Identification of malodourous emissions of wood pellets during storage

BARBARA PÖLLINGER-ZIERLER[1], Irene Sedlmayer[2,3], Hermann Hofbauer[3], Elisabeth Wopienka[2] and Barbara Siegmund[1]

[1] *Institute of Analytical Chemistry and Food Chemistry, Graz University of Technology Stremayrgasse 9/2, 8010 Graz*

[2] *BIOENERGY 2020+ GmbH, Gewerbepark Haag 3, A 3250 Wieselburg-Land*

[3] *Institute of Chemical Engineering, Technical University of Vienna, Getreidemarkt 9/166, 1060 Vienna*

Abstract

During storage of pellets, various compounds like e.g. carbon monoxide (CO), carbon dioxide (CO_2) and partly malodourous volatile organic compounds (VOCs) can be formed. Research on this so-called off-gassing phenomenon is focusing on the one hand on the identification and characterization of the unpleasant odour-active VOCs and on the toxic atmosphere caused by formation of CO and depletion of oxygen (O_2). On the other hand, the mechanism behind the off-gassing phenomenon is a further topic in research. However, both topics have in common that they are necessary research questions in order to prevent insecurity due to the formation and enrichment of harmful CO and complaints by the end-user because of malodourous smell in pellet storage places.

Thus, the aim of this study was to identify and quantify the malodorous VOCs and find correlations with the released amounts of CO. To identify odour-active components in wood pellets, sensory and analytical methods were applied. A trained sensory panel established olfactory descriptors for the wood pellet samples. By means of instrumental methods like GC-MS, volatile and potentially odour-active components were identified. The total amount of VOCs was determined using a flame ionization detector and CO was analysed with a gasanalyzer. The results showed significant differences concerning both types of emission - VOCs and CO - between sensory unremarkable wood pellets and pellets with a pronounced off-flavour. Terpenes, short chain fatty acids and saturated aldehydes were identified to have major impact on the aroma profile of wood pellets.

Introduction

In recent years, a significant increase in the demand of wood pellets has been observed. Besides beneficial characteristics for the combustion process (e.g. wood pellets exhibit a high energy density) the customer also expects a natural wood pellet flavour of the product [1]. During storage of wood pellets, various compounds like carbon monoxide (CO), carbon dioxide (CO_2) and volatile organic compounds (VOCs) are formed, and the oxygen (O_2) in the surrounding air decreases [2]. Simultaneously, partly malodourous compounds may be formed leading to unpleasant and disturbing smell in the pellet storage facilities. The formation pathways of the unpleasant odour-active VOCs and CO are not completely clear, but the degradation of natural wood components like resins or fatty acids seem to be one reason for the release of the emissions. In addition, secondary metabolites of microbial growth on the raw material can lead to off-flavour formation during storage [3].

The aim of this study was the identification of odour-active components in wood pellets. To reach this aim, sensory and analytical/gas chromatographic methods were applied on wood pellets (with or without off-odour) made of spruce or/and pine in various ratios. Different sensory unremarkable and malodourous wood pellets were analysed.

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Experimental

For the analysis of the volatile compounds the pellets were crushed using a laboratory scale mill. For the extraction and enrichment of the volatile compounds from the pellets prior to the GC analysis, headspace solid phase micro extraction (HS-SPME) was used. 100 mg of ground pellet samples were analysed and 50/30 µm DVB/Carboxen/PDMS fibres (2 cm stable flex, Supelco) were used for the enrichment of the volatile compounds. The fibre was exposed into the headspace of the samples for 20 minutes at 40°C while stirring the samples. The separation and the identification of the volatile compounds were performed on an Agilent GC-MS system (GC 7890 with MS 5975c VL MSD, electron impact ionisation 70 eV) using a nonpolar analytical column (HP5MS, 30m*250µm*1 µm) and on a Shimadzu GC-MS system (GC2010 with GCMS-QP 2010 Plus, Shimadzu Europa GmbH, electron impact ionisation 70 EV) system with a polar analytical column (ZB-Wax plus, 20m*180µm* 0.18µm). The identification of the compounds was based on the comparison of the obtained mass spectra with mass spectra from literature or from MS databases as well as the calculation of linear temperature programmed retention indices and comparison with retention indices from authentic reference compounds or data from literature.

Moreover, for the determination of emitted amounts of CO and total VOCs (TVOC, i.e. the sum of all volatile compounds that can be emitted from the wooden material) the pellets samples were stored in closed glass bottles for five days at 22°C. Thus, this method is called storage experiment. For the measurement of CO concentration, a gasanalyzer (Emerson, NGA 2000) and for the determination of total VOCs concentration a flame ionization detector (Thermo-FID) were used [4]. The release of emissions is explained as release of gas per kg pellets on dry basis per day enabling the comparison of different pellet samples.

A sensory panel consisting of 15 well trained panellists performed descriptive analysis of sensory unremarkable and malodourous wood pellets and established corresponding olfactory descriptors.

Results and discussion

The results of the study show that terpenes (e.g. α-pinene, β-pinene or camphene), short chain fatty acids and saturated aldehydes have major impact on the composition of the wood pellet volatiles. The composition of the volatile compounds of pellets with and without detected off-odour differs significantly. Figure 1 shows the comparison of the aldehyde and free fatty acid distribution, receptively, of a reference sample produced from spruce and pine (50/50) and a rejected, malodourous pellet sample. On the one hand, shifts of the compound ratios were discovered which could be one reason for the detected off-flavours in pellets. Increasing concentrations of compounds like hexanoic acid and aldehydes like octanal or nonanal are supposed to negatively influence the pellet odour. On the other hand, some compounds were detected which are most likely produced by microorganisms as secondary metabolites during microbial growth on sawdust (e.g. 3-methyl-butanoic acid). These VOCs present in higher concentrations in the pellets with malodour most probably influence the off-odour formation.

