

Review



# **Emissions of Volatile Organic Compounds (VOCs) as Safety Indicators in the Development of Wood-Based Binderless Boards**

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Abstract: Wood-based panels are ubiquitous in our daily lives, both as building materials and as furnishing materials. Numerous studies have revealed that these materials emit volatile organic compounds, such as formaldehyde, into indoor air, which can be harmful to human health. These volatile organic compounds come both from the wood itself, more specifically cellulose, hemicellulose, and lignin, and from the resins used to bind the wood fibers or particles together. Today, new panels bonded with bio-based adhesives and binderless panels are emerging. The aim of this article is to highlight the importance of measuring VOC emissions from binderless wood-based panels, and more specifically, to identify the VOCs, originating from the wood and thermal transformation processes, likely to be emitted during the production of such panels, as well as how to sample them and measure their emissions. This work provides a useful approach to identifying and quantifying VOC emissions from these new materials. These methodologies should be applied more widely to gain knowledge about VOCs, which are relevant indicators for the development of environmentally friendly materials.

**Keywords:** lignocellulosic material; pollutants; volatile organic compounds; wood-based composites; sustainable materials; free formaldehyde



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# 1. Introduction

The wood industry is a major worldwide industry. The global forest products trade was estimated in 2020 by the Food and Agriculture Organization of the United Nations [1] and represented over USD 234 billion in imports and over USD 226 billion in exports. Forest products englobes roundwood; wood charcoal, chips and particles, residues, pellets, and other agglomerates; sawnwood and veneer sheets; wood-based panels; pulp and recovered paper; and paper and paperboard. In 20 years, wood-based board global production increased from 178 million of m<sup>3</sup> in 2001 to 396 million of m<sup>3</sup> in 2021 [2], for use in various sectors such as construction and furniture, depending on the board characteristics. As the panels are manufactured from different wood species, in various sizes and shapes, bonded with different petrochemical binders and using diverse manufacturing processes, they have different specificities, particularly in terms of mechanical strength and hydrophobicity [3–5].

These wood-based panels are more than ever present in our homes, workplaces, or schools, yet building and furnishing materials including wood-based panels have been found to emit volatile organic compounds (VOCs) [6]. Emissions of these VOCs depend on environmental factors, such as temperature or humidity [7–10], but also on factors intrinsic to the boards themselves [11–13]. Some VOCs have been classified as carcinogenic, genotoxic, and reprotoxic molecules, in particular formaldehyde [14]. The nature and quantity of VOCs emitted from wood-based boards can originate, among other things, from the petrochemical binders used in the process of production to bond particles or fibers together.

Over the last decades, numerous studies have been carried out to replace these petroleum-based binders with biobased binders [15–17] or even to produce binderless

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boards, based on the self-adhesive properties of the various raw materials used, due to their chemical composition [18–21]. These boards show great promise, particularly in terms of mechanical properties. To be able to replace existing industrial boards, biobased and binderless boards need to offer similar or even higher mechanical resistance, as well as complying with VOC emission standards.

This paper aims to highlight the importance to measure the VOC emissions of woodbased binderless boards and specifically to identify the VOC from wood and thermal transformation processes that are likely to be emitted during the production of such wood panels, as well as how to sample them and measure their emissions.

## 2. Wood and Its Pectocellulosic Cell Wall Organization

Lignocellulosic materials such as wood are complex materials, composed of a variety of cells with very different functions. All these cells have in common a pectocellulosic wall, composed mainly of cellulose, hemicelluloses, lignin, and pectins, organized to protect the cell [22].

*Cellulose* is a homopolymer of  $\beta$ -D-glucopyranose units, linked by  $\beta$ -(1-4) glycosidic bonds [23–27]. It is thus formed by long linear chains that can reach a degree of polymerization of 15,000 [24,28]. As each unit has alcohol functions, the linear chains come together through hydrogen bonds and Van der Waals forces to form cellulose microfibrils [25,29–31]. When the microfibrils are perfectly ordered, they are referred to as crystalline cellulose or non-accessible cellulose [23–25,29]. The cellulose microfibrils can then combine to form a cellulose fiber or macrofibril. The cellulose, arranged in microfibrils and macrofibrils, thus provides mechanical strength to the cell wall, enabling the plant to expand in height [28,29].

*Hemicelluloses* are heteropolymers of pentoses (xylose and arabinose), hexoses (mannose, glucose, and galactose) and acid oses (uronic acids), linked by  $\beta$ -(1-4) osidic bonds, with degrees of polymerization ranging from 100 to 300 [23,24,32]. There are four types of hemicelluloses [33]:

- Xyloglucans: backbone of β-(1-4)-linked glucoses, with branches of xylose, galactose, and fucose;
- Glucuronoxylans and glucuronoarabinoxylans: skeleton of xyloses linked by β-(1-4) bonds, with glucuronic acid and arabinose branches;
- Mannans and glucomannans: skeleton made up entirely of mannose (for mannans and galactomannans) or glucose and mannose (for mannans and galactoglucomannans), linked by β-(1-4) bonds;
- $\beta$ -(1-3,1-4)-glucans: backbone of glucoses linked by  $\beta$ -(1-3) or  $\beta$ -(1-4).

The type of hemicelluloses and their quantities depend on the organism studied. In fact, xyloglucans are found in greater quantities in the primary cell walls of plants, particularly hardwoods. Glucuronoxylans are mainly found in the secondary cell walls of hardwoods. As for galactoglucomannans, they are mostly found in the secondary walls of softwood [33]. Hemicelluloses bind to cellulose microfibrils via hydrogen bonds. They thus play a bridging role between cellulose microfibrils, but also with other wall components. Hemicelluloses also bind to lignin via covalent bonds. In this way, hemicelluloses reinforce the cell wall [23,24,28,33].

*Lignin* is an amorphous, three-dimensional heteropolymer made up of three monomers called monolignols (phenylpropanoids): *p*-coumaryl alcohol (H unit), coniferyl alcohol (G unit), and sinapyl alcohol (S unit) [24,25,34,35]. Each unit is found in different quantities depending on the plant type: hardwood lignin is predominantly composed of S and G units, while softwood lignin is predominantly constituted of G units. All these monolignols are linked together by various ether bonds of different strengths [35]. Lignin therefore has a highly complex structure. Lignin gives cells rigidity, enabling woody plants to grow vertically. Lignin also helps protect cells from microbial and fungal attack by rendering wall polysaccharides inaccessible [36,37].

