose in the chips enough to reduce the energy required to produce fiber (Maloney, Particle Generation, Conveying, and Storage, 1993c). The high temperature degradation of lignin and cellulose results in the generation of many organic compounds including volatiles that will ultimately be emitted as process emissions following the refining process (Granstrom, 2005).

Wood chips are refined to a fine hair-like fiber using high energy pressurized refiners. The digestor is producing up to 8 atmospheres pressure and heating chips to 100°C utilizing steam while simultaneously pressing the chips into the refiner (Maloney, Particle Generation, Conveying, and Storage, 1993c). The refiner utilizes two opposite-facing plates that are covered in teeth-like blades to refine the wood chips down to fiber. One plate is fixed while one plate is rotated by a large motor to generate centripetal force and the energy to slice the wood chips down to fiber (Figure 1) (Maloney, Particle Generation, Conveying, and Storage, 1993c).

Figure 1: Side view of pressurized refiner and cross-section of refiner plates



The fiber is forced into a large, low pressure volume called the flash tube dryer operating at 200-300°C and 1 atmosphere, which causes a significant percentage of the moisture to flash off of the wood as steam along with an assortment of organic compounds from the breakdown of the wood cellulose in the digesting and refining process (Maloney, Drying Principles and Practices, 1993a). Wood is collected in the drying process via cyclones and sent to a hot press to be made in to solid panels and cut to size for customer demands (Maloney, Drying Principles and Practices, 1993a). The focus of this project is around the pressurized refining and drying processes as the steam and gases collected from the cyclones must be controlled.

The specific fiberboard process being studied is based just south of Raleigh, North Carolina. The site has a capacity to convert over 280,000 oven dry tons of Southern yellow pine wood residuals per year into wood-based fiberboard. Wood residuals are industrial wood waste byproducts from saw mills, band mills, plywood plants, and other wood products facilities that make solid wood products but end up with residual wood materials. The facility has conducted numerous source tests of the refining and drying processes of federal hazardous air pollutants and other organic compounds for State and Federal compliance purposes. The emissions tests will provide an archive of historical information to compare new data with. The process is being studied in North Carolina (Figure 2).

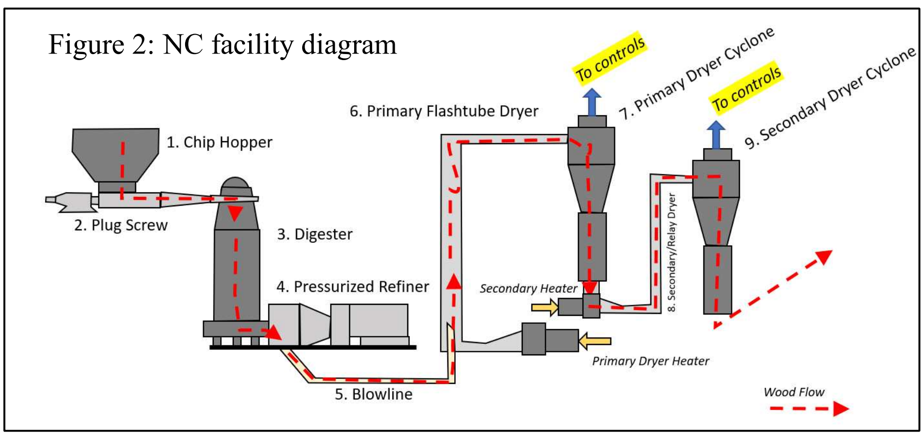


Figure 2: NC facility diagram

The refining and drying emissions of the North Carolina facility will be the focus of this project. These processes represent the largest known source of volatile organic pollutants in fiberboard production (US EPA, 2002). As a result, there are significant public health and regulatory implications for the control of pressurized refiners and flash tube drying.

Emission factors are derived by monitoring emissions of specific compounds from a point source of pollution and weighting the emissions versus the process throughput. Using emission factors is the simplest means for estimating long-term emissions from a process without the need for continuous emissions monitoring. The US EPA has published emission factors for emission sources in a wide range of industries since 1972 under the designation of Compilation of Air Pollution Emissions or AP-42 (US EPA, 2020a). Chapter 10 of AP-42 is dedicated to wood products emission factors and the US EPA compiled emissions testing from a wide range of wood products sources including fiberboard refining and drying processes (US EPA, 2002). According to AP-42 Chapter 10.6.3 data, the drying process accounts for over 80% of the organic emissions in the manufacture of fiberboard (US EPA, 2002).

The compounds that make up the majority of the fiberboard process emitted volatile organic emissions according to AP 42 Chapter 10.6.3 include formaldehyde, methanol, acetaldehyde, acetone, alpha-pinene, and beta-pinene (US EPA, 2002). Many of these documented compounds are found in the US EPA Integrated Risk Information System (IRIS) due to epidemiological evidence of chronic or acute toxicity (US EPA, 2020b). Acetaldehyde and formaldehyde are probable human carcinogens according to IRIS while methanol, acetone, formaldehyde, and acetaldehyde are documented as having several acute effects in the IRIS database (EPA, Acetaldehyde CASRN 75-07-0, 2020e; EPA, Acetone CASRN 67-64-1, 2020f; EPA, Formaldehyde CASRN 50-00-0, 2020c; EPA, Methanol CASRN 67-56-1, 2020d).

