

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS' EMISSIONS FROM WOOD PROCESSING

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ABSTRACT

Volatile organic compounds (VOCs) have received a great deal of attention due to their high abundance during the drying process of wood particles. This is a potential environmental issue due to being low level ozone precursors. This work aimed to study the emissions of VOCs during drying in the particleboard manufacturing process. In this study, wood particles were dry and VOCs were collected using a sorption tube. The VOCs were analyzed with gas chromatography-mass spectrometry to explore the effect of temperature on the composition of main components. The results indicated that α -pinene and D-limonene were the dominant components. The results also indicated that using natural gas or wood dust as a heat source did not have a major impact on the emission characteristics of VOCs.

KEYWORDS: Wood particle board, drying, emission, volatile organic compound.

INTRODUCTION

Global production of all major wood products is steadily growing. Softwoods are more homogenous than hardwoods, and are preferred in particleboard production due to their advantageous physical and technical properties (Paczkowski et al. 2013) and cost. However, softwoods have disadvantages in terms of their high emission of VOCs (Englund and Nussbaum 2000, Banerjee 2001, Granström 2003). Much research on wood processing waste during recent decades has focused mainly on the emissions. In the last decade, extensive research has been conducted in this area and there is now a good understanding of the problem (Johansson

et al. 2004, Granström 2009, Dahlen et al. 2011, Roffael et al. 2015, Huang et al. 2016). A wide spectrum of sources can contribute to the emission of VOCs. Wood has a heterogeneous structure and many other properties affect the drying process. There are many factors that affect the release of VOCs from the drying of wood: species, location, dimension, time of harvest, storage time, temperature, drying medium, and moisture content (Becker and Mehlhorn 1995, Granström 2009, Dahlen et al. 2011, Roffael et al. 2015, Huang et al. 2016). The VOCs can be released from wood products through different thermo-chemical processes and also can be formed from native wood. Softwoods, like pine and spruce, usually contain a high extractive content including mainly monoterpene and diterpene compounds that are predominate in the emission of VOCs (Roffael et al. 2015). Hardwoods, like beech, birch, and poplar, contain almost no emittable terpene compounds (Poblete and Roffael 1985, Risholm-Sundman et al. 1998). The released compounds at normal drying temperatures are volatile extractive compounds, mainly terpenes, carboxylic acids, aldehydes, and alcohols (Johansson et al. 2004). Aldehydes and carbon monoxide formation are the results of thermal degradation of wood (Svedberg et al. 2004). Terpenes are highly reactive in the atmosphere and may contribute to the formation of ground level ozone (Wimmerstedt 1995).

The aim of this study is to determine the composition and concentration of VOCs in emissions from the drying of aspen and spruce wood chips. It is also important to determine if the drying media has any effect on the total amount of VOCs emissions from the drying process.

MATERIAL AND METHODS

Material

In this study, VOC emissions from a wood chip dryer at a particleboard factory in Europe were analyzed. To produce the particleboards, the factory where emissions were tested uses aspen and spruce wood chips that are produced either on site by milling roundwood or supplied directly by wood mills located in the vicinity of the factory. Emissions from the wood chip dryer are first directed to a wet electrostatic precipitator for removal of dust and partial removal of mainly hydrophilic VOCs, before being released to the atmosphere.

Sampling

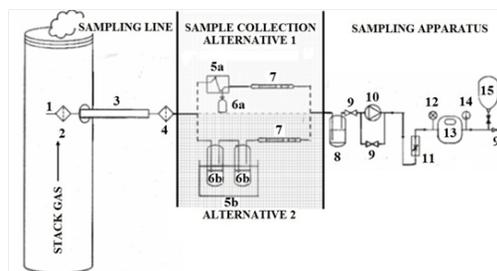


Fig. 1. Schematic diagram of non-isokinetic sampling.

The sampling probe (1) from a suitable corrosion-resistant material (stainless steel), the filter (2) from inert material (ceramic or metal) with appropriate pore size, the heated sampling line (3; the sampling line temperature must be higher than the temperature of flue gas in the chimney to prevent effluent condensation), and the filter inert material (4; ceramic or metal) with appropriate pore size (Fig. 1).

Sample collection (alternative 2)

The sampling cooler (5b) is used to separate water vapor from the flue gas before the gases enter into the sample collector (7). The dew-point temperature of 5°C shall not be exceeded, the cooler flask is (6b) for capturing condensable compounds from effluent, the sorption tubes (7; 6 mm diameter) are filled with appropriate sorbent (TENAX), to collect VOC, drying tower (8) filled with silica gel, the flow regulator (9) and control, pump (10), flow meter (11; the sampling rate of about 500 mL·min⁻¹, sampling period is 30 min), the temperature sensor (12), gas meter (13), and pressure gauge (14; vacuum meter).

