Assessing VOC Emission by Wood Pellets Using the PTR-ToF-MS Technology

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Wood pellets are important fuel in heat and power production with a high potential to grow in the future. Pellets represent a well spread commodity for energy production in Europe with a rapidly increasing market. To analyze the Volatile Organic Compounds (VOCs) emitted from wood pellets, 21 samples have been collected in triplicate. Seventeen samples are commercial pellets and 4 are pellets produced at laboratory scale. Based on the in-force ISO standard, the commercial pellets belong to the high-quality classes A1 and A2. To analyse Volatile Organic Compounds (VOCs) emissions, each sample were introduced in a glass jar connected to PTR-TOF 8000 (Ionicon Analytik GmbH, Innsbruck, Austria) and each one analyzed with a zero-air generator. The tool was set in the standard configuration using H3O+ as proton donor in the transfer reaction. The raw data were acquired by the TofDaq software (Tofwerk AG, Switzerland) using a dead time of 20 ns for the Poisson correction, and subsequently they were converted in ppbv (part per billion by volume). A total number of 53 VOCs were selected as more informative. A multivariate ordination technique (Principal Component Analysis - PCA) were applied on the matrix 60 (pellet samples) x 53 (VOCs) in order to observe the pellet sampled in a reduced space. On the negative side of the first (51.1%) and second (13.0% of the explained variance) PCA axes were positioned the samples characterized by chestnut, beech, or mixed pellets containing these wood species. The samples located close to the origin consist of a mix of different pellets samples, while the coniferous pellets were located along the positive side of PC1 and PC2. Moreover, was observed a sort of a gradient, from the negative to the positive side of the first axis and from hardwood to softwood pellet. Using the entire dataset of VOCs, it has been observed a lack of a clear distinction between groups of pellets belonging to different wood species which could be due to several reasons such as the intrinsic variability of the wood, the pellet manufacturing process (*e.g.*, the temperature of the extruder), the addition of additives and the different geographic origin of biomass.
Keywords: pellet; VOCs; multivariate statistics; quality.

1. Introduction

Renewable wastes such as biomass-related agricultural agri-food residues, and forestry residues are being increasingly recognized as valuable feedstock for bioenergy production (Negri *et al.,* 2016; Zambon *et al.,* 2016). The potential benefits for the environment are the reduction of CO2 emissions and sequestration of carbon, and for the farmers additional income through energy production and solid renewable fuels (Parmar *et al.,* 2014; Usman *et al.,* 2015; Colantoni *et al.,* 2016). The world energy demand is increasing very fast as a consequence of economic growth and development. The global total primary energy supply more than doubled between 1971 and 2011 and is expected to increase at higher rates in the next decades (Zanetti *et*