As a result of gaps perceived by environmental groups and state agencies, state regulatory agencies began developing local Air Toxics programs to regulate the emissions of toxic compounds from various industrial processes that were not already regulated by the National Ambient Air Quality Standards (NC Division of Environmental Quality, 2020). North Carolina, for example, developed its own air toxics program starting in 1985 and created fence-line standards for several toxic air pollutants by 1989 (NC Division of Environmental Quality, 2020).

There are a number of fiberboard facilities subject to various state air toxics programs requiring control of toxic air pollutants down to regulatory fence-line thresholds. The state air toxic program and regulatory citations for existing US fiberboard manufacturers are listed in Appendix Table A.1. To show variation from program to program at the state level, Table 2 shows the relative fence-line concentration requirements for formaldehyde in each of the aforementioned fiberboard producing states. The different states have selected different ambient air concentrations, different implications for exceeding concentrations, and different averaging periods for the exact same compound. The lack of programs in many states and sheer variation of state programs demonstrates the lack of consistency and approach from each state when regulating air toxics.

The 1990 Clean Air Act Amendments directed the US EPA to establish standards for many toxic air pollutants (US EPA, 2017a). These non-criteria air pollutants were designated "hazardous air pollutants." In 1992, the United States EPA created a list of industry categories documenting major and area sources of hazardous air pollutants requiring additional regulation, and potentially, controls (US EPA, 1992).

Plywood/particleboard manufacturing was listed in Table 1 in this initial 1992 list (US EPA, 1992). The 1992 lists initiated the development of national emission standards for hazardous air pollutants on a sector by sector basis. The plywood and composite wood products (PCWP) national Maximum Achievable Control Technology (MACT) emission standard for hazardous air pollutants was promulgated by the US EPA in 2004 and applied to a wide range of manufacturers of wood products including fiberboard (US EPA, 2004). The PCWP MACT directed manufacturers to apply maximum achievable control technology to specific pieces of process equipment in order to significantly reduce emissions of hazardous air pollutants from the wood products manufacturing sector.

The designation for maximum achievable control technology for pressurized refiners and fiberboard dryers is 90% reduction of total hydrocarbons, formaldehyde, or methanol as indicated in Table 1B of the final PCWP MACT rule (US EPA, 2004).

As part of the US EPA process for reviewing new control technologies and updating risks of industries, the US EPA is required to complete a technology review every eight years for every sector's hazardous air pollutant MACT standard (US EPA, 2017b). This review process is being completed right now for the current PCWP MACT standard to determine whether or not the MACT standards lowered risk below acceptable thresholds with an ample margin of safety. As part of the review, the US EPA sends a comprehensive survey called an information collection request (ICR) to all of the companies and facilities in the sector to collect emissions data, process information, and control device information (US EPA, 2017b). All of the inputs received in the information collection request are then used to conduct a comprehensive air dispersion model of the industry to determine its residual risk after implementation of MACT controls. A significant input for the model – where site specific emissions data are not available - is the AP-42 emission factor database (Sroka, 2019).

The compilation in AP-42 shows the gap in knowledge around speciated volatile organic compounds in the exhaust of the pressurized refining and drying process of fiberboard plants. Table 1 summarizes four fiberboard refiners+dryers grouped by tree species that were tested and compiled in the AP-42 Chapter 10.6.3:

Table 1 – Sample Emission Factors from AP-42 for fiberboard dryers[3]

VOC Species	Indirect Fired Softwood	Resin+ Hardwood	No Resin+ Hardwood	Direct-Fired Softwood
Total "VOC" as propane[2]	*5.60E+00*	*4.80E+00*	*1.20E+00*	*6.70E+00*
acetaldehyde	2.00E-02	1.30E-02		
acetone	2.50E-02		1.60E-02	
alpha-pinene	2.10E+00			
beta-pinene	4.30E-01			
camphene	1.20E-01			
formaldehyde	2.20E-01	2.60E-01	8.50E-03	8.60E-01
limonene	1.10E-01			
methanol	8.70E-01		9.60E-01	
MIK	4.90E-03			
phenol	2.30E-02			
subtotal speciated compounds	***3.92E+00***	***2.73E-01***	***9.85E-01***	***8.60E-01***
% of total "VOC" identified	***70.05%***	***5.69%***	***82.04%***	***12.84%***

Notes: 1. units = lbs compound/ton of wood processed
2. Total "VOC" is estimate based on FID and wet impinger testing
3. AP-42 document does not clearly delineate facilities in Malvern, AR; Urania, LA; Eugene, OR; Rocklin, CA; Mt. Jewett, PA

Several studies of other wood products systems show that there are additional compounds that should be included when defining emissions from a fiberboard refining and drying process. Acetic acid and formic acid, in particular, are cited in multiple studies as large constituents resulting from the breakdown of wood in the drying process (Granstrom, 2005) (Jain, 2011) (Risholm-Sundman, 1998). Georgia-Pacific conducted studies on oriented strandboard (OSB) raw material and found that smaller wood particles released more mass VOC per unit mass of wood than larger particles (Banerjee S. O., 1998). Typical wood particles in the OSB process are the size of a dollar bill while wood refined in a fiberboard plant's pressurized refiner is at most 3 mm long and 35 micrometers in diameter. This difference would result in a significantly higher surface area per unit mass of wood in a fiberboard dryer than more traditional wood product dryers.