*Pectins* are polysaccharides found mainly in the middle lamella and primary wall. There are different types of pectin [38,39]:

- Homogalacturonans: linear chains of uronic acids linked by  $\alpha$ -(1-4) bonds, which account for around 65% of pectin. The homogalacturonans are often methylated and sometimes acetylated.
- Rhamnogalacturonans I: homogalacturonan and rhamnose skeletons, with arabinose and galactose branches on the rhamnose units. The uronic acid units of the backbone can be methylated and sometimes acetylated. Rhamnogalacturonanes I account for between 20 and 35% of pectin.
- Rhamnogalacturonans II: branched homogalacturonan skeletons with more than 12 types of sugar and 20 different types of bonds. The rhamnogalacturonans II account for around 10% of pectin.
- Xylogalacturonans: homogalacturonan skeletons with some branches of  $\beta$ -(O-3)-xylose.

The non-methylated units of homogalacturonans are negatively charged and can interact with calcium Ca<sup>2+</sup> to form a gel. A hypothetical structure called the "egg box" represents the compaction of homogalacturonans that occurs during Ca<sup>2+</sup>-induced gelation. This phenomenon accounts for 70% of the pectic gel in pectocellulosic walls [29,38]. The different types of pectin are thought to be linked by covalent bonds between their skeletons. Pectins are also linked to other wall polysaccharides, such as xyloglucans or xylans, by covalent bonds [38,39]. Thanks to these interactions, pectins contribute to the mechanical strength (non-methylated homogalacturonan blocks linked by ionic bonds with calcium), adhesion, and rigidity of the pectocellulose wall [38].

Cellulose, hemicelluloses, lignin, and pectins thus form a complex network of molecules protecting the plant cell and providing the rigidity and flexibility required for the development of lignocellulosic material.

## 3. Wood-Based Composite Boards

Numerous wood-based boards exist. They are characterized by their manufacturing process; the nature, size, and geometry of the raw material; and the presence or not of a binder, and if so, the nature of the binder.

#### 3.1. Wood-Based Boards Containing a Binder

The rising price of wood during the 20th century led manufacturers to develop new materials, less expensive but with the same or even better characteristics of solid wood. This is how wood-based panels emerged.

Different varieties of wood-based panels were then developed with different properties depending on their composition. Figure 1 shows the variety of wood-based industrial composite panels that exist, as well as their manufacturing processes. Wood can be simply ground to produce boards from particles, or it can undergo a thermomechanical process to preserve longer fibers. Wood-based boards that are currently on the market can be divided into three groups: fiberboard, particleboard, and veneer panels.

## 3.1.1. Different Types of Industrial Wood-Based Boards

Fiberboards are made from wood fibers using a thermomechanical process. Fiberboards are produced by adding a synthetic binder to fibers, followed by a thermocompression process involving heat and pressure. There are different types of fiberboards, depending not only on the process used but also on the final density of the board, ranging from a few hundred kg m<sup>-3</sup> to over 800 kg m<sup>-3</sup> [40]. Among fiberboards, the following are particularly worthy of mention medium density fiberboard (MDF), hard density fiberboard (HDF), or hardboard (HB), most of which are used in furniture.

The particleboard group includes panels made from wood ground into a variety of grain sizes and geometries. Particles can range from a few millimeters (particleboard in particular) to tens of centimeters (for the oriented strand board or OSB) [40]. Like fiberboards, particleboards are manufactured by thermocompression, with the addition of a petrochemical binder. These panels are used in furniture and construction.



Figure 1. Variety of wood-based boards (adapted from [40]).

Finally, the last group of wood-based panels is called veneer panels. These boards have the distinctive feature of being manufactured from solid wood, which can be either thin layers of wood or planks. Wood can be glued in a variety of ways, depending on the intended application and therefore on mechanical requirements (in case of a use in construction) or aesthetics (for furnishings). Plywood panels, glued laminated panels, or laminated veneer lumber boards (LVL) are used in construction, as their particular structure (gluing sheets together) gives them high mechanical strength at lower cost than solid wood. Finger-jointed panels, on the other hand, as their name implies, are glued at the edge of the panel. The aesthetics of solid wood are conserved, and these boards are used for furnishings.

Panels made from reconstituted wood (MDF or particleboard) and intended for furniture use can then be laminated (i.e., covered with a wood veneer to give them the appearance of solid wood) or laminated (covered with a layer of plastic of a certain color) for aesthetic purposes. These boards account for the majority of wooden furniture on the market today.

All these boards are bonded with an adhesive system. Numerous binders have been developed to respond to the diverse characteristics expected of the panels, but also for economic reasons. Numerous synthetic petrochemical binders are used in panel manufacturing today, classified into two categories: thermosetting binders and thermoplastic binders (Table 1).

Categories	Resin Type	Typical Adhesive System
	Amino	Urea-formaldehyde (UF) Melamine-formaldehyde (MF) Melamine-urea-formaldehyde (MUF)
Thermosetting	Phenolic	Phenol-formaldehyde (PF) Resorcinol-formaldehyde (RF) Phenol-resorcinol-formaldehyde (PRF)
	Isocyanate	Diphenylmethane-4,4'-diisocyanate (pMDI)
Thermoplastic	Vinyl	Polyvinyl acetate (PVAC) Polyvinyl alcohol (PVA)

 Table 1. Wood-based panel adhesives.

#### 3.1.2. Development of New Panels with Biobased Binders

A considerable amount of research has been carried out to develop boards with non-petrochemical binders. New bio-based binders have emerged from tannins [41], lignin [18,19,42], proteins [43–46], carbohydrates [47], or unsaturated oils [48].

These new binders will not be developed further in this paper, since numerous reviews have already covered the subject [21,49–54].

#### 3.2. Wood-Based Binderless Boards

In order to replace binders derived from the petroleum industry, another solution today is to produce panels without any binder (binderless boards) by activating the intrinsic adhesive properties of the lignocellulosic raw material. By applying heat and/or pressure, the components of the raw material are transformed and create bonds. Various reviews have already reported on the characteristics of binderless panel production, mentioning the various raw materials used, as well as the processing and self-adhesion mechanisms [55–60]

#### 3.2.1. Self-Adhesion Mecanisms for Wood-Based Binderless Boards

Binderless panels can be made from lignocellulosic materials, since these have intrinsic adhesive properties that can be activated when certain components are subjected to elevated temperature or pressure. Several reactions such as hydrolysis, dehydration and thermal oxidation have been observed [55,58]. Hemicelluloses have lower temperature stability unlike cellulose and lignin, so hemicelluloses are the first components of the lignocellulosic material modified during the panel-forming process, releasing compounds such as organic acids and acetone [61]. These organic acids, such as acetic acid, will then catalyze degradation reactions of cellulose and hemicelluloses [62], releasing furan compounds from pentoses or hexoses in the hemicellulose. These furan compounds include furfural or hydroxymethylfurfural, which can later recondense or establish new bonds with other compounds during cooling [63].