Concerning the acid composition, a drastic decrease of acetic acid but also of butanoic and pentanoic acid was observed from the ‘good’ to the ‘bad’ sample, as well as a simultaneous increase of hexanoic and heptanoic acid were observed. The methyl branched fatty acid 3-methyl-butanoic acid shows slightly higher concentration in the malodorous pellet than in the ‘good’ one. Due to its low odour threshold (OT;

0,0018mg/m³; [5]) 3-methyl-butanoic acid is considered to be of importance for the pellet off-odour. Regarding aldehydes, hexanal concentrations were reduced while pentanal, octanal and nonanal showed higher concentrations in the malodourous sample. These compounds shift results in pellets with a very strong lacquer-like flavour, whereas the typical woody odour mainly caused by terpenes was no longer detectable. The total concentration of terpenes decreased in the malodourous samples as well as the total concentration of VOCs. The loss of hexanal might be also responsible for the loss of fresh notes.

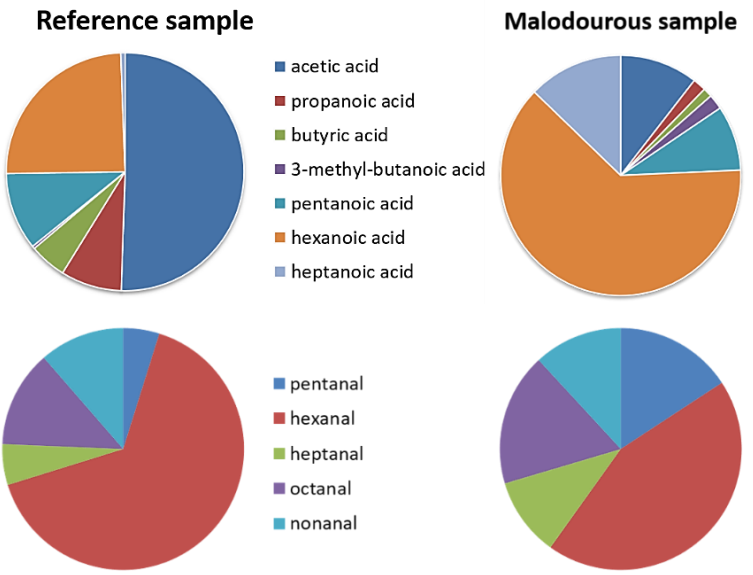

Figure 1: Odour-active components in pellets samples

Figure 2 shows the results from CO and TVOC analysis. Interestingly, the so-called reference sample (i.e. good sample) shows a significantly higher emission of CO and total VOCs, respectively, than the malodourous sample.

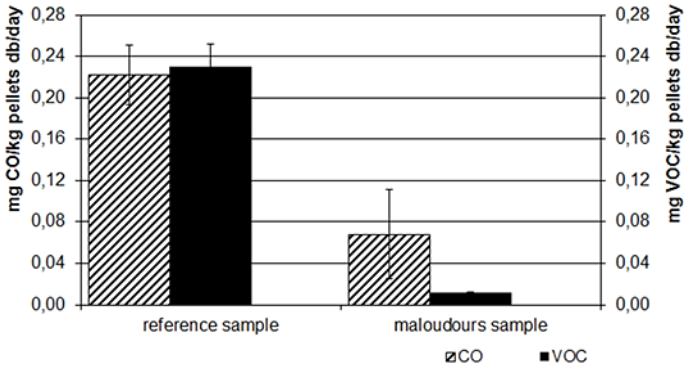

Figure 2: Release of CO and total VOCs

The formation pathways for odour-active VOCs, total VOCs and CO have not been explained yet. The identities of the detected compounds indicate that the (oxidative) degradation of natural wood components like resins or fatty acids is one reason for the release of emissions from the pellets.

Results from previous studies show (data not shown), that the microbial spoilage of raw material during storage could be an additional way for the formation of VOCs (especially for aldehydes and acids).

Moreover, interestingly the pellet sample with pronounced off-odour did not emit more CO and total VOCs than an odour unobtrusive pellet sample. Although the pellet sample was rejected due to a distinct off-odour, a decrease of total VOCs could be detected in GC-MS analysis. The results of the study show a shift of different odour-active substances as a reason for the existing off-odour. Thus, the total amount of VOCs is not the decisive parameter alone for the evaluation of a malodourous smelling pellet sample. Since odour of pellets is dependent on the concentration in combination with the odour thresholds (OT) of the respective component (e.g. OT of hexanal 58mg/m³, OT of 3-methylbutanoic acid 0,0018mg/m³) [5], quantification is inevitable to be able to judge the sensory relevance of the compounds of interest.

The results of this study show that the determination of CO emission and the measurement of total VOC release from the pellets are not sufficient to evaluate off-odour formation in wooden pellets. The detailed investigation of the sensory properties in combination with the GC-MS analysis of the potentially (mal)-odorous volatiles is necessary to obtain a comprehensive picture of pellet (off)-flavour. The results serve as a basis for future investigations to elucidate off-flavour formation pathways in wood pellets.

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