Typical wood product systems are operated at 1 atmosphere of pressure while a pressurized refiner can operate at 8 atmospheres (Maloney, Particle Generation, Conveying, and Storage, 1993c). According to Maloney, increasing pressure in a refiner from 3 atmospheres to 8 atmospheres can double the potential acid produced from wood fiber (Maloney, Particle Generation, Conveying, and Storage, 1993c). This makes quantifying organic acid generation from a high pressure system like fiberboard production likely to result in a greater understanding of volatile organic emissions from the fiberboard process.

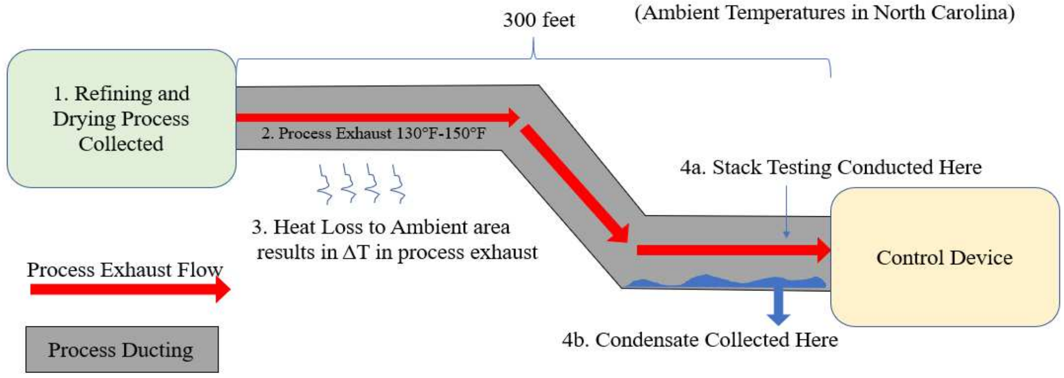
The goal of the project is to speciate and apportion the organic compounds originating from the refining and drying process at a fiberboard production facility in North Carolina to provide better understanding of the emissions from a fiberboard refining and drying process. As stated previously, compounds are generally unknown or poorly documented for this type of system because this is a relatively small, specialized segment of the wood products industry and the focus of similar studies was on larger parts of the wood products sector like lumber, OSB, and veneer (Banerjee S. a., 2007) (Banerjee S. O., 1998) (Banerjee S. O., 1995) (Jain, 2011) (Risholm-Sundman, 1998). It is expected that there will be significantly higher mass of volatiles and extractives released from fibrous wood at these elevated pressures and temperatures compared with low pressure, low energy systems that are used in the rest of the wood products industry.

II. Methods

A. Condensate Testing

The exhaust must travel 300 feet through a large stainless steel duct. The process exhaust leaves the dryer saturated with moisture, and it ranges in temperature from 130°F-150°F. Therefore, the exhaust cools as it travels the length of stainless steel ducting, reducing the exhaust's carrying capacity for water vapor and resulting in water condensate. At the end of this duct, there is a collection system installed to collect and purge condensate prior to the installed control device for this exhaust (Figure 3).

Figure 3: Collection Apparatus



Condensate samples from the process exhaust were analyzed to identify the presence and concentration of specific compounds known to originate from wood drying processes, based on (Jain, 2011) and the US EPA AP-42 emission factors database (US EPA, 2002).

The condensate purge system is checked every 12 hours by employees at the North Carolina facility to ensure it is flowing properly to prevent accumulation of wood fiber and water soluble compounds like fatty acids or formaldehyde. Samples of condensate will not be preserved or chilled for local laboratory testing while samples being sent overnight were originally chilled and packed in ice. However, attempts at shipping overnight during the pandemic conditions have resulted in samples being received multiple days later at ambient temperatures.

Condensate samples are collected from a drain attached to the stainless steel duct using appropriate gloves due to presence of hazardous chemicals and liquid temperatures in excess of 140°F. Headspace must be minimized in the collection jars to reduce chances of volatiles loss at laboratory. The samples will be taken directly to the lab or shipped expeditiously, where they will be refrigerated until processed.

Initial screening of the samples was conducted using two different laboratories. One laboratory is a commercial laboratory owned by Montrose Environmental located in Durham, North Carolina. utilizing certified methods for specific individual organic compounds to analyze the condensate. Table 2 summarizes the methods used to evaluate concentrations of identified compounds of interest. There may be some atypical organic compounds that do not have an official certification from the State of North Carolina. In the case of these compounds, the laboratory is required to provide the method detection limit and initial demonstration of capability study for the compound according to the NC Department of Environmental Quality.