The compounds released by cellulose and hemicelluloses will then take part in other reactions, notably with lignin. Lignin undergoes plasticization under the effect of heat; its glass transition temperature is exceeded, and it begins to soften [64–66]. The inter-monomer bonds will thus break, making the lignin more condensed on the one hand and, on the other hand, allowing for the creation of bonds with other compounds, such as cellulose and hemicelluloses [63,67,68]. An increase in the number of  $\beta$ -O-4 bonds in lignin was observed by Sun et al. [69].

Thus, as a result of the reactions undergone by the components of lignocellulosic material with an increase in temperature, acidic compounds are released from hemicelluloses, catalyzing the degradation of cellulose and hemicelluloses. The compounds then recondense with each other, forming a natural resin, or form bonds with lignin. Lignin, having undergone plasticization, surrounds the cellulose and hemicelluloses before hardening when the temperature is lowered at the end of the process. This plays an important role in the mechanical properties of the final material. Lignocellulosic materials, thanks to their various components and properties, are therefore perfectly suited to the production of binderless panels.

The parameters of the production process of these binderless boards have an impact on panel properties. It has been demonstrated that increasing the temperature and/or the pressure applied during the process can lead to binderless boards with better mechanical characteristics and water resistance [70,71]. The time of process, the size, shape, quantity, and moisture content of the raw material also influence the properties of the binderless boards produced depending on the raw material [72–75].

## 3.2.2. Some Examples of Wood-Based Binderless Boards

A wide range of lignocellulosic raw materials have been used to produce binderless panels. These raw materials can be divided into two groups: woody raw materials, i.e., wood, and non-woody raw materials. Many non-woody raw materials have been used to manufacture binderless boards, from bagasse [76,77] to kenaf [67,78] or even coconut husk [66,79].

Concerning the wood-based binderless boards, various wood species have been studied, as mentioned in Table 2 for the production of wood-based binderless boards by the compression-cooking process.

Wood Species	Pretreatment	References
Abies alba and Pinus insignis	Steam explosion	[80]
Oil palm trunk	/	[70]
Oil palm trunk	/	[72]
Picea mariana bark	Refining	[81]
Oil palm trunk	/	[82]
Pinus radiata	Fenton reaction	[83]
Aspen	Steam stabilization	[84]
Picea abies and Fagus sylvatica	Fenton reaction	[85]
Populus euramevicana	/	[86]

Table 2. Wood-based binderless boards.

/: no pretreatment.

## 4. Why and How to Measure Volatile Organic Compound Emissions from a Material?

Volatile organic compounds (VOCs) have many definitions, depending on the organizations that publish them and the regulations to which they apply. The World Health Organization (WHO) [87] characterizes VOCs as compounds with boiling points between 50–100 °C and 240–260 °C. Based on this definition, many compounds are included in VOCs, with diverse compositions and structures: aliphatic hydrocarbons (alkanes, alkenes and alkynes), alicyclic hydrocarbons (cyclic hydrocarbons derived from the aliphatic series), aromatic hydrocarbons (including some polycyclic aromatic hydrocarbons), and substituted hydrocarbons (halogens, alcohols, aldehydes, ketones, ethers and esters, acids, amines, amides, and nitriles).

Although there is no universal definition of VOCs, their impacts on human health and on the environment are acknowledged worldwide [88,89]. First, VOCs affect human health with direct and indirect effects. VOCs can be toxic substances at various levels, with some VOCs even classified as carcinogenic, mutagenic, and reprotoxic (CMR), such as formaldehyde or benzene. Furthermore, since VOCs are precursors of ozone in the air, they can lead to an overproduction of ozone, a gas that is itself toxic, causing various symptoms in humans depending on the level of exposure: coughing, shortness of breath, nasal, eye and throat irritation, among others. Ozone can also have harmful effects on vegetation, altering plant resistance to pathogens and accelerating the degradation of certain materials. Moreover, the overproduction of ozone generates an additional greenhouse effect. It should be noted that VOCs can generally be of biogenic or anthropogenic origin. Table 3 presents some VOCs commonly studied.

Table 3. Some	VOCs and some of	their characteristics.
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	Compound	CAS	MW (g mol $^{-1}$ )	Bp (°C) [90,91]	CMR Classification [14]
C <sub>1</sub>	Formaldehyde	50-00-0	30	-19	Carc. 2
C	Acetaldehyde	75-07-0	44	21	Carc. 2
C <sub>2</sub>	Acetic acid	64-19-7	60	118	Carc. 3
	Acetone	67-64-1	58	56	Carc. 3
C	Acrolein	107-02-8	56	52	Carc. 3
$C_3$	Propanal	123-38-6	58	48	Carc. 3
	Tetrachloroethylene	127-18-4	166	121	Carc. 2
C	Butanal	204-646-6	72	75	Carc. 3
$C_4$	2-Butenal	4170-30-3	70	102	Muta. 2
C <sub>5</sub>	Furfural	98-01-1	96	162	Carc. 2
	Benzene	71-43-2	78	80	Carc.1, Muta. 2
C	2-Butoxyethanol	111-76-2	118	170	Carc. 3
$C_6$	1,4-Dichlorobenzene	106-46-7	147	173	Carc. 2
	<i>n</i> -Hexane	110-54-3	86	69	Repr. 2
C-	Benzaldehyde	100-52-7	106	179	Carc. 3
C7	Toluene	108-88-3	92	111	Repr. 2

	Compound	CAS	MW (g mol $^{-1}$ )	Bp (°C) [90,91]	CMR Classification [14]
	Ethylbenzene	100-41-4	106	136	Carc. 3
	Štyrene	100-42-5	104	145	Carc. 3
C	Vanillin	121-33-5	152	285	Carc. 3
$C_8$	<i>m</i> -Xylene	108-38-3	106	139	Carc. 3
	o-Xylene	95-47-6	106	144	Carc. 3
	<i>p</i> -Xylene	106-42-3	106	138	Carc. 3
C	Syringaldehyde	134-96-3	182	192	Carc. 3
<b>C</b> 9	1,2,4-Trimethylbenzene	95-63-6	120	169	Carc. 3
0	Naphtalene	91-20-3	128	218	Carc. 2
$C_{10}$	Sabinene	3387-41-5	136	163	Carc. 3
C <sub>11</sub>	Undecane	1120-21-4	156	196	Carc. 3

## Table 3. Cont.

Bp: boiling point; CMR: carcinogenic, mutagenic, reprotoxic.

#### 4.1. How to Sample and Analyse VOCs

## 4.1.1. VOC Sampling

VOC sampling techniques are diverse. They depend in particular on the matrix being studied, the compounds being sampled, the equipment available, and the cost of the various devices. A distinction is generally made between sampling without preconcentration and sampling with preconcentration [92,93].

