Short communication

# Optimizing storage emissions of wood flakes by gas sensor controlled thermal oxidation of lipids

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## ABSTRACT

Emissions in pellet storages caused by the autoxidation of lipids have a negative impact on human health and lead to unpleasant odors. This study investigates (1) the emissions of softwood flakes during temperature treatments (150°C-240 °C), (2) the online monitoring of these emissions with gas sensors, (3) the impact of the thermal treatments on the lipid content in the flakes and (4) the correlation between the lipid content and the storage emissions. The results show a correlation between the temperature during the treatment, the α-pinene, furfural, and 2-methoxyphenol emissions, and the gas sensor response. The decrease of the lipid content is correlated to a decrease in storage emissions, especially hexanal and carbon monoxide. It is discussed if higher drying temperatures during pellet production can reduce the storage emissions of the pellets. The increasing fire risk in the dryer could be controlled by the gas sensors.

## 1. Introduction

The chemistry of wood is a complex mixture of natural polymers (hemicellulose, cellulose, and lignin) and extractives. Part of these extractives are triacylglycerids, which contain mainly unsaturated fatty acids with species specific chain length. Therefore, wood pellets can emit gases via direct evaporation or autooxidation. Terpenes are extractives that are directly emitted and are abundant in softwood pellets at high concentrations. Short chain aliphatic aldehydes and pentylfuran are the reaction product of the oxidation of fatty acids [1]. These degradation products were found in the volatile profile of several softwood and hardwood species [2,3]. These odors are described as unpleasant. Hexanal can cause headache and discomfort in the eyes and nose [4]. Carbon monoxide (CO) is emitted by stored pellets [5] and has a higher affinity to the erythrocytes than oxygen. In a few reported cases it caused fatal accidents in pellet storages [6,7]. Its origin is assigned to fatty acid oxidation, as well, although the exact reaction mechanism is not elaborated. The emissions in the storage follows a first order kinetic [8]. Therefore, an intense drying that degrades the fatty acids prior to storing the biomass can reduce the storage emissions [9,10]. However, increasing drying temperatures are avoided in the industry in order to prevent the outbreak of a fire in the dryer. Conventional temperature sensors are not sufficient to identify a fire, as the retention time of some flakes in the dryer can be very long due to

adhesion to the surface or interception by metal surfaces. While these flakes slowly heat up until they ignite, they emit temperature correlated degradation products of the wood, e.g. furfural or 2-methoxyphenol. Semi-conductor metal oxide gas sensors are sensitive towards these volatile organic compounds (VOCs). They change their conductance due to the reduction or oxidation of the oxygen on the surface of the sensor, which is induced by VOCs. This mechanism has the potential to enables the online identification of an increasing fire risk in wood flake dryers [11]. This study aims at reducing the storage emissions of wood pellets by a thermal treatment that simulates elevated drying temperatures, which are controlled by a semi-conductor metal oxide gas sensor array. Also, the relation of fatty acid degradation and volatile emission should be proven in this study by a combined analysis of VOCs in the flue gas and fatty acids in the wood flakes before and after the thermal treatment.

## 2. Material and methods

### 2.1. Samples

Flakes were obtained from a local saw mill (Dold Holzwerke GmbH, Buchenbach, Germany) from the infeed of a band dryer. The flakes contained app. 20% fir (*Abies alba*) and 80% spruce wood (*Picea abies*).

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## 2.2. Thermal treatment

The flakes were chaffed to a particle size of app. 1 mm and 1,5 g were put into a gas tight stainless steel cylinder with a volume of 200 ml. The cylinder was put in a reconstructed GC oven (Perkin Elmer, Autosystem GC-FID, Norwalk, USA). Synthetic air (80% $N_2$, 20% $O_2$, Messer Industriegase GmbH, Bad Soden, Germany) was led through the cylinder at a flow rate of 2 L/min. Three temperature treatments were applied in order to investigate the temperature dependent VOC profile: (1) 25 °C–150 °C in 50min, (2) 25 °C–200 °C in 36 min, and (3) 25 °C–240 °C in 40 min. The temperature in the cylinder was monitored by a Testo flue gas sensor (testo 320 basic, Testo SE & Co. KGaA, Lenzkirch, Germany) operated in temperature mode.

## 2.3. VOC analysis

The VOCs in the flue gas were sampled with charcoal tubes (1,8 mg charcoal pellet, CLSA Filter, Daumazan sur Arize, France) for 60 s at 25 °C, 100 °C, 130 °C, and 150 °C (treatment 1) at 25 °C, 100 °C, 150 °C, and 200 °C (treatment 2), and at 25 °C, 150 °C, 200 °C, and 240 °C (treatment 3). The charcoal tubes were eluted with 100 μl of a methanol/acetone solution (1:1 v/v). The eluates were analyzed by GC-MS. 1 μl was injected at 230 °C with a 1:40 split in a GC-MS system (Trace 1300, Thermo Fisher Scientific, Waltham, USA) with a TraceGOLD SQC column (15 m, 0.25 mm film thickness, Thermo Fisher Scientific, Waltham, USA). The temperature program started at 30 °C with a hold of 2min, proceeding with a ramp of 40 °C/min to 250 °C and a final hold of 2min. The MS detector (ISQLT, Thermo Fisher Scientific, Waltham, USA) was operated in scan mode (mz 35–400 per 0.3s) with an ionization energy of 35 mV. The spectral data was analyzed with the Thermo Xcalibur Qual Browser (Thermo Fisher Scientific, Waltham, USA) and the Mass Spectral Search Library of the National Institute of Standards and Technology NIST (Gaithersburg, USA). The identity of VOCs was further confirmed by calculating the linear retention index (C7 to C24 straight-chain hydrocarbons [12] by using purchased standard compounds at $10^{-4}$ dilution. The area of the most abundant ion in the standard spectra was used for quantification (Appendix 1). The emission rate was calculated in μg/L/min. The Ws (Watt second) was calculated as the integral of the time/temperature curve for each VOC sample. The Ws resembles the sum of the energy applied to the wood flakes at the respective temperature. This enabled the comparison of the different temperature ramps were the same temperature was reached after different time intervals. The heating capacity of spruce wood (2.3 J/g × K) was multiplied with the dry mass of the sample (1.5 g) and the temperature increase in the respective time interval with 298 K (25 °C) as the starting temperature $\left( Ws = 2.3 \frac{Ws}{g \times K} \times 1.5g \times (xK - 25K) \right)$.

