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Storage-induced emissions from different wood species

Abstract: In this study, the extractive contents and the storage-induced emissions from chips of *Salix alba*, *Betula pendula*, *Populus tremula*, and *Alnus glutinosa* are compared with emissions from *Pinus sylvestris* chips. Soxhlet extraction was performed, and carbon monoxide (CO) and O₂ concentration in the gas phase as well as gas chromatography-mass spectrometry analysis of volatile organic compounds were analyzed. *Pinus sylvestris* showed the highest extractive content in the petrol ether fraction and emitted CO in the highest concentration. *Salix alba*, *B. pendula*, *P. tremula*, and *A. glutinosa* have lower extractive contents in the petrol ether fraction and the CO concentrations decreased in the headspace accordingly. The emission of aldehydes was lower in the case of woods with lower petrol ether contents (*P. sylvestris*, *S. alba*, and *B. pendula*), but the situation was not as clear for *P. tremula* and *A. glutinosa*. The origin of CO and aldehyde emissions is discussed in view of the possible oxidative degradation processes of lipids and terpenes.

Keywords: *Alnus glutinosa*, *Betula pendula*, CO, emissions, *Pinus sylvestris*, *Populus tremula*, *Salix alba*, VOC, volatile organic components, wood chip storage

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Introduction

The wood consumption is increasing worldwide (Rupar and Sanati 2005; Kuang et al. 2008). The shortage of fossil fuels also contributes to wood demand on the energy sector. There is a competition for wood in the fields of sawn timber, wood composites, paper production, and energetic utilization. In the first three application fields, softwoods are preferred due to their advantageous physical and technical properties despite their lower density.

Softwoods are also more homogenous than hardwoods (deciduous woods). However, the availability of softwoods is limited. Softwoods have also disadvantages in terms of their high emission of volatile organic compounds (VOCs); this effect is very typical for pinewood (Englund and Nussbaum 2000; Banerjee 2001; Granström 2002). The measurement of VOC emissions is relevant in the context of traditional technological processes (Barry and Corneau 1999; Englund and Nussbaum 2000; Banerjee 2001; Wiglusz et al. 2002; Bengtsson and Sanati 2004; Radhakrishnan and Banerjee 2004; Makowski and Ohlmeyer 2006a,b; Ayrlmis and Kaymakci 2012).

The VOC emissions of wood-based panels are partly due to the genuine VOC emission of the wood itself (Makowski et al. 2005) additionally to the emission of the adhesive (Schneider and Dix 2006). At high concentrations, the VOCs are perceptible as an unpleasant odor and they are considered an environmental problem and a health hazard (Granström 2002, 2009; Svedberg et al. 2004). The extractives (accessory compounds), such as terpenes, fats, or fatty acids, undergo oxidative/thermal degradation during production or storage leading to elevated VOC emissions. Thermal degradation yields VOCs, such as aldehydes and carbon monoxide (CO) (Frankel 1983; Risholm-Sundman et al. 1998; Back and Allen 2000; Svedberg et al. 2004; Arshadi 2005; Arshadi et al. 2007, 2008, 2009; Neuenschwander et al. 2010), which can be detected in pellet piles during storages at high concentrations (Svedberg et al. 2004; Kuang et al. 2008).

The background of the present article is the substitution of softwoods by the underutilized hardwoods such as willow, birch, poplar, and alder to diminish the competition in the wood markets in Europe. One of the prerequisites to this purpose is the estimation of their VOC emission behavior. The present study is focusing on the emission of aldehydes and CO from the chips of the wood species listed above in comparison with pine chips. The experimental conditions were selected, which lead probably to thermal oxidation of fats and fatty acids as the main sources of VOC emission. Furthermore, the study is aiming at the evaluation of the relation between the accessory compound content of woods and their VOC and CO emission properties.