Tab. 1: Conditions of sampling and of collections onto sorption tube source of emissions- wood dust was used as a fuel.

Sampling	Sample 1		Sample 2		Sample 3	
Tube	1	2	3	4	5	6
Tube number	196409	196410	196407	196408	196405	196406
Temperature of gas (°C)	128	128	130	127	133	132
Gas velocity (m·s ⁻¹)	24.7	24.7	24.7	24.7	24.7	24.7
Gas flow (m ³ ·h ⁻¹)	157055	157055	157055	157055	157055	157055
Sampling parameters						
Gas temperature (°C)	7	7	7	7	7	7
Gas flow (L·min ⁻¹)	0.5	0.5	0.5	0.5	0.5	0.5
Sampling time (min)	30	30	30	30	30	30
Gas volume (m ³)	0.015	0.015	0.015	0.015	0.015	0.015

Tab. 2: Conditions of sampling and of collections onto sorption tubes source of emissions- natural gas was used as a fuel.

Sampling	Sample 4		Sample 5	
Tube	7	8	9	10
Tube number	196404	196403	196402	196401
Temperature of gas (°C)	130	128	132	130
Gas velocity (m·s ⁻¹)	24.7	24.7	24.7	24.7
Gas flow (m ³ ·h ⁻¹)	157055	157055	157055	157055
Sampling parameters				
Gas temperature (°C)	7	7	7	7
Gas flow (L·min ⁻¹)	1	1	1	1
Sampling time (min)	20	20	20	20
Gas volume (m ³)	0.020	0.020	0.020	0.020

Thermal desorption (TD) and gas chromatography (GC)/mass spectrometry (MS) analyses Sorbent tubes (filled with Tenax TA/Carbograph) were thermally desorbed by a thermal desorption unit (Unity 2, Markes International Ltd., Pontyclun, UK) coupled to a gas chromatograph (7890A gas chromatograph Agilent Technologies, Wilmington, USA) and to a mass spectrometer detector (MSD; 5975C, Agilent Technologies, Wilmington, USA). Thermal desorption of sorbent tubes was performed in a two-step mode. In the first step, the collected compounds were desorbed from sorbent tubes for 2 min at 250°C with a flow rate of 20 mL·min⁻¹ of He, carried through a 100 mg Tenax™ TA cryogenic internal trap, and cooled at -10°C. Thereafter, in the second step, the trap was desorbed at 300°C for 1.5 min with fast heating (900°C·min⁻¹).

The GC/MS analysis was made on a 30 m × 250 μm × 0.25 μm internal diameter fused silica capillary column HP-5MS (Agilent Technologies, Wilmington, USA). The temperature program was as follows: 40°C for 2 min; 300°C at a rate of 20°C·min⁻¹; and final hold for 5 min. The injector temperature was 250°C and splitless mode was used. Helium was used as the carrier gas with a flow of 1.2 mL·min⁻¹. The end of the column was introduced into the ion source of the mass selective detector (MSD) operated in electron impact ionization (70 eV) mode. The data acquisition system used was Agilent MSD ChemStation software (E.02.02.1431, Wilmington, USA).

Qualitative and quantitative analysis

In the qualitative analysis by mass spectrometry, individual VOC compounds were identified by comparing the obtained mass spectra with the spectra stored at the National Institute of Standards and Technology (NIST) and Wiley libraries. The quantitative analysis of VOC emitted from the examined samples was carried out by using the method of addition of octadecane as an internal standard.

RESULTS AND DISCUSSION

Analyses of the amount of emitted VOCs can be affected by the method of collection of compounds. Furthermore, if the test material is too small, some emissions will be lower than the detection limit. Additionally, some compounds, such as formic, acetic, and oxalic acid, methanol, and ethanol, are polar compounds and soluble in water. According to different publications, these compounds are emitted during the drying of wood (Risholm-Sundman et al. 1998, McDonald et al. 2004). Most of these identified compounds can also be found in the extracts of untreated wood sources such as bark (Jablonsky et al. 2017). Qualitative and quantitative analysis of VOCs in five different samples collected from the outlet of the wet electrostatic precipitator were performed.

Samplings (1 through 3) were carried out in the conditions where wood dust was used as a fuel to produce hot air for drying of wood chips. Other samplings (4 and 5) were carried out in the conditions where natural gas was used as a fuel.

In the first three samples 129 (sample 1), 140 (sample 2), and 156 (sample 3) different volatile organic compounds were identified. In the next two samplings, 155 (sampling 4) and 109 (sampling 5) volatile compounds were identified.