Table 2 - Testing Conducted at Montrose in Durham, North Carolina		
Compound	Sampling Location	Analysis Method
Formaldehyde	Condensate	High pressure liquid chromatography derivatization analysis
Methanol	Condensate	Gas chromatography analysis
Fatty Acids (Acetic, Formic)	Condensate	High pressure liquid chromatography
Limonene, α-pinene, β-pinene, acetone, ethanol, camphene, phenol, m-xylene, p-xylene	Condensate	Gas chromatography extraction analysis

For quality control, the laboratory in Durham is conducting a known concentration spiked sample test to ensure the testing equipment is recovering an adequate percentage of the compounds and confirming equipment is not contaminated by analyzing blanks in parallel with the condensate. Blanks were generated in the laboratory and were not provided during the sampling. The laboratory also prepared known concentrations for spike analysis to ensure accuracy of equipment during testing. Two test runs were conducted on every compound for each sample analyzed in the Durham laboratory and the result for the sampling event is the average of the two test runs. Equipment calibration curve data are provided with every final sample report.

The second laboratory conducting initial screening of compounds is owned by the National Council of Air and Stream Improvement (NCASI). This lab is a private laboratory located in Gainesville, Florida. The NCASI laboratory has built a library of organic compounds typically generated in wood products wastewaters that can be identified in the laboratory's mass spectrometer. The NCASI laboratory is utilizing a calibrated mass spectroscopy that has been verified against known concentrations of compounds typically found in wood-based wastewaters. Detailed quality assurance was not provided for the mass spectrometer as the mass spectrometry was conducted pro bono and the goal was primarily to identify any potential compounds in the water not to quantify concentrations.

B. *Air Stream Sampling*

After building a list of identified compounds from wet chemistry testing, the identified compounds were tested in the air stream for concentrations and mass flow rate. EPA approved source testing methods were utilized in the air stream to identify concentrations of compounds based on compounds found in the liquid condensate. Table 3 summarizes the US EPA approved test methods utilized in the air stream and what compounds were assessed by each method.

Table 3 - Testing Methods Conducted in Air Stream	
Method	Compound(s)
EPA Method 320	Formaldehyde Methanol Acetic acid Formic acid Ethanol Acrolein Acetone Furfural p-Xylene Acetaldehyde Phenol
EPA Method 18	Methane Alpha-pinene Beta-pinene
EPA Method 25A	Total hydrocarbons

Concentrations of speciated organic compounds were compared to total hydrocarbon mass emission rates. During the source testing, concurrent total hydrocarbon testing using flame ionization was conducted with speciated VOC testing using Fourier transform infrared spectroscopy (FTIR) to create a mass balance between non-speciated and speciated total VOC. The contractors conducting the testing had completed the Source Evaluation Society's qualified source testing individual program. The source testers utilized EPA Method 320 for speciated VOC and EPA Method 25A for total hydrocarbons. EPA Method 18 will be to identify presence terpenes as larger molecules may condense in the FTIR sampling system and produce lower than expected concentrations.

EPA Method 320 described vapor phase organic compound detection by FTIR. The FTIR operates by pulling a known volume of gas through an infrared beam (OAQPS U. E., Test Method 320, 2019). Every compound elicits a unique infrared spectrum when passing through the infrared beam, allowing the FTIR system to extract not only the identity of the compounds but the signal strength of the spectrum indicating concentration (OAQPS U. E., Test Method 320, 2019). The EPA method states that the FTIR operator will have conducted calibrations and verified accuracy of his or her sampling equipment with known concentrations of target compounds prior to testing in the field. The source tester must procure digital calibration standards that were developed by the FTIR supply company to ensure confidence in the results within the target testing concentrations.

In EPA Method 320, potential factors affecting accuracy are broken into two categories: sample-independent factors and sample-dependent factors (OAQPS U. E., Test Method 320, 2019). Sample-independent factors are related to operator skill, equipment configuration, and reference spectra accuracy. The EPA Method 320 is a relatively expensive method compared to EPA Method 25A, so there are fewer operators experienced with using Method 320 compared with Method 25A. An FTIR continuous monitoring system used for Method 320 can cost over $100,000 while a handheld FID used for Method 25A can cost as little as $5,000. High moisture sources like the North Carolina facility's dryer exhaust provide also substantial interference for certain compounds like methanol. The process variables are sample-dependent factors.

The option selected in EPA Method 18 was collection using glass flasks filled with deionized water. The method collects gases via a heated probe and pumps the gases through a heat exchanger system to condense organic gases into flasks. The glass flasks are air tight in series with the probe and located in packed ice to condense the target organic gases in to a liquid form for later analysis. The organic compounds collected in the flasks are then separated via gas chromatography and quantified in the gas chromatograph system (OAQPS, 2019).

EPA Method 25A utilizes flame ionization detection (FID) to incinerate organic compounds and then measure the mass flow rate of carbon in the form of CO_2 as a result of the combustion of organics (OAQPS U. E., Method 25A, 2017). Similar to EPA Method 320, Method 25A pulls a set flow rate of gas from the sampled airstream for analysis. The method expresses mass flow rates of carbon as propane because the FID analyzers are calibrated using known concentrations of propane and resultant concentrations of CO_2 (OAQPS U. E., Method 25A, 2017).