Sampling without preconcentration involves isolating a portion of the air in which the compounds to be studied are present, with no selection of compounds. In this way, all the compounds in the matrix are considered in the analysis. This sampling method is known as "whole-air sampling". It can be carried out using

- a bag (made from the following materials: polyvinyl fluoride (tradename: Tedlar), polytetrafluoroethylene and fluorinated ethylene propylene copolymer (tradename: Teflon), polyethyleneterephtalate (tradename: Nalofan), polyvinylidene difluoride (tradename: Altef)...) offering a wide range of volumes (from a few mL to several dozen liters) and being low-cost but fragile;
- a polished stainless-steel canister, reusable, with a range of volumes from a few mL to several dozen liters, but are expensive;
- a glass vial or ampoule, infinitely reusable after cleaning.

The advantage of these collection devices is that several analyses can be carried out on the same sample. However, when sampling "whole air", the humidity of the sample is the same as that of the air and can therefore be high. This can lead to artefacts during analysis. It is therefore important to dehumidify the sample when this type of sampling is carried out. Even et al. [94] highlighted the points that still need to be explored towards the standardization of a suitable procedure, in particular investigations on sorbent combinations and the suitability of chromatography columns. The major challenge is that strong sorbents adsorb water together with very VOCs.

Pre-concentration sampling involves the absorption or adsorption of compounds on a substrate in order to extract them from the air. The choice of sorbent depends on the type of compounds to be studied and the sampling method chosen: passive or dynamic. Sampling is considered to be dynamic if the air is pumped through the collection medium to fix the compounds. Dynamic sampling can be carried out using sorbent(s) contained in a cartridge. A multitude of adsorbents are available: graphitized carbons (Carbograph, Carbotrap, Carbopack) for carbon number C3 to C30, carbon molecular sieves (Carbosieves, Anasorb, Carboxen) for carbon number C1 to C9, and porous organic polymers (Tenax, Porapak, Chromosorb) for carbon number C6 to C26 [94]. As each adsorbent has specific properties, it is essential to study them carefully to select the most appropriate one [94,95]. Adsorbent beds can be built up to extend the range of compounds studied.

In contrast, with passive sampling, there is no movement of the matrix, only the diffusion of analytes comes into play. Passive sampling of analytes can be performed with

- a solid-phase microextraction (SPME) fiber;
- a stir bar sorption extraction system (SBSE);
- a passive dosimeter containing a sorbent, as previously mentioned, with various ge-ometries (Radiello tube, badge G.A.B.I.E, 3M type 3500, PerkinElmer tube).

The choice of sampling method depends on the matrix under study and the sensitivity of the detection equipment. If the detection equipment is sufficiently sensitive, sampling without preconcentration may be sufficient for the sample to be directly analyzed. On the other hand, if matrix is very low concentrated in VOCs, it is preferable to consider a preconcentration step. It may also be possible to sample compounds without preconcentration, then concentrate them a posteriori by sorption (e.g., sampling in a bag and adsorption on SPME fiber).

For some VOCs, it is necessary to go through a derivatization stage before analysis, during sampling. This is particularly the case for certain carbonyl compounds [96]. Derivation consists in grafting a group visible with conventional detection methods onto non-detectable compounds. There are a number of different derivatization methods, as well as various derivatization agents. For carbonyl compounds, 2,4-dinitrophenylhydrazine (DNPH) and O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) are frequently used. If analytes are sampled using a SPME fiber, the derivation can be carried out either in the sampling matrix or directly on the SPME fiber. If the analytes are sampled on an adsorbent cartridge, the derivatization agent is located directly on the cartridge (DNPH-impregnated silica gel cartridges).

There may be artefacts linked to the presence of water or ozone in the sampled atmosphere. Palluau et al. [97] demonstrated that the presence of ozone in samples taken from canisters led to a decrease in the concentration of certain unsaturated reactive compounds such as ethylene and propylene. This can also be observed in the study of terpene compounds collected on Tenax TA<sup>®</sup> cartridges [98]. Palluau et al. [99] also demonstrated that there is a loss of compounds on Carbotrap/Carbosieve adsorbent cartridges when these are exposed to humidity (90% relative humidity).

It should be noted that emissions from a material can also be studied by thermodesorption and pyrolysis analysis [100,101].

## 4.1.2. VOC Analysis

There are two families of VOC analysis techniques: off-line and on-line. For off-line techniques, a sample is taken from the matrix, the compounds are stored in/on their collection media, and then they are usually analyzed by gas or liquid chromatography technics coupled with mass spectrometry or flame ionisation and UV detection, respectively. On-line analysis techniques can also be used, in particular PTR-MS and SIFT-MS [102–104].

When analyzing VOCs by gas chromatography, the notion of total VOCs (TVOCs) is often introduced, being defined in the European standard ISO is ISO 16000-6 [105] as "the sum of volatile organic compounds, sampled on a Tenax TA<sup>®</sup> cartridge which elutes between *n*-hexane and *n*-hexadecane included on a non-polar capillary column, detected by flame ionization or mass spectrometry and quantified by converting the total surface area of the chromatogram in this range into toluene equivalent". Consequently, the TVOC parameter differs from the sum of all the VOCs detected.

## 4.2. How to Measure VOC Emission Rates from Wood-Based Materials?

There are a variety of emission chambers, depending on their size (from a few cm<sup>3</sup> to several hundred liters), material (glass, stainless steel), operating temperature, etc. Thanks to their flexibility, emission cells have become the benchmark for VOC analysis and are frequently used for standardized analyses. Table 4 lists the various emission chambers found in the literature, together with the associated method and emission parameters. Finally, Table 5 presents the characteristics of some commercially available chambers and cells.