The concentration of total VOCs was in the range from 20,473 μg·m⁻³ to 60,471.5 μg·m⁻³. In order of samplings 1 to 5, the concentrations of total VOCs were as follows: 20,473 μg·m⁻³, 60,471.5 μg·m⁻³, 24,113.3 μg·m⁻³, 40,053.3 μg·m⁻³, and 54,601.2 μg·m⁻³. These measurements describe the real state of generated VOCs during the drying process. The range of identified compounds (109 to 156) cannot clearly describe the influence of the drying medium. The VOCs constituted the largest proportion of emissions from the treated samples via different type of drying medium such as wood dust and natural gas (Tabs. 3 and 4).

Tab. 3: Analysis of major volatile organic compounds (sources of emissions in dryer – wood dust used as fuel).

Sample 1		Sample 2		Sample 3	
Compound	Amount ($\mu\text{g m}^{-3}$)*	Compound	Amount ($\mu\text{g m}^{-3}$)*	Compound	Amount ($\mu\text{g m}^{-3}$)*
α -Pinene	2657.4	α -Pinene	4697.9	α -Pinene	3003.3
β -Pinene	1688.3	D-Limonene	2822.1	D-Limonene	1962.4
D-Limonene	1485.6	β -Pinene	2795.6	laevo- β -Pinene	1917.2
α -Pinene, (D)-	1231.4	Thunbergol	2150.3	α -Pinene, (D)-	1700.0
Cembrene	962.0	3-Carene	2111.2	m-Ethyltoluene	515.1
Toluene	772.0	Manool oxide	1501.0	Longifolene	478.5
Thunbergol	682.2	α -Terpineol	1449.3	Thunbergol	439.8
Camphene	646.9	δ -Cadinene	1376.6	β -Myrcene	394.3
Longifolene	625.1	Toluene	1338.7	α -Terpinolene	380.8
δ -Cadinene	593.2	Camphene	1193.6	Camphene	369.6
α -Terpinolene	530.8	α -Muuroolene	1168.5	Epizonarene	350.1
α -Curcumene	527.2	Pimarinal	1126.7	Acetone	317.6
α -Muuroolene	483.0	Longifolene	1120.7	1,3,5,7-Tetramethyl-adamantane	276.0
Manool oxide	429.7	2-Methyl-3-phenyl-propanal	969.9	Toluene	263.2
1,5,9-Cyclotetradecatriene, 1,5,9-trimethyl-12-(1-methylethenyl)-	424.7	α -Curcumene	931.9	α -Bergamotene	221.2
(+)-4-Carene	400.2	1,5,9-Cyclotetradecatriene, 1,5,9-trimethyl-12-(1-methylethenyl)-	886.5	α -Longipinene	205.1
Epizonarene	396.8	L- α -Terpineol	869.3	Bornyl acetate	200.4
p-Xylene	360.6	β -Panasinsene	867.6	Cyclofenchene	185.3
Benzaldehyde	356	α -Terpinolene	863.8	Acetophenone	168.9
α -Bergamotene	290.8	Cembrene	847.4	L- α -Terpineol	164.6
Pimarinal	269.5	p-Xylene	817.1	δ -Muuroolene	160.2
δ -Muuroolene	257.6	Hexanal	803.9	δ -Cadinene	140.8
Terpinen-4-ol	237.9	.tau.-Muurolol	797.6	α -Muuroolene	138.9
α -Amorphene	223.8	Benzaldehyde	768.5	Nonanal	135.2

*in wet conditions

Tab. 4: Analysis of major volatile organic compounds (sources of emissions in dryer- natural gas used as fuel).

Sample 4		Sample 5	
Compound	Amount ($\mu\text{g m}^{-3}$)*	Compound	Amount ($\mu\text{g m}^{-3}$)*
Thunbergol	2209.0	α -Pinene	6386.2
α -Pinene	2033.3	α -Pinene, (D)-	5771.0
D-Limonene	1431.9	D-Limonene	5768.4
β -Pinene	1372.8	β -Pinene	4079.8
trans-Geranylgeraniol	1233.0	β -Myrcene	2237.1
α -Pinene, (D)-	1149.4	p-Cymene	1563.5
Pimarinal	1113.1	α -Terpineol	1538.9
Cembrene	1102.2	Cyclohexene, 4-methyl-3-(1-methylethylidene)-	1331.9
Methyl dehydroabietate	984.7	Toluene	1316.4