When comparing compounds of varying molecular weights to EPA Method 25A, a normalization will need to be made to account for organic carbon atoms in a mass balance. The molecular weight of carbons in the compound measured is divided by the total molecular weight of that compound. The measured mass emission rate is multiplied by this ratio to obtain an estimate of the total mass emission rate as carbon.

III. Results

A. Water Quality Results

Condensate testing was initiated in December 2019 to identify potential compounds originating from the medium density fiberboard dryer process air stream. Initial testing was focused on the most well documented, water soluble compounds such as formaldehyde, methanol, acetic acid, formic acid, and butyric acid. Testing was conducted at Montrose's Durham, North Carolina laboratory. The water condensate had a pH ranging from 4 to 5 and acetic, formic, and butyric acid were prevalent in prior wood products studies (Jain, 2011). Acetic acid is also subject to North Carolina toxics air quality standards (Quality, 2018). Methanol and formaldehyde have already been detected in the air stream in every historical air emissions tests for the North Carolina fiberboard facility being studied. Table 4 summarizes concentrations of each compound of interest in the condensate and sample dates collected from December 2019 to June 2020.

Table 4 - Water quality testing of condensate on water soluble compounds					
Date	***12/19/2019***	***1/30/2020***	***1/29/2020***	***3/20/2020***	***6/1/2020****
Compound	***mg/L***	***mg/L***	***mg/L***	***mg/L***	***mg/L***
Butyric Acid	<MDL	<MDL	<MDL	NT	NT
Acetic Acid	28.6	13.1	11.1	20.7	109
Formic Acid	9.85	3.97	4.01	9.66	34.6
Methanol	NT	84.8	85.1	70.7	71.3
Formaldehyde	NT	29.1	30.7	10.9	3.66
Acetaldehyde	NT	NT	NT	NT	0.0175

NT – no test
MDL – method detection limit
* - acetone, α-pinene, β-pinene, camphene, ethanol, limonene, phenol, and p-xylene were not detected in testing on 6/1/2020 (MDL ~0.5 mg/L) but were not tested for prior to 6/1/20

To identify unknown compounds, condensate was sent to NCASI's Gainesville, Florida laboratory for analysis via mass spectroscopy. Higher concentrations and more individual compounds were identified in the condensate in early March sampling than testing conducted in warmer weather months April through June. Concentrations became very low and many compounds were no longer detectable from March 31 onward. Table 5 summarizes compounds detected in mass spectroscopy at NCASI's laboratory that were not already detected via Montrose's testing in Durham.

Table 5 - Mass spectroscopy attempts to tentatively identify compounds that had condensed in condensate collection system			
3/2/2020	***3/31/2020***	***4/6/2020***	***4/22/2020***
2,3,3-Trimethyl-1,4-pentadiene			
Furfural			furfural
α-pinene	α-pinene	α-pinene	α-pinene
phenol			
			p-xylene

B. Air Stream Results

Initial sampling of the air stream was conducted in February 2020. The resulting spectra generated by the FTIR sampler has been re-analyzed as new compounds were identified in subsequent water quality testing of condensate. Based on EPA Method 320, the following concentrations were identified. Compounds with <0.1 ppm concentration in the air stream are denoted as <0.1 as the operator could not definitively distinguish these compounds from background and moisture interferences. Table 6 summarizes the average concentration over the testing period in February 2020 for each of the speciated VOCs. EPA Method 18 identified trace (<1 ppm) methane in the sample air stream and significant presence of α-pinene as shown in Table 6.

Table 6 - Observed concentrations of identified compounds in air stream and method utilized		
Compound	**_C_{wet}_** **_ppm_**	**_Method_**
Methanol	88.1	EPA Method 320
α-Pinene	48.5	EPA Method 18
Formaldehyde	46.0	EPA Method 320
Acetic Acid	16.3	EPA Method 320
Formic Acid	3.57	EPA Method 320
β-Pinene	1.16	EPA Method 18
p-Xylene	0.980	EPA Method 320
Methane	0.490	EPA Method 18
Furfural	0.150	EPA Method 320
Acrolein	<0.1	EPA Method 320
Ethanol	<0.1	EPA Method 320
Acetaldehyde	<0.1	EPA Method 320
Phenol	<0.1	EPA Method 320
Acetone	<0.1	EPA Method 320

EPA Method 25A yielded a concentration of 325 ppm as carbon on a wet basis. A moisture content of 14% was observed in an average air flow rate of 157,264 DSCFM. Table 7 details the concentration, molecular weight, and mass emission rate of the compounds detected in EPA Methods 320 and 18. Molecular weight is necessary for calculating mass emission rate.