Reference	Associated Standard	Volume of the Chamber (L)	Chamber Model (Material)	Emission Surface (m <sup>2</sup> )	Air Flow (L min <sup>-1</sup> )	Specific Air Flow Rate (m <sup>3</sup> m <sup>-2</sup> h <sup>-1</sup> )	Air Velocity (m s <sup>-1</sup> )	Loading Rate (m <sup>2</sup> m <sup>-3</sup> )	Air Change Rate (h <sup>-1</sup> )	Temperature, Relative Humidity (°C, %)
[108]	ASTM D5116-06 [109]	216	(Polished stainless steel)	/	1.8	/	/	/	0.5	25 °C.
[110]	QB 1952.2–2011 [111]	1000	/	0.4	/	/	0.2	0.4	1	50%
[112]	/	1000	(Stainless steel)	0.9	/	/	0.1–0.3	0.9; 1.8 and 3.6	1	23 °C, 45%
	203	Model VCE 200, Vötsch Industrietechnik (polished stainless steel)	$26.6  imes 10^3$	/	3.83	/	0.131	0.502		
[113]	/	24	Designed for the study using a desiccator (glass)	$60 \times 10^3$	/	4.04	/	0.250 1.01 25 °C 0.0250 1.01	– 25 °C, 50%	
		0.044	μ-CTE, <i>Markes</i> (stainless steel)	$0.267 \times 10^3$	/	4.28-5.06	/	6.07	26.1–30.7	
[114] EN 7	EN 717-1 [115]	225	(Stainless steel)	0.225	/	/	0.1–0.3	1	1	23 °C, 45%
	ASTM D 6007-02 [116]	1000	(Aluminum)	4.84	/	/	2–5	0.43	2	24 °C, 50%
	EN 717-2 [117]	4	(Glass)	0.02	1	/	/	/	60	60 °C, ≤3%
[118]	/	30	/	0.588	$\begin{array}{c} 15\times10^3 \text{ or} \\ 30\times10^3 \end{array}$	/	/	19.6	0.5 or 1	23, 35, 50, or 60 °C, 50%
[119]	/	$60 \times 10^{-3}$	MOSEC (Glass)	0.0017	/	/	/	/	/	23 °C
[120]	/	8000	(stainless steel)	/	/	/	/	/	/	_
[121]	/	0.044	μ-CTE, <i>Markes</i> (stainless steel)	/	/	/	/	/	/	40, 60, or 80 °C
[122]	ENV 13419-1 [123]	1000	Glass	/	/	1	0.1–0.3	1.5; 1 and 1.35	/	
[124]	ISO 16000-9 [125]	50.9	CLIMPAQ, <i>Climtech</i> (glass, stainless steel, and aluminum)	0.099	/	0.16	/	1.96	0.3	– 23 °C, 50%
[126]	ISO 16000-10 [127]	0.035	FLEC, <i>Chematech</i> (stainless steel)	0.0177	/	0.0106	/	506	514	

 Table 4. Examples of emission cells used in studies and associated parameters.

/: unspecified information.

Emission Chamber	Chamber Volume(s) (Internal Dimensions)	Т (°С)	RH (%)	d (L min <sup>-1</sup> )	ACR (h <sup>-1</sup> )	Examples of Standards
Model VCE 200 or 1000, Vötsch Industrietechnik	200 L (61 cm $\times$ 61 cm $\times$ 56 cm) 1000 L (75 cm $\times$ 163 cm $\times$ 75 cm)	20–130	5–95	/	0.1–1.8	ISO 16000-1 [128] ENV 13419-1 [123]
μ-CTE, Markes	44 mL 114 mL	20–120 20–250	/	10–70 50–500	/	ISO 16000-25 [129] ISO 12219-3 [130] ASTM D7706-17 [131]
CLIMPAQ, Climtech	50 L (21 cm $\times$ 81 cm $\times$ 22 cm)	ambient	/	/	0.02–140	EN 717-1 [115] ISO 16000 [132]
FLEC, Chematech	35  mL ( $\Phi = 150 \text{ mm}; h_{max} = 18 \text{ mm}$ )	ambient	/	/	/	ISO 16000-10:2006 [127]

Table 5. Characteristics of some emission cells mentioned previously.

RH: relative humidity; T: temperature; d: air flow; ACR: air change rate, /: unspecified information.

The surface emission rates (SER) in  $\mu$ g m<sup>-2</sup> h<sup>-1</sup> can be calculated for every compound or for the TVOCs using the following equation:

$$SER = \frac{m - m_0}{V} \times \frac{q}{S}$$
(1)

where m is the mass of the compound(s) studied ( $\mu$ g), m<sub>0</sub> is the mass of compound(s) already present in the environment ( $\mu$ g), V is the the sampled volume (m<sup>3</sup>), q is the the sampling rate (m<sup>3</sup> h<sup>-1</sup>), and S is the sample surface area (m<sup>2</sup>).

VOC emissions from materials depend on three parameters: the initial emittable concentration ( $C_0$ ), the diffusion coefficient ( $D_m$ ), and the partition coefficient (K) [106,107]. Emissions from materials have been modeled and shown to be influenced by factors such as temperature, humidity, and air flow, through the three parameters mentioned above.

# 5. Wood-Based Panel Emissions

# 5.1. Wood Panels Bonded with an Adhesive

5.1.1. VOC Emissions from Wood-Based Panels with a Petrochemical Binder

Formaldehyde is the most widely researched compound. It has been found in the emissions of various wood-based boards such as MDF [133,134], particleboards [118,134], OSB [133–135], or plywood [114,134,136,137]. Formaldehyde was found to originate in a larger amount from the formaldehyde-based binders used, but also from the wood species, in smaller quantities. Other VOCs have been identified in the emissions of wood panels bonded with petrochemical resins (Table 6).

Table 6. Type of wood boards and their emissions.

Type of Wood Panel	VOCs Identified in Emissions	References
	Formaldehyde *	[133]
MDF	Formaldehyde, acetaldehyde, hexanal	[134]
	Acetic acid, tetrahydrofuran, $\alpha$ -pinene, styrene, hexane, camphene, p-xylene, dichloromethane, naphthalene	[138]
	Formaldehyde, acetaldehyde, propanal, hexanal, pentanal, benzaldehyde, acrolein, acetone	[134]
Particleboards	Formaldehyde, <i>n</i> -hexane, 3-methylheptane, 2,2-dimethylhexane, undecane, dodecane, toluene, benzene, xylenes, 1,4-dichlorobenzene, naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 2-methylfuran, 2,3-dimethylnaphthalene, 1,7-dimethylnaphthalene, pentanal, hexanal, nonanal, decanal, 2-pentanone, 4-methyl-2-pentanone, 2-ethylhexanol, isobutanol, n-butanol, ethyl acetate, <i>n</i> -butyl acetate, isoocyl acetate, dibutyl phthalate, dimethyl carbonate, trichloromethane, phthalic anhydride, TVOCs	[118]

Type of Wood Panel	<b>VOCs Identified in Emissions</b>	References
	Formaldehyde, hexanal, and $\alpha$ -pinene, among others	[135]
OSB	Formaldehyde, acetaldehyde, propanal, pentanal, hexanal, benzaldehyde, furfural, acrolein	[134]
	Formaldehyde *	[133]
Dimused	Formaldehyde *	[114,134,136,137]
Plywood	Formaldehyde acetaldehyde, propanal, hexanal, pentanal	[134]

Table 6. Cont.

\*: Compound specifically researched.