α -Muurolene	968.4	Cyclopentene, 3-isopropenyl-5,5-dimethyl-	1191.9
δ -Cadinene	866.1	Longifolene	1177.2
Manool oxide	814.4	Benzaldehyde	1165.8
Longifolene	782.5	2,4,6-Octatriene, 3,4-dimethyl-	1164.1
L- α -Terpineol	737.8	p-Xylene	1140.3
α -Curcumene	603.1	Hexanal	1043.1
α -Cadinol	564.4	Allo-Ocimene	820.2
Dehydroabietal	551.0	(-)-4-Terpineol	798.0
Alloaromadendrene oxide-(1)	533.9	4-Methylbenzaldehyde	765.9
α -Amorphene	513.7	α -Elemene	666.3
β -Panasinene	453.4	α -Muurolene	624.0
Benzocyclododecene, 2,3-diethyl-4a,5,6,7,8,9,10,11,12,13-decahydro-	449.7	δ -Muurolene	558.2
1-Phenanthrenemethanol, 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-, [1S-(1.alpha.,4a.alpha.,10a.beta.)]-	435.7	2-Carene	543.1
β -Cubebene	421.5	Bornyl acetate	493.5
Camphene	416.4	endo-Borneol	487.0

*in wet conditions

The major compounds identified were α -Pinene, β -Pinene, D-Limonene, α -Pinene, (D)-Cembrene, Toluene, Thunbergol, Camphene, Longifolene, δ -Cadinene, α -Terpinolene, α -Curcumene, α -Muurolene, and Manool oxide. Other compounds, including aromatic hydrocarbon, alkenes, and esters, were identified. In the work Yazar et al. (2011), carcinogenic air pollutants, such as toluene, cymene, benzene and xylene, have also been detected in very low amounts. Huang et al. (2016) detected the largest proportion of VOC emissions from the treated bamboo terpene compounds such as cedr-8-ene, α -copaene, β -cedrene, D-limonene, cis-thujopsene, longifolene, α -pinene, β -myrcene, and γ -muurolene. Sesquiterpenes, such as α -cedrene, α -copaene, β -cedrene, cis-thujopsene, and longifolene, accounted for the largest proportion of terpenes, while the monoterpenes, including D-limonene, α -pinene, and β -myrcene, were minimally represented.

These results are consistent with the authors' results, in which mainly terpenes were identified. A study on monoterpene emissions showed their dominance during the heat-treatment of wood (Milota 2000, Banerjee 2001).

For eucalyptus wood, which was treated by heat, similar results were found. Johansson et al. (2004) and Granström (2009) found that during the drying processes initial terpenes of 80% to 90% are released.

Up to 50% of the original terpene content is removed in a very short time after contact with the drying medium (Johansson et al. 2004). It was confirmed in other scientific papers that with rising temperature, the content of VOCs also increased. Granström (2003) observed that the relative amount of less volatile monoterpenes increased with drying medium temperature (140°C, 170°C, and 200°C). In contrast, Huang et al. (2016) noted that the influence of rising temperature in range of 150 °C, 180 °C, and 210 °C does not have an obvious effect on the amount of released VOCs. The papers showed no influence of exposition time (1 h, 2 h, and 3 h) for released quantity of VOCs. These results showed that the quantity of VOCs depended mostly on the type of drying material.

The release of VOCs during the drying of wood feedstocks is a potential environmental problem. In particleboard production, the drying process is the dominant source of VOC emissions. These VOCs may contribute to air pollution or eutrophication (Rupar and Sanati 2003). Detailed information about the emissions of volatile hydrocarbons is important because different hydrocarbons have different toxicological properties (Granström 2003). The knowledge relating to the nature of the substances emitted during the drying of the feedstock of biomass such as wood, wood dust, and particleboard, is necessary to assess environmental and health effects. In some works, the amount of VOCs emitted affects the drying medium, drying, and other parameters (Becker and Mehlhorn 1995, Rupar and Sanati 2003, Granström 2009, Dahlen et al. 2011, Roffael et al. 2015, Huang et al. 2016).

In cases when hot air or steam was used as a drying medium, it was shown that the medium has an impact on the change of distribution between different group of terpenes compounds according to the used drying procedures (Rupar and Sanati 2003). The feedstock of biomass emitted different concentrations of VOCs even at low temperature, because it is the natural property of this material. Thus, it was clear that during the drying process VOCs will always be released from any wooden material.

In the authors' experiments (heating medium temperature of 127°C to 133°C), no obvious effect of the drying medium type on the formation of the major identified substances and their quantity was identified.

CONCLUSIONS

The results of the authors' experiments showed that the combination of TD with GC/MS was the best suitable method for the determination of volatile compounds emitted during the drying of wood material for production of particleboard. In total, 156 different volatile organic compounds were identified in 5 different sampling conditions. The major volatile compounds found in the emissions were: α -Pinene, β -Pinene, D-Limonene, α -Pinene, (D)-Cembrene, Thunbergol, Camphene, Longifolene, δ -Cadinene, α -Terpinolene, α -Curcumene, α -Muurolene, etc. (Tabs. 3 and 4). These compounds are of natural origin and were not formed in the technological process of drying in the production of particle boards. The amount and the composition of released VOCs did not depend on the fuel typically used to produce hot air as drying medium, i.e. natural gas or wood dust.

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