al., 2017). Pellets are solid biofuel with excellent technological properties. In the last two decades European demand for wood pellets has increased steadily, mostly stimulated by public policies and governmental supports (Olsson *et al.*, 2011; Sikkema *et al.*, 2011). Wood pellets are important fuel in heat and power production with a high potential to grow in the future. Compared with other biofuels, pellets have higher energy density, lower transportation and storage costs and their regular shape allows the automation of feeding procedure in burning appliances (García-Maraver *et al.*, 2001; Monteiro *et al.*, 2012). These are some of the reasons why wood pellets have a wide diffusion on the biofuels market. However not all pellets do present the same quality which is expression of different parameters depending on both, intrinsic feedstock characteristics and treatment or production conditions (Sgarbossa *et al.*, 2014). The properties owing to the raw materials affect pellets quality because their constituents are found practically unchanged in the final product (Pallottino et al., 2016). In fact, they have a high density (more than 1000 kg.m^{-3} solid), a high bulk density (more than 500 kg.m^{-3} loose), a low moisture content (less than 10%) and, consequently, a higher calorific value per volume unit compared to other traditional woody fuels (Dhamodaran and Afzal, 2012). The properties of pellets allow them to be burned with a high combustion efficiency and to be used in domestic appliance thanks also to their regular shape and small dimensions that allow them to be stored and handled like a fluid (Stelte *et al.*, 2012). The pelletizing process is strongly affected by the tree species used, the characteristics of which are then reflected in the final pellet quality (Nielsen *et al.*, 2009; Gil *et al.*, 2010). The pelletizing pressure, the hold time of pellets in the die channel (i.e.: compaction ratio) and the extruding temperature are directly related to feedstock characteristics. By pelletization, raw biomass can be converted into a pellet form with improved fuel quality such as increased bulk density, and uniformed shape and size (Liu *et al.*, 2014). However, the use of different raw materials may have opposite effects on the final densified product (). The pellets quality is crucial to ensure a high combustion performance and it is guaranteed by European and International standards. The pellet market in the European Union (EU) shows a continuous expansion over the years. Europe produced 13.5 million of tons and consumed 18.8 million tons of pellets in 2014 (AEBIOM, 2015). The production and use of traditional or technologically improved woody biofuels can contribute to the overall greenhouse gases (GHG) reduction (Katers et al., 2012) due to their close-to-neutral carbon emission (Sjølie and Solberg, 2011). Many European countries have developed pellets quality standards. Pellet quality depends on chemical, mechanical and physical properties of biomass (Obernberger and Thek 2004). Some parameters are related to raw material (Arshadi *et al.*, 2008) and some to quality management of the manufacturing process (Lehtikangas, 2001). This has strongly encouraged many European countries to set up subsidy schemes for the substitution of oil, coal and gas residential and industrial heating systems or power plants by others run on biomaterials. Aside from the physico-mechanical and chemical characteristics that high-quality pellets must meet, the consumers evaluate them according to the characteristics perceivable through the senses, such as color and smell. In details, consumers consider that dark color pellets have a lower commercial value than light wood pellets (Lam *et al.*, 2012), and wrongly consider their pungent smell because of the gluing additives used in pellets manufacturing, additives that are permitted by the quality standards only in small quantities (≤2%) (UNI EN ISO 17225-2:2014). GC-MS (gas chromatography-mass spectrometry) is a commonly technique employed to identify volatile compounds from woody samples but is rather slow and requires sample preparation (Taiti et al., 2016). Nowadays, PTR-TOF-MS (proton transfer – time of flight –mass spectrometer) represents an innovative technique and a new instrument that enables the real-time separation and quantification of volatile organic compounds(VOCs) from trace levels up to parts per million, with a low fragmentation level. The key advantages of this tool, that allow its use in a wide range of fields, are: (1) unprecedented number of VOCs can be detected simultaneously and (2) there is no need of any sample preparation. It is an useful method previously used for fingerprinting and screening volatile emissions from different material (Mancuso et al 2015, Vita et al., 2015, Kim et al., 2009). In this context, the aim of this work was to assess whether the PTR-ToF-MS instrument would be able to detect different VOCs emitted by different woody plant pellet (commercial and not). The VOCs were exploratory examined using an ordination technique (Principal Component Analysis – PCA).

2. Materials and methods

2.1 Pellet samples

Table 1 indicates the species and origins of the 21 pellets analysed in this study. 17 samples are commercial pellets and 4 are pellets produced at laboratory scale. Among them, there are 10 pure spruce pellets, 3 mixed spruce and beech, 2 chestnut, 2 pine and 5 mixed broadleaves-coniferous. Based on the in-force ISO standard ISO 17225-2:2014, the commercial pellets belong to the high-quality classes A1 and A2.

2.2 PTR-ToF-MS and VOCs analysis

PTR-ToF-MS (model 8000, Ionicon Analitic GmbH, Innsbruck, Austria) has been used in this study as the detector for the organic compounds emitted by wood pellets. A description of this instrument, with its advantages and disadvantages, can be found elsewhere (Blake et al., 2009; Taiti et al., 2016). the volatile analysis was performed using H_3O^+ as reagent ion for the proton-transfer reaction. Briefly, 40 gr of each pellet samples was placed into 0.75 L glass jar (Bormioli, Italy) provided of glass stopper fitted with two Teflon tubes connected respectively to the tool and the zero-air generator (Peak Scientific instruments, USA).