Table 7 - Mass Emission Rates of speciated VOC excluding methane			
	_C_{wet}_	**_Mol. Wt._**	**_Mass Emission Rate_**
Results	**_ppm_**	**_g/mol_**	**_lbs/hr as VOC_**
α-Pinene	48.5	136	174
Methanol	88.1	32.0	74.2
Formaldehyde	46.0	30.0	36.3
Acetic Acid	16.3	60.1	25.7
Formic Acid	3.57	46.0	4.32
β-Pinene	1.16	136	4.15
p-Xylene	0.98	106	2.55
Furfural	0.15	96.1	0.35

The resulting 325 ppm concentration observed in Method 25A translates to 102 lbs/hr total hydrocarbons emitted on a carbon basis. Table 8 shows the FID concentration reading, the molecular weight of carbon, and the calculated mass emission rate as carbon.

Table 8 - Calculated carbon emission rate from 25A flame ionization method			
	C_{wet}	***Mol. Wt.***	***Mass Emission Rate***
Results	***ppm***	***g/mol***	***lbs/hr as C***
Method 25A as C	325	12.0	102

To compare the speciated results of Methods 320 and 18 to Method 25A, the overall speciated results were converted to a carbon basis. Table 9 summarizes the mass emission rate of each speciated compound as carbon versus its emission rate on a speciated VOC basis. As illustrated in Table 9, 321 pounds per hour of VOC is being emitted but only 213 pounds per hour of carbon atoms are being emitted from the same source based on the molecular make up of these compounds.

Table 9 – Calculated mass emission rates as carbon for species identified in Method 320				
	Mass Emission Rate	***C***	***Mol. Wt.***	***Mass Emission Rate***
Results	***lbs/hr as VOC***	***#***	***g/mol***	***lbs/hr as C***
α-Pinene	174	1	136	153
Methanol	74.2	1	32.0	27.8
Formaldehyde	36.3	1	30.0	14.5
Acetic Acid	25.7	2	60.1	10.3
Formic Acid	4.32	1	46.0	1.13
β-Pinene	4.15	1	136	3.66
p-Xylene	2.55	8	106	2.31
Furfural	0.35	5	96.1	0.22
Total VOC	321			213

C. Comparison to Published Emission Factors

The production rate through the dryer process during the testing was 36.4 short tons of dry wood per hour. To get the resulting emission factor for each compound, the emission rates as VOC were divided by the production rate to get a normalized factor to compare to published AP-42 factors in Table 10.

In AP-42 Chapter 10.6.3, there were four processes similar to the North Carolina fiberboard facility. These facilities reported emission factors for Method 25A (total hydrocarbons as C), acetaldehyde, acetone, α-pinene, β-pinene, camphene, formaldehyde, limonene, methanol, MIK, phenol, and acrolein. During the project, ethanol, acetic acid, formic acid, furfural, and p-xylene were tested for in addition to the AP-42 compounds. Limonene and MIK were not tested for in the North Carolina process air stream.

Table 10 – Comparison of Field Testing versus AP-42 published emission factors.					
	Lb VOC/dry ton of wood				
	Project Testing	***AP-42 10.6.3***			
VOC Species	***Direct-Fired Soft/ Hardwood Mix***	***Indirect Fired Softwood***	***Resin+ Hardwood***	***No Resin+ Hardwood***	***Direct-Fired Softwood***
Total hydrocarbons as C	*2.82*	*4.40*	*3.70*	*1.00*	*4.80*
acetaldehyde	0.00	0.020	0.0130		
acetone	0.00	0.0250		0.016	
α-pinene	4.21	2.10			
β-pinene	0.101	0.430			
camphene	NT	0.120			
formaldehyde	1.00	0.220	0.260	0.0085	0.860
limonene	NT	0.110			
methanol	2.04	0.870		0.96	
MIK	NT	0.00490			
phenol	0.00	0.023			
acrolein	0.00	0.00			
ethanol	0.00				
acetic acid	0.71				
formic acid	0.12				
furfural	0.00097				
p-xylene	0.070				
subtotal speciated compounds	***8.26***	***3.92***	***0.273***	***0.985***	***0.860***

IV. Discussion

A. FID Results Significantly Less than speciated Compounds

The total carbon results from the flame ionization method underestimated total volatile organic emissions from the source. The α-pinene alone, which should 100% combust in a flame ionization detector (FID), is greater in carbon mass than the entirety of the results from Method 25A. This could be an erroneous result from sampling error or some other factor such as non-concurrent sampling. Historical testing concentrations generated from previous FID tests on this source indicate much higher mass flow rates of total hydrocarbons, based on EPA Method 1 for measuring flow rates. These concentrations are detailed in Table 11.

Table 11 – Historical Method 25A concentrations from dryer exhaust					
Concentrations	3/8/2018	3/29/2018	4/26/2018	2/27/2019	2/27/2020
Method 25A as propane	171 ppm_w	141 ppm_w	156 ppm_w	173 ppm_w	138 ppm_w

Similar sources utilizing softwood species in AP-42 had 56-70% more carbon emissions detected in Method 25A. The facility in North Carolina primarily uses Southern yellow pine – a softwood – and Southern hardwood species like oak as raw material. The raw material variation at this site in North Carolina can range from 50% or more hardwood on certain production runs and significant hardwood raw material could be contributing lower than expected total hydrocarbon results. The primary VOC from pine is pinenes and terpenes and the high results for α-pinene indicate there was likely underestimation in the Method 25A results or overestimation from Method 18.

