Biomass and Bioenergy xxx (2017) 1–13

Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: http://www.elsevier.com/locate/biombioe

Research paper

Development of a compact technique to measure benzo(a)pyrene emissions from residential wood combustion, and subsequent testing in six modern wood boilers

Franziska Klauser [a, b