Before the analyses, each sample has been incubated for 300 seconds, and VOC sampling were performed in conditioned rooms with a constant temperature of 25°C±1. For each sample were analyzed three replicates employing three different glass jar. Analysis has been performed using the instrumental set up and parameters presented previously by Taiti et al., 2016. The internal calibration of ToF spectra was based on m/z = 29:997 (NO^+), m/z = 59:049 ($C_3H_7O^+$) and m/z = 137:132 ($C_{10}H_{17}^+$) and was performed off-line after dead time correction; for peak quantification, the resulting data were corrected according to the duty cycle. Data were recorded with the software TOF-DAQ (Tofwerk AG, Switzerland), the sampling time for each channel of TOF acquisition was 0.1 ns, acquiring 1 spectrum per second, for a mass spectrum range between m/z 20 and m/z 220. Finally, the raw data, expressed as signal intensities (cps) were converted in ppbv using the formula described by Lindinger et al. (1998) to calculate the concentration for each VOC.

Table 1: Specie and origin of pellets

Sample number	Specie	Origin
1	Spruce	Russia
2	Chestnut	Italia - Piemonte
3	Spruce-beech	Italia - Basilicata
4	Spruce-beech	Bosnia & Erzegovina
5	Pine	Italia - Toscana
6	Corsican Pine	Italia - Calabria
7	Beech (60%) Pine L. (20%) Alder (20%)	Italia - Calabria
8	Pine L. (50%) Chestnut (50%)	Italia - Calabria
9	Chestnut	Italia - Calabria
10	Spruce	Italia - Veneto
11	Spruce	Italia - Trentino
12	Spruce	Bosnia & Erzegovina
13	Spruce	Bosnia & Erzegovina
14	Spruce	Germany
15	Spruce	Austria
16	Spruce	Italia - Lombardia
17	Spruce	Italia - Emilia Romagna
18	Spruce	Austria
19	Beech - Spruce	Bosnia & Erzegovina
20	Acacia (30%) Pine (30%) Gum tree (40%)	Vietnam
21	Acacia (30%) Pine (40%) Gum tree (30%)	Vietnam

2.3 Multivariate analysis

In this study an ordination technique (PCA) was performed to observe how the pellet samples, and their wood origin species, disposed within the VOCs space. PCA is an ordination technique based on a projection method which allows the display of information in a data matrix considering the influence of each in a limited number of components expressed as linear function of the original ones. The data matrix, consisting of 53 VOCs emitted by 60 samples belonging to 20 different wood pellet (commercial and not). The first two (*i.e.*, the most informative) principal components (PC) were selected to be graphically reported. The results allow to visualize the samples according with their scores. Similar scores along a component detect similarities for variables with a high loading for that component. PCA was performed using PAST software (Hammer et al., 2001).