The FID was calibrated using propane onsite prior to stack testing. However, there is a possibility that operator error in the installation of the probe resulting in poor collection efficiency could have resulted in lower than expected concentrations. Alpha pinene as carbon should have resulted in over 150 lbs/hr of carbon emissions from the FID but the FID only detected approximately 102 lbs/hr of carbon emissions. The raw data showed extremely low concentrations of carbon emissions from the FID ranging from 80-100 ppm_w. This source in previous tests has been shown to have carbon emissions from the FID ranging from 130-170 ppm_w. The autoignition temperature for alpha-pinene is significantly lower than propane meaning it should be easier to burn in a FID so the most likely explanation is that the FID was not accurately collecting emissions from the source.

B. *Fatty acids not in AP-42*

Formic acid and acetic acid account for 10% of the total mass of VOC emitted from the medium density fiberboard dryer and are not documented as emissions in AP-42. Neither compounds are US EPA listed hazardous air pollutants. In North Carolina, however, acetic acid is a regulated toxic air pollutant and would be volatile at medium density fiberboard operating temperatures and should be accounted for in a State emission inventory and air toxics evaluations. Acetic acid is not specifically addressed in the plywood and composite wood products NESHAP meaning this compound is not exempt from NC State air toxics evaluation against the State's ambient air quality standard for acetic acid (Quality, 2018).

C. *Detection limits of methods*

The data were collected on one day of source testing. Based on the collected knowledge and information, it would be beneficial to retest all of the lower molecular weight compounds in the air stream with FTIR paired with Method 18 for higher molecular weight compounds. There could potentially be additional constituents like limonene and camphene making up significant portions of the fiberboard air stream. Phenols were detected in early condensate testing in March 2020 but were not detected in significant concentrations in the air stream using Method 320. Method 320 has a detection limit for most compounds ranging from 0.1 to 1 ppm, which was not quite sensitive enough to accurately capture some of the compounds being emitted at relatively high rates (~1 lb/hr).

Additional sampling days and more parallel test methods could be used to verify emissions and find additional chemical constituents in the air stream. In particular, a NICM approach could be run in parallel with FTIR to verify accuracy of the FTIR but also to quantify trace acetaldehyde, phenol, acrolein, and other compounds that would not be distinguishable on the FTIR spectra in this air stream.

D. *Condensate testing as a surrogate for stack testing*

Condensate and water quality testing was found to be an adequate estimate for approximating emissions of water soluble compounds. Normalizing the four compounds tested via water quality testing and air emissions testing versus methanol shows relatively similar ratios of these compounds in the water versus the air. The mass emission rates compared to the condensate concentrations in Table 12 successfully ranked them in order of concentration despite varying levels of solubility in water. Stack testing would still be required to accurately account for the concentrations in air due to very different chemical properties. Also, testing on 6/1/2020 discussed later shows flaws in the condensate collection system.

Table 12 - Comparison of condensate testing mass ratios versus stack testing

Ratio	FTIR Mass Ratio	Condensate Mass Ratio*
Acetic Acid/Methanol	0.19	0.35
Formic Acid/Methanol	0.07	0.06
Methanol/Methanol	1.00	1.00
Formaldehyde/Methanol	0.29	0.49

* - Excludes 6/1/2020 condensate sampling.

Initial sampling and attempts to tentatively identify organic compounds via mass spectroscopy yielded only the presence of phenol, xylene, furfural, and α-pinene. α-pinene concentrations ranged from 4 mg/L to 170 mg/L when tested at the NCASI laboratory. This could be a function of the NCASI laboratory's limitations in testing capabilities during pandemic conditions or the chemicals not condensing in quantifiable concentrations due to warmer ambient temperatures in the warmer months.

Testing was conducted on June 1, 2020 and showed a potential flaw in using condensate as a surrogate for source testing. Acetic acid was 109 mg/L and formic acid was tested to be 34.6 mg/L while formaldehyde was extremely low at 3.66 mg/L. Both acids are soluble in water without limit and the process temperature is much lower than the boiling point of these two acids so the acids were accumulating in the collection system and potentially preventing formaldehyde from accumulating at expected air:liquid equilibrium concentrations with the air. This shows the importance of ensuring the purge is continuously flowing and not stagnating in the process flow.

E. *Comparison of Historical Methods with Modern Testing Methods*

US EPA provides an addendum table compiling test methods used to derive emission factors called the AP-42 detailed data tables. Two outdated methods were utilized for speciated VOC testing in Table 10: CARB Method 430 (formaldehyde) and US EPA Method 0011. A third method was also used in Table 10: NCASI impinger/canister method (NICM). Analysis of the CARB Method 430 and EPA Method 0011 have found that there was significant potential for interference from reactions occurring between compounds and the Dinitrophenylhydrazine used in the collection train (NCASI, 1992). NICM is the NCASI impinger/canister method and this method has been shown to have relatively high spike recovery between 80 to 120% (NCASI, 1992). The NICM uses a water filled impinger to capture water soluble compounds and a cannister to capture less soluble compounds. This method allowed for detection of low concentrations of water soluble acetaldehyde, phenol, and acetone and high molecular weight insoluble compounds limonene and camphene. However, the data from the NICM method is mixed with the CARB 430 and Method 0011 results.