Materials and methods

Wood species

Stemwood with a diameter between 20 and 25 cm of *Pinus sylvestris*, *Salix alba*, *Betula pendula*, *Populus tremula*, and *Alnus glutinosa* was felled and debarked in a stand near Spangenberg (D-34286, Hessen, Germany). The pine stems had a relative heartwood content between 25% and 33%.

Extraction procedure

The stems were reduced to chips with a grinder from Retsch GmbH (Haan, Germany) working with a mesh size of 1 mm. Seven grams (calculated as dry matter) of each wood species were Soxhlet extracted in five successive steps with solvents of increasing polarity according to the method of Kübel et al. (1988): (1) petrol ether, (2) diethyl ether, (3) acetone/water (9:1), (4) ethanol/water (8:2), and (5) water (60°C). Each step lasted 6 h, and after each step, the dry weight of the evaporated extracts was weighed. The extraction was repeated twice for each wood species.

Sampling of VOCs and analysis

Chips produced with a drum chipper and a knife ring flaker were dried at 80°C to a moisture content of 8%. Two chip samples from each species (2 kg, calculated as dry matter) were separately put into gastight 50 l stainless steel containers. The containers had two valves for volatile sampling. They were stored at 50°C for 5 days in a cabinet dryer.

The containers were taken out daily of the cabinet dryer and conditioned at room temperature for 1 h. A portable gas sampling device (Testo 330-2 LL; Testo AG, Lenzkirch, Germany) was inserted through the upper sampling valve for CO sampling (precision: $\pm 0.0001\%$, ± 1 ppm) and O₂ sampling (precision: $\pm 0.1\%$, ± 1000 ppm). Each container was sampled twice.

VOCs with higher molecular weight were sampled after 5 days by a membrane pump (Thomas Division, Sheboygan, WI), which was connected with Teflon tubes to both sampling valves (closed loop) and sucked 36 l h⁻¹ of the headspace in the container through a calibrated charcoal filter tube (1.8 mg charcoal; CLSA Filter, Daumazan sur Arize, France). The filter tubes were eluted with 75 μ l of a mixture of CCl₂H₂/MeOH (2:1). One microliter of the solution was injected into a 6890N Network GC System onto a nonpolar column (30 m $\times$ 0.25 mm HP-5 MS filled with 95% dimethyl/5% diphenyl-polysiloxane; 0.25 μ m film thickness). Both systems were from Agilent Technologies (Santa Clara, CA, USA). Temperature program: 40°C for 2.5 min $\rightarrow$ 6.2°C min⁻¹ to 250°C (hold of 10 min). A quadrupole mass spectrometer (type 5973; Agilent Technologies) was operated in the scan mode in the range of 20–354 m/z (acquisition time of 0.5 s). A solvent delay was used to increase the lifetime of the detector by discriminating large amounts of CCl₂H₂/MeOH and this approach restricted the identification of compounds with a linear retention index (LRI) >800. The chromatograms were evaluated by the Enhanced Chemstation Version D00.00.38 software from Agilent Technologies, Mass Spectral Search Library of the National Institute of Standards and Technology (Gaithersburg, MD, USA), and MS Interpreter

Version 0.9f (Gaithersburg, MD, USA). The authentic standards in CCl₂H₂/MeOH (2:1) dilution of 100 ppm (g/g) were used for compound identification and as reference for quantification. The LRIs were calculated based on straight-chain hydrocarbons (C₇–C₂₄) (Castello et al. 2009).