3. Results and discussion

Figure 1 represents the scatter plot of the pellet scores on the first two axes of the PCA. The first PC represents a sort of a gradient, from the negative to the positive side of the first axis, from hardwood (mainly chestnut) to softwood (mainly spruce) pellet. The samples located close to the origin consists of a mix of different pellets samples, while the coniferous pellets were located along the positive side of PC1. The lack of a clear distinction between groups of pellets belonging to different wood species could be due to several reasons such as the intrinsic variability of the wood, the pellet manufacturing process (*e.g.*, the temperature of the extruder), the addition of additives or the different geographic origin of biomass. A total of 57 VOCs, with protonated masses ranging from 27.022 to 205.195 m/z, were obtained from 21 different pellet samples (Figure 2). Some differences in terms of VOC composition and concentration were found for some compounds. Given the botanical nature of the material used the high variability observed could be due by the different chemical composition of each samples. Previous studies reported that volatile compounds are produced by the oxidation of residual fatty acids contained in the pellet (Sveldberg et al., 2004, Arshadi and Gref 2005). Furthermore, in some pellets (e.g., pine) are contained a typical aroma compounds, that are related to the terpenoids production. In details, methanol, acetic acids, acetone and formic acid were showed in high amounts, instead, terpenes, other aldehydes and organic acids were found in substantially lower levels. Moreover, in Figure 2 are shown the scores of the wood pellet together with the vectors of the VOCs on the first two axes. On the first axis, the VOCs are greater on the positive side (the side of softwood pellets). VOCs (with their Putative Identifications) which highly contribute on that side have the following protonated masses: 77.04 (PI: Alkyl fragment), 67.05 (PI: terpenes fragment), 109.1 (PI: terpenes fragment), 71.05 (PI: 2-butenal) and 57.07 (PI: alkyl fragment hexenol).
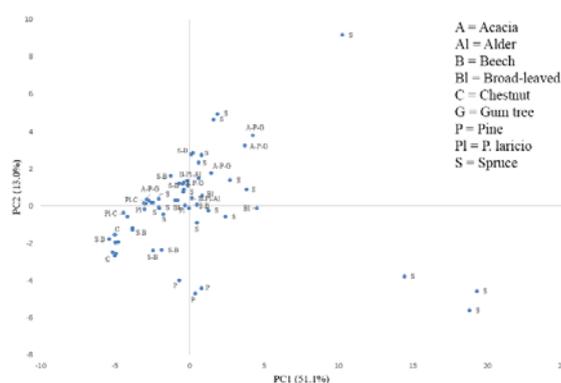

Figure 1: Graphical layout of the PCA results. The x-axis represents the PC1 while the y-axis the PC2. The value in brackets represents the variance explained by that PC (total variance explained: 64.1%). The scores of the wood pellet and their wood origin were reported
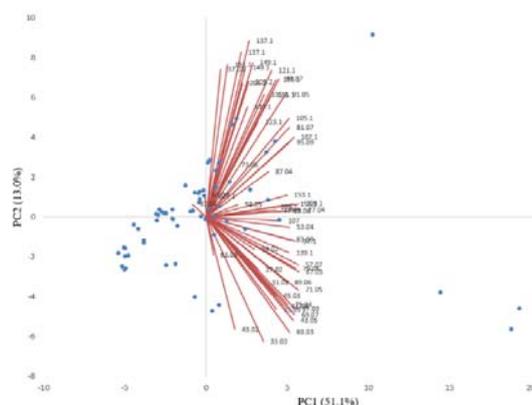

Figure 2: Graphical layout of the PCA results. The x-axis represents the PC1 while the y-axis the PC2. The value in brackets represents the variance explained by that PC (total variance explained: 64.1%). The scores of the wood pellet (blue points) together with the VOCs loadings (red vectors) were reported. The wood origin of the pellets was reported in Figure 1.

4. Conclusions

The goal of this study was to detect the VOCs emitted by different wood pellets (commercial and not). 21 pellets have been analysed: 17 samples were commercial pellets and 4 were pellets produced at laboratory scale. Among them, there were 10 pure spruce pellets, 3 mixed spruce and beech, 2 chestnut, 2 pine and 5 mixed broadleaves-coniferous. An multivariate ordination technique (Principal Component Analysis – PCA) to exploratory analyse the VOCs emitted by pellets. The VOC analysis of pellets has produced 57 VOCs, responsible among other of smell of the pellets. The results of PCA showed a sort of a gradient, from the negative to the positive side of the first axis, from hardwood (mainly chestnut) to softwood (mainly spruce) pellet. The lack of a clear distinction among pellets groups is probably a consequence of the high variability of the wood species chemical composition as well as the different biomass origins.

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