## 2.4. Flue gas monitoring

Three gas sensors (GGS5330 WO$_2$, GGS2330 SnO$_2$, and GGS1330 SnO$_2$, UST-Umweltsensortechnik, Geschwenda, Germany) were operated at 5 V and 200 Ω, 200 Ω, and 75 Ω, respectively. The sensors were calibrated with selected flue gas components (α-pinene, furfural, 2-methoxyphenol) in $10^{-3}$, $10^{-4}$, and $10^{-5}$ dilutions. Each dilution step was tested three times at a synthetic air flow rate of 1.5 L/min. The VOCs emitted during the thermal treatments were led through a sensor chamber and the resistance of the sensors was measured in intervals of 1s.

## 2.5. Weight loss

The samples were weighted before and after the thermal treatment. The weight loss was calculated in % and the initial moisture content of the flakes was subtracted. The moisture content was 52% ± 1.7% and determined according to DIN EN 15414-3:2011-05.

## 2.6. Elemental analysis

20 mg of treated and untreated flakes were wrapped in a tin foil and analyzed by a CHNS analyzer (varioMAKRO cube, elementar, Germany), which was calibrated with sulfanilamide. Each treatment was repeated three times and each sample was analyzed three times. The O/C and H/C ratio was calculated on molar basis. All results were tested for normal distribution with the Shapiro Wilks test and as at least one data set was not normally distributed the Whitney Mann *U* Test was always applied to test for significant differences.

## 2.7. Calorific value

The calorific value of five 1 g samples of untreated or thermally treated flakes were determined with a calorimeter (C200, IKA, Stauffen, Germany) according to DIN 51900-2:2003-05. All results were tested for normal distribution with the Shapiro Wilks test and as at least one data set was not normally distributed the Whitney Mann *U* Test was always applied to test for significant differences.

## 2.8. Lipid analysis

15 g of untreated or thermally treated flakes (N = 3) were successively extracted in dichloromethane (DCM) and methanol for 6 h per solvent. After each extraction step the residues were vacuum dried and weighted. Both fractions were transesterified in 15 ml of a 1% methanolate/methanol solution for 2 h at 70 °C with a stirring rate of 500 rpm. The solution was neutralized with an aqueous 1% HCl solution and vacuum dried. The residue was desalinated with a 20 ml water/DCM mixture (1:1 v/v) in a separating funnel. The DCM fraction was air dried and the residue was solved in a 20 ml acetone/methanol solution (1:1 v/v) for GC-MS analysis. The parameters of the analysis were the same as described in "VOC analysis". The identity of the compounds was further confirmed by calculating the linear retention index (C7 to C24 straight-chain hydrocarbons [12]) by using purchased standard compounds at $10^{-4}$ dilution. The area of the most abundant ion in the standard spectra was used for quantification. Three fatty acid methyl esters (oleic acid methyl ester, linoleic acid methyl ester, and linolenic acid methyl ester) were quantified.

## 2.9. Storage experiments

Three Erlenmeyer flasks with a volume of 180 ml were each filled with 20 g of treated or untreated flakes. The flasks were closed and kept at room temperature (22 °C ± 2 °C). In 24 h intervals, VOCs and CO were sampled with charcoal tubes and a CO sensor (testo 320 basic with CO$_{low}$ sensor, sampling range 0–500 ppm, Testo SE & Co. KGaA, Lenzkirch, Germany), respectively. The testo sensor circulated the gases with a flow rate of 8.1 L/min for 9min. The final value of the CO$_{low}$ sensor was recorded and the VOCs were analyzed as described in section "VOC analysis".

## 3. Results and discussion

All treatments showed only a slight dry weight loss of $-0.44 ± 1.18$ after treatment, which was due to the loss of extractives (Table 1) and volatile degradation products (Fig. 1). This corresponds to the slight increase of the HHV, which was accompanied by a decrease of the oxygen content and an increase of the carbon content (Table 1).

The VOC emission pattern of the three thermal treatments is shown in Fig. 1. The emissions can be divided in three phases. In the initial phase between 25 °C and 150 °C the terpenes are released [13]. In the second phase from 150 °C to 200 °C, furans (mainly furfural) are emitted as degradation products of hemicellulose [14–16]. The third phase from 200 °C to 240 °C shows the additional emission of methoxyphenols from the degradation of lignin [17]. The Ws are given in order