Results and discussion

Expectedly, the pine chips contain a lot of unpolar compounds in the petrol ether and diethyl ether fraction (Table 1; Figure 1) due to their high contents of triacylglyceride (Arshadi et al. 2009; Schlechtriem et al. 2010) and terpene (Englund and Nussbaum 2000; Banerjee 2001; Granström 2002; Rupar and Sanati 2005; Péres et al. 2006). Both triacylglycerides and terpenes are mainly solved in the petrol ether fraction, whereas terpenes can also be solved in the diethyl ether (Nostro et al. 2000). The pine chips have the highest extractive content in the petrol ether and diethyl ether fraction (1.84%/1%) and the other wood species extractive content below 1.0% in both solvents (Table 1; Figure 1a). There is a correlation between the extractive contents and the O₂ and CO emissions (Table 1; Figure 2a and b) during storage. The chips with a high extractive content in the petrol ether fraction show an increasing emission of CO and decreasing O₂ concentration, whereas, in chips with low extractive contents, these changes are less pronounced (Table 1; Figures 1a and b and 2a and b).

These results are in general accordance with those of Kuang et al. (2008) and can be interpreted as manifestations of oxidative reactions during storage of wood chips at elevated temperatures. The fat and terpene content of the woods seems to induce an accumulation of CO (i.e., CO emissions are high in wood species with a high fat or terpene content), which can be extracted by unpolar solvents. Especially, poplar and alder show a very low CO emission, but any of the four investigated wood species have a lower CO emission in comparison with pinewood. This is an advantage in the utilization of these wood species as boards, for example.

Birch, poplar, and alder show the main decrease of O₂ and the main increase of CO in the first 24 h. The O₂ decrement is high in the time range of 48–120 h (birch 0.1%, poplar 0.1%, and alder <0.1°C), but the CO increment is low (birch 64 ppm, poplar 48 ppm, and alder 26 ppm). This discrepancy can be caused by the differences of the sensor sensitivities toward O₂ and CO, which does not allow the precise quantification of O₂ concentration below $\pm 0.1\%$ (± 1000 ppm).

The VOC emission with higher molecular weight is displayed in Figure 1b and shows a high terpene and aldehyde emission from pine and a high aldehyde emission

Table 1 Compilation of data concerning lipid containing petrol ether fraction, O₂ decrease, CO increase, and aldehyde concentration after 120 h at 50°C.

Wood species	Extractive content in		Decrements/increments		Aldehyde conc. (ppm)
	Petrol ether (%)	Petrol+diethyl ether (%)	O ₂ 0–120 h (%)	CO 24–120 h (ppm)	
Pine	1.8	2.8	-0.7	+208	758
Willow	0.6	0.8	-0.4	+103	777
Birch	0.4	0.7	-0.3	+64	173
Poplar	0.2	0.3	-0.2	+48	1016
Alder	0.1	0.3	-0.2	+26	442

from willow and poplar. Alder and especially birch emitted less aldehydes (Table 1; Figure 1b). Hexanal, 2-hexenal, and nonanal contributed to a large extent to the aldehyde emission of all five wood species (Table 2), whereas 2-pentylfuran and furan were the only furans detected. There is evidence that 2-pentylfuran derived from fatty acid oxidation, as well, and not exclusively from beginning hemicellulose oxidation (Snyder et al. 1988; Risholm-Sundman et al. 1998). In this study, the emission of 2-pentylfuran is lower than the emission of the straight-chain aldehydes. Furans are a typical product of thermal degradation of hemicelluloses and cellulose (Manninen et al. 2002). The

experimentation time (5 days at 50°C) in this study was not sufficient to yield high amounts of furfural (Table 2), whereas the wood in the study of Manninen et al. (2002) was treated with hot steam (230°C) for 1 day.

The emission of the group of alcohols, comprising 1-hexanol and 1-octen-3-ol, plays a minor role in the overall volatile pattern and can be assigned to thermally induced oxidative reactions in lipids (Frankel 1983).

In this context, the differences in defense mechanism of the trees in focus are remarkable: Salicaceae woods emit low amounts of terpenes (α -pinene, β -pinene, and limonene) (Table 2; Figure 1b), whereas they emit large

Figure 1 (a) Relative extractive contents (%; based on dry weight of untreated material) of the wood species indicated and (b) concentration of selected VOCs at the end of the storage time (5 days) (ppm).

Figure 2 Plots of the gas contents in the headspace of stored wood chips (collected in stainless steel containers) versus the storage time (h) at 50°C: (a) O₂ content and (b) CO concentration.

Table 2 VOCs detected and quantified (ppm) by gas chromatography-mass spectrometry.

Compounds	CAS-No.	LRI ^a	Wood species				
			Pine	Willow	Birch	Alder	Poplar
Aldehydes							
Hexanal	66-25-1	826	469	498	118	406	783
Heptanal	111-71-7	910	17	16	3	4	49
2-Heptenal	18829-55-5	963	151	74	20	20	76
Octanal	124-13-0	1003	–	88	14	5	48
Nonanal	124-19-6	1118	116	86	15	6	50
Decanal	112-31-2	1219	6	14	4	2	10
Alcohols							
1-Hexanol	111-27-3	885	19	10	5	5	–
1-Octen-3-ol	3391-86-4	989	153	46	26	–	33
1-Octanol	111-87-5	1084	31	–	–	–	–
Furans							
Furfural	98-01-1	860	–	–	–	7	–
2-Pentylfuran	3777-69-3	1002	323	333	29	170	657
Terpenes							
α-Pinen	80-56-8	937	1760	8	–	–	6
3-Caren	498-15-7	1013	1823	–	–	–	–
Limonene	138-86-3	1037	280	–	–	–	–

^aThe identification and quantification was confirmed by authentic standard compounds. The substances are listed in the order of their LRIs on a nonpolar column. LRI, linear retention index.

amounts of terpenes from their leaves in living trees in response to damages induced by herbivores (Frost et al. 2007; Schnitzler et al. 2010). On the contrary, conifer species defend their wood against fungi and xylophagous insects by terpenes and terpenoids.

Acetic acid is a common volatile product of the thermally induced deacetylation of hemicelluloses (Risholm-Sundman et al. 1998; Manninen et al. 2002), but it was not detected in this study because of the experimental conditions. As mentioned above, the mass spectrometer operated with a solvent delay, which restricted the detection of compounds to those with an LRI above 800 on a nonpolar column. Acetic acid has an LRI of approximately 690 on a nonpolar column.

The data of VOC analysis do not correlate perfectly with the results of the Soxhlet extraction and the CO quantification. Because aldehydes are products of fatty acid oxidation in wood (Frankel 1983; Snyder et al. 1988; Risholm-Sundman et al. 1998; Manninen et al. 2002; Svedberg et al. 2004; Arshadi 2005; Roffael 2006), the expectation is that the emission is high in the case of species with high yields of extracts with the unpolar petrol ether. As described by Frankel (1983), this process consumes O_2 , which corresponds to the results in Table 1: high O_2 consumption and high aldehyde concentrations in the extracts for pine and willow, whereas the opposite is true for birch. On the contrary, poplar and alder emit large amounts of aldehydes and their O_2 consumption and CO accumulation are low. This indicates that aldehydes might evolve also from other sources than lipid oxidation. The aldehydes that might already be present in the wood could be emitted directly without affecting the CO or O_2 concentration. This would explain the slow increase of the CO and slow decrease of the O_2 of poplar and alder

from the third to the fifth day (Figure 2b). Theoretically, aldehydes could evolve from oxidation of terpenes at 120°C, but the formation of straight-chain aldehydes from terpenes, as identified in this study, is not reported (McGraw et al. 1999; Neuenschwander et al. 2010).

Conclusion

There is a relation between fat content, CO formation, and O_2 depletion in wood chips. This confirms the oxidative CO formation from fatty acids proposed by other authors. The oxidation of terpenes could also contribute to CO formation. The behavior of the wood species is different with this regard and storage time, storage conditions, and, mainly, the temperature govern the CO emissions during production processes or storage. The aldehyde emissions are not solely linked to the lipid concentration and CO formation. They might evolve from other sources and more analytical efforts are needed to clarify this issue.

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