These VOCs can be emitted for months or even years after panel production [139,140]. The nature of these VOCs emitted is linked to a wide range of factors, such as wood species, binder rate, or binder type [141], including carbonyl compounds (formaldehyde, benzaldehyde, hexanal) and terpene compounds ( $\alpha$ - and  $\beta$ -pinene, camphene, limonene) [139,140,142].

## 5.1.2. VOC Emissions from Wood-Based Panels with Bio-Based Adhesive

Tupciauskas et al. [143] produced biobased panels from birch. They extracted suberinic acid from the wood, mixed it with birch particles, and thermocompressed it at 226 °C for 9.5 min. They then studied the molecules emitted by these panels by SPME-GC-ToF-MS and detected 49 compounds, including furfural, acetic acid, and 5-methylfurfural as the majority compounds with relative peak areas of 21, 14, and 13%, respectively.

Jia et al. [48] elaborated plywood panels bonded with phenolic resins (PF) based on bio-oil, obtained by the pyrolysis of birch co-products. Emissions of formaldehyde and other VOCs by these panels were then measured according to the percentage replacement of phenol by bio-oil. We observed an increase in formaldehyde emissions with the percentage of bio-oil. The panels also emitted various compounds such as furfural, acetic acid, and hexanal. In addition, some toxic VOCs were detected, such as *N*,*N*-dimethylformamide, furfural, and phenol, which are carcinogenic mutagenic reprotoxic (CMR) compounds, or benzofuran, suspected of being carcinogenic.

Panels made with biobased binders therefore emit compounds linked to the thermal degradation of raw material components, such as furfural or acetic acid. In the case of panels bonded with bio-based resins with the phenol-formaldehyde adhesive system, compounds typical of these resins have been identified, notably formaldehyde.

Bio-based panels therefore offer an alternative to petrochemical resins, but the result does not seem entirely satisfactory, since they may emit higher levels of compounds such as formaldehyde [48] than industrial panels marketed today.

## 5.2. Wood Panels Bonded without Adhesive

Since few studies have tracked VOC emissions from unbonded panels and since the thermocompression process can be likened to heat treatment of the raw material, a state of the art on the impact of heat treatment on the VOCs emitted by wood is presented.

#### 5.2.1. VOC Emissions from Heat-Treated Softwoods

Scots pine has been extensively studied. In particular, Manninen et al. [11] compared emissions from simply dried pine with those from pine heat-treated (at 230 °C with steam for 24 h). They identified 41 volatile organic compounds, but only 14 were common to both untreated and treated pine. They showed that the main VOCs in untreated pine are terpenes (notably  $\alpha$ -pinene and  $\alpha$ -terpinene) and aldehydes (mainly hexanal), accounting for 71% and 25% of total emissions, respectively. Alcohols, ketones, and aromatic hydrocarbons were also detected in small quantities. In the case of treated pine, the main compounds emitted were aldehydes, accounting for 35% of emissions (notably furfural), and carboxylic

acids and their esters, accounting for 30% (mainly acetic acid). Ketone emissions also increased compared to untreated pine (from 1% before treatment to 16% following heat treatment). On the other hand, terpene emissions dropped sharply with heat treatment, accounting for just 10% of total emissions. It is important to note that terpene composition changed with heat treatment, as the authors identified 13 terpenes in emissions from untreated pine, compared with 5 in emissions from treated pine.

Mayes and Oksanen [144] also studied VOC emissions from pine (*Pinus sylvestris*) in connection with Thermowood heat treatment at 180 °C or 230 °C. TVOC emissions decreased after heat treatment (1486  $\mu$ g m<sup>-2</sup> h<sup>-1</sup> for untreated wood versus 828  $\mu$ g m<sup>-2</sup> h<sup>-1</sup> and 235  $\mu$ g m<sup>-2</sup> h<sup>-1</sup> for pine treated at 180 °C and 230 °C, respectively). Emissions from untreated pine were mainly terpenes:  $\alpha$ -pinene (174  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>), camphene (232  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>), and limonene (191  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>). Hexanal was also emitted by untreated pine (43  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>). Terpene and hexanal emissions decreased with heat treatment temperature (between 180 °C and 230 °C): from 312 to 24  $\mu$ g m<sup>-2</sup> h<sup>-1</sup> for  $\alpha$ -pinene, from 32  $\mu$ g m<sup>-2</sup> h<sup>-1</sup> to below the detection limit for camphene, from 153 to 1  $\mu$ g m<sup>-2</sup> h<sup>-1</sup> for limonene, and from 8  $\mu$ g m<sup>-2</sup> h<sup>-1</sup> to below the detection limit for hexanal. Conversely, acetic acid emissions increased with heat treatment temperature 3  $\mu$ g m<sup>-2</sup> h<sup>-1</sup> for pine treated at 180 °C. Furfural was emitted in greater quantities at 180 °C (29  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>) than at 230 °C (10  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>).

Sivrikaya et al. [145] also studied VOC emissions from Scots pine (sapwood or heartwood) but subjected to two types of treatment: heat treatment and vacuum heat treatment, at temperatures of 180 °C or 200 °C. VOC emissions from untreated pine were measured for comparison with those from heat treatment. VOC emissions from untreated heartwood were found to be more than 10 times higher than those from untreated sapwood (413 mg m<sup>-2</sup> h<sup>-1</sup> and 33 mg m<sup>-2</sup> h<sup>-1</sup> respectively). The main compound emitted by untreated heartwood and sapwood was  $\alpha$ -pinene, with 714 mg m<sup>-2</sup> h<sup>-1</sup> for heartwood and 77 mg m<sup>-2</sup> h<sup>-1</sup> for sapwood. Camphene,  $\beta$ -pinene, hexanal, and limonene were also identified as the main compounds in heartwood emissions, with 9 mg m<sup>-2</sup> h<sup>-1</sup>, 8 mg m<sup>-2</sup> h<sup>-1</sup>, 6 mg m<sup>-2</sup> h<sup>-1</sup>, and 5 mg m<sup>-2</sup> h<sup>-1</sup>, respectively. For sapwood emissions, hexanal and pentanal represent 51 mg m<sup>-2</sup> h<sup>-1</sup> and 17 mg m<sup>-2</sup> h<sup>-1</sup>, respectively. TVOC emissions increased for both heat treatments between 180 °C and 200 °C for heartwood and sapwood. Terpene emissions ( $\alpha$ -pinene,  $\beta$ -pinene, camphene, limonene) from heartwood decreased after both types of heat treatment and were lower at 180 °C than at 200 °C, except for pinenes, which were higher at 200 °C for vacuum heat treatment. Sapwood terpene emissions were lower after heat treatment at 180 °C, but higher after heat treatment at 200 °C, except for  $\beta$ -pinene, whose emissions after heat treatment were all higher. Aldehyde emissions varied from compound to compound. The aldehydes initially emitted (pentanal and hexanal) were emitted in very low quantities, or were no longer emitted (pentanal) after heat treatment. Other aldehydes, such as furfural, crotonaldehyde, and benzaldehyde, appeared after treatment or were emitted in larger quantities, although these remained low (<1 mg m<sup>-2</sup> h<sup>-1</sup>). Other compounds were also released after heat treatment, including alcohols (1-methoxy-2-propanol), ketones (cyclohexanone), and aromatic hydrocarbons (benzene, toluene, and their derivatives), but the quantities emitted were low (<1 mg m<sup>-2</sup> h<sup>-1</sup>).

Three Tunisian pine species (*Radiata pine, Pinus pinaster*, and *Pinus halepensis*) were subjected to different heat treatment severities by Elaieb et al. [146]. Heat treatments were evaluated in terms of sample mass loss: 0% (untreated), 8%, 10%, or 12% mass loss. The three pine species showed similar behavior with regard to VOC emissions. Firstly, the untreated sample emitted significantly more VOCs than the treated samples. The main compounds emitted were hexanal,  $\beta$ -pinene, camphene, nonanal, isobornyl acetate, caryophyllene, humulene, and caryophyllene oxide. Most of these VOCs are no longer emitted after heat treatment. However, at heat treatment corresponding to 8% mass loss, some monoterpenes such as pinene and terpenyl acetate were still detected, and furfural appeared in the emissions. After the most severe heat treatment (12% mass loss), only

acetic acid, due to the thermal degradation of hemicelluloses, vanillin, and guaiacylacetone, the first lignin degradation products, were detected.

Hyttinen et al. [147] studied emissions from untreated and treated wood (spruce, Scots pine, and aspen) for 28 days. They showed that TVOC emissions from spruce and Scots pine decreased with heat treatment (from 550  $\mu$ g m<sup>-2</sup> h<sup>-1</sup> to 220  $\mu$ g m<sup>-2</sup> h<sup>-1</sup> and from 2000  $\mu$ g m<sup>-2</sup> h<sup>-1</sup> to 240  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>, respectively). The main emissions from untreated spruce were  $\alpha$ -pinene (40–120  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>), limonene (40–140  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>), and  $\beta$ -pinene (20–66  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>). In treated spruce, acetic acid (17–53  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>), furfural (14–23  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>), and  $\alpha$ -pinene (3–18  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>) were detected in the majority of cases. For untreated Scots pine, the compounds emitted in the greatest quantities were  $\alpha$ -pinene (410–890  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>),  $\Delta$ -3-carene (340–680  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>), and hexanal (22–70  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>), while for treated Scots pine were acetic acid (4–86  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>), furfural (11–26  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>), and hexanal (10–17  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>).

Peters et al. [148] studied Thermoholz-treated wood (spruce, maple, beech, and ash) at 180 and 200 °C and compared it with its untreated peers. Emissions from untreated spruce were mainly terpenes (mono-, sesqui-, and diterpenes), accounting for around 95% of total VOC emissions. After heat treatment, carboxylic acid and aldehyde emissions increased (representing 25% and 10% of total emissions, respectively), while terpene emissions decreased. However, terpene emissions remained in the majority after treatment, accounting for around 65% of total emissions. Peters et al. [148] identified over 50 terpenes emitted by untreated spruce:  $\alpha$ - and  $\beta$ -pinene, sylvestrene, caryophyllene, and  $\gamma$ - and  $\delta$ -cadinene were the main compounds. As for aldehydes, hexanal accounted for 70% of aldehydes emitted by untreated spruce. After treatment, hexanal accounted for only 1.4% of aldehyde emissions, while furfural and 5-methylfurfural accounted for a very high 96% of the aldehyde fraction.

All these studies concluded that the compounds emitted by untreated softwood were mainly terpene compounds, in particular pinenes, limonene, or camphene, as well as a few aldehydes in smaller quantities (hexanal). On the other hand, after heat treatment, the total quantity of VOCs emitted was lower than before heat treatment, with aldehyde compounds predominating, notably acetic acid and furfural.

#### 5.2.2. VOC Emissions from Heat-Treated Hardwoods

Hyttinen et al. [147] compared emissions from poplar (*Populus tremula*) before and after heat treatment at 190 °C and found that poplar before heat treatment emitted more VOCs than after (513  $\mu$ g m<sup>-2</sup> h<sup>-1</sup> vs. 109  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>). In addition, they observed that the VOCs most emitted before and after treatment were carbonyl compounds. Before treatment, emissions were mainly represented by hexanal, acetic acid, and pentanal, with respective emission rates of 330  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>, 54  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>, and 46  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>. In contrast, after heat treatment, acetic acid and furfural were the major compounds, with emission rates of 88  $\mu$ g m<sup>-2</sup> h<sup>-1</sup> and 77  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>, respectively.

Čech and Tesařová [149] studied VOC emissions from untreated poplar and poplar heat treated at 180 °C or 200 °C, demonstrating in particular that VOC emissions from poplar increased with heat treatment and with treatment temperature. Indeed, 3 h after heat treatment, poplar emissions were linked to 31  $\mu$ g m<sup>-3</sup>, 73  $\mu$ g m<sup>-3</sup>, and 178  $\mu$ g m<sup>-3</sup> concentration in the emission chamber for untreated wood, wood treated at 180 °C, and wood treated at 200 °C, respectively. They observed a strong influence of treatment temperature on furfural and phenol emissions in particular, which are typical compounds of hemicellulose and lignin degradation.

VOC emissions from heat-treated poplar were analyzed by Xue et al. [145]. For this, the authors compared untreated poplar with poplar treated at 160 °C, 180 °C, 200 °C, or 220 °C. Like Čech and Tesařová [149], they found that VOC emissions were higher after wood treatment. Xue et al. [150] classified VOC emissions by compound type (alcohols, aldehydes, furans, aromatic compounds, esters, and alkanes). Aldehydes were the compounds emitted most at all treatment temperatures (except 220 °C), with a maximum contribution of 83% at 180 °C. For untreated poplar, aldehyde emissions accounted for 30% of total emissions,

with decanal (10% of total VOC emissions), 2-nonenal (10% of total VOC emissions), and nonanal (5% of total VOC emissions) as the main compounds. However, the main compound emitted by untreated poplar was a carboxylic acid: oxalic acid (32% of total VOC emissions). Aromatic compounds were the second most emitted by untreated poplar, along with naphthalene (6% of total VOC emissions) and methylnaphthalene (12% of total VOC emissions). At 160 °C and 180 °C, aldehydes remained the dominant compounds, accounting for over 70% of emissions at 160 °C and over 80% at 180 °C. Indeed, 2-nonenal, furfural, and decanal represented, respectively, 40%, 4%, and 11% of total VOC emissions at 160 °C and 43%, 17%, and 5% of total VOC emissions at 180 °C. At 200 °C, furfural became the majority aldehyde, accounting for 27% of total VOC emissions. However, at 200 °C, phenol appeared and was emitted in greater quantities than furfural, accounting for 29% of total VOC emissions. Emissions of aromatic compounds generally increased with temperature, reaching 30% of total VOC emissions at 220 °C, with phenol (16% of total VOC emissions), methylnaphthalene (10% of total VOC emissions), and naphthalene (4% of total VOC emissions). Esters appeared at 180 °C and increased with temperature, accounting for 13% of total emissions at 220 °C, with methyl benzoate (9% of total VOC emissions) the main compound at 220 °C.

Peters et al. [148] studied emissions from maple (*Acer pseudoplatanus*), beech (*Fagus sylvatica*), and ash (*Fraxinus excelsior*) before and after heat treatment at three temperatures: 60 °C, 180 °C, and 200 °C. The main compounds emitted by the three species before treatment were aldehydes and carboxylic acids. In the case of ash, aldehydes accounted for almost 90% of pre-treatment VOC emissions, while carboxylic acids accounted for around 55% of emissions from maple and poplar. For all three species, hexanal was the aldehyde most emitted by untreated wood. Following heat treatment at 180 °C, aldehyde emissions from all three species decreased, while carboxylic acid emissions increased (particularly acetic acid). On the other hand, when comparing treatment at 180 °C with treatment at 200 °C, carboxylic acid emissions decreased and aldehyde emissions increased (largely dominated by furfural) for all three species studied.

The VOCs emitted by native hardwoods therefore appeared to be very diverse. On the other hand, when subjected to heat treatment, an increase in carbonyl compounds (carboxylic acids and aldehydes) was observed, reflecting the degradation of the various wood components (hemicelluloses and cellulose), as seen above.

#### 5.2.3. VOC Emissions from Binderless Boards

To our knowledge, only two studies published results concerning VOC emissions from binderless panels obtained by cooking-compression. The first one concerns binderless panels made from an extrusion-refined coriander straw and a deoiled coriander press cake [151,152]. These cakes were obtained by extrusion and were then thermopressed at 205 °C for 5 min under 21.6 MPa pressure. Acetaldehyde, linalool, camphor, and *p*-cymene were identified as the majority emitted compounds, with emission rates of around 31 µg m<sup>-2</sup> h<sup>-1</sup>, 23 µg m<sup>-2</sup> h<sup>-1</sup>, 9 µg m<sup>-2</sup> h<sup>-1</sup>, and 4.4 µg m<sup>-2</sup> h<sup>-1</sup>, respectively. Linalool and camphor emissions were attributed in particular to the residual presence of essential oil in the materials. Formaldehyde emissions were below the detection limit estimated at 0.2 µg m<sup>-2</sup> h<sup>-1</sup>, while those of MDF and chipboard determined under the same conditions were, respectively, 42 and 84 µg m<sup>-2</sup> h<sup>-1</sup>. For these two materials, formaldehyde was the main compound emitted.

The second study concerns binderless boards produced from *Quercus robur* under various processing parameters (time, pressure, temperature) to observe their impact on the board VOC emissions [101,153]. VOC from these panels were studied in two ways. Firstly, emissions were measured in emission chambers. Secondly, the panels were pyrolyzed. Twenty-eight VOCs were identified by the pyrolysis of the binderless boards such as acetic acid, furfural, oak lactone, isoeugenol, vanillin, coniferaldehyde, and sinapaldehyde. Quantification of the VOC emissions led to the identification of acetaldehyde, formaldehyde,

acetic acid, and furfural as the major emitted compounds at, respectively, 109  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>, 44  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>, 180  $\mu$ g<sub>eq toluene</sub> m<sup>-2</sup> h<sup>-1</sup>, and 126  $\mu$ g<sub>eq toluene</sub> m<sup>-2</sup> h<sup>-1</sup>.

It clearly appears that binderless boards, although free of petrochemical or bio-based binders, can lead to emission of compounds known for their toxicity (formaldehyde, furfural, etc.) in significant quantities. It is therefore essential to take them into account as part of any strategy to develop such materials.

## 6. Conclusions

Wood is a natural heteropolymer made up of a number of polymers: cellulose, hemicelluloses, and lignin. These three components vary in quantity, composition, and size, depending on the nature of the wood. They provide both rigidity and flexibility to plant cells, enabling lignocellulosic organisms to grow both in width and height. Cellulose, hemicelluloses, and lignin also confer certain properties to the material. When subjected to heat, hemicelluloses and lignin undergo chemical changes. Hemicelluloses release acetic acid, which catalyzes future depolymerization reactions, releasing furan compounds such as furfural or 5-methylfurfural. At the same time, lignin plasticizes, enabling it to encapsulate cellulose fibers and hemicelluloses. On cooling, the lignin congeals, while the furan compounds released earlier resinify. Thanks to these self-adhesive properties, many lignocellulosic materials have been used to develop binderless panels.

Moreover, indoor air quality, and in particular the presence of VOCs in indoor air, has become a major concern for health authorities. Techniques for sampling and analyzing VOCs have developed to enable the analysis of numerous compounds with ever-lower detection limits, facilitating, among other things, the identification of sources emitting VOCs into indoor air. Numerous laws and decrees have been published over the past two decades to reduce emissions from building materials in particular. While existing materials are subject to studies aimed at reducing their VOC emissions, new materials are in the development phase.

Therefore, binderless panels are now showing their potential as bio-based materials that can be produced from co-products, and as an alternative to the industrialized woodbased panels using petrochemical resins. Numerous studies have been carried out to determine the optimum processing conditions for a given material, in order to obtain panels with satisfactory mechanical strength, dimensional stability, and water resistance. However, very few studies have focused on VOC emissions from these panels. It is nevertheless necessary to identify and quantify the compounds emitted, in order to judge the suitability of binderless panels for use today in sectors such as construction or furnishings, or even to replace existing panels.

This review provides an overview of the main methodologies used to analyze volatile substances in materials, together with examples of standards. It may offer a useful approach to identify and quantify VOC emissions of materials. Such data could be used in life cycle assessment evaluation of bio-based materials in order to reinforce wood binderless boards market attractiveness as regards sustainability representing an alternative to the current wood market. Only a few applications are available, and these methodologies should be more widely applied to gain knowledge on VOCs, which are relevant indicators for the development of environmentally friendly materials.

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