F. *FID/US EPA Method 25A Accuracy or potential field errors*

There is a potential for sampling error using EPA Method 25A and EPA Method 18 that resulted in unexpectedly high Method 18 results and unexpectedly low Method 25A results. A poor seal on the sampling train for Method 25A could have resulted in excessive collection of fresh air and dilution of the process exhaust. This may explain the relatively low carbon emissions from the flame ionization detector compared to the Method 18 results. The Method 18 sample train could have collected fiber or some other particulate when analyzed, resulting in abnormally high pinene results. Alternately, the chromatography sample preparation and measurement could have calculation or methodology errors because the chromatography is conducted offsite not in parallel with the active sampling methods like Method 320 and Method 25A.

V. Conclusions

The emphasis on testing volatile organics in the wood products industry since the implementation of 1990 Clean Air Act amendments has been focused primarily on the original 187 hazardous air pollutants and the non speciated total hydrocarbons test EPA Method 25A. Formaldehyde and methanol emissions are documented in US EPA's AP-42 emissions for a wide range of wood products emission sources because these are target compounds in the plywood and composite wood products NESHAP. However, there are other State regulated organic compounds emitted from these processes that have not been as well documented including fatty acids and terpenes.

Acetic acid and formic acid were found to make up 10% of the volatile organic emissions from the medium density fiberboard process emissions. Any medium density fiberboard plants constructed in States with acetic acid or formic acid air toxics standards would need to account for these emissions in their compliance demonstrations. North Carolina, for example, maintains an acetic acid air quality standard but does not have a formic acid air quality standard. A wood products facility emitting acetic acid in North Carolina would need to evaluate compliance against the State's ambient air quality standard for acetic acid because acetic acid is not specifically addressed in the wood products NESHAP (Quality, 2018).

Beyond increasing knowledge of speciated compounds, there are regulatory implications related to accurately accounting for total VOC emissions in the Prevention of Significant Deterioration Program. The use of the flame ionization detection EPA Method 25A might be a misleading surrogate for total VOC emissions, as suggested by the results of this project. Using Method 25A source tests as the sole source of VOC estimates could potentially mislead an industrial source or regulators during permitting and compliance demonstrations. In the case of this study, Method 25A underestimated total speciated VOC emissions from the North Carolina medium density fiberboard process by almost 75%. US EPA's 2007 interim guidance for calculating wood products' VOC emissions takes into account formaldehyde's zero response in Method 25A but would similarly still underestimate total VOC emissions by 45%.

These VOC estimations and species accounting need to be as accurate as possible in order to appropriately permit, model, and control sources, which ultimately better protects the public and environment.

V. Appendix

Table A.1 – Selected Chemicals Properties			
Organic Compound	Mol. Wt g/mol	B.P. °F	Log K_{ow}
Acetaldehyde	44.1	69.0	-0.34
Acetic Acid	60.0	244.0	-0.17
Acetone	58.1	133.0	-0.24
Acrolein	56.1	126.0	-0.01
Alpha-pinene	136.0	313.2	4.83
Beta-pinene	136.0	329.0	4.16
Camphene	136.2	318.2	4.22
Ethanol	46.1	173.1	-0.31
Formaldehyde	30.0	-6.0	0.35
Formic Acid	46.0	213.3	-0.54
Furfural	96.1	323.1	0.41
Limonene	136.2	348.8	4.57
Methane	16.0	-258.0	1.09
Methanol	32.0	148.3	-0.77
Phenol	94.1	359.1	1.46
p-Xylene	106.2	280.9	3.15

Table A.2 – State air toxics standards in States with fiberboard processes	
State	Air Toxics Standard
Arkansas	ADEQ Non-Criteria Pollutant Control Strategy
Georgia	Toxic Impact Assessment Guideline
Louisiana	LAC 33:III Chapter 51
Michigan	R 336.1224-1225 Air Toxics Evaluations
Minnesota	Ambient Air Toxicity Values
Mississippi	N/A
Missouri	N/A
Montana	N/A
North Carolina	**15A NCAC 02D.1100 Control of Toxic Air Pollutants***
Oklahoma	252:100-42 Control of Toxic Air Contaminants
Oregon	OAR 340-246 Oregon State Air Toxics Program
Pennsylvania	N/A
South Carolina	61-62.5 Standard No. 8 Toxic Air Pollutants
West Virginia	45 CSR 27 Air Toxics Best Available Technology
Virginia	9VAC5-60 Hazardous Air Pollutant Sources

Note* - the project is based in North Carolina

State	Table A.3 - Example Formaldehyde Fence-line Standards in µg/m³				
	<1-Hour	1-Hour	8-Hour	24-Hour	Annual
Arkansas			14.74		
Georgia	245 (15 min)				0.77
Louisiana			3.2		
Michigan				30	0.8 | 0.08
Minnesota		94			2 | 9
North Carolina		**0.15**			
Oklahoma				8	
Oregon					3
South Carolina				15	
Virginia		62.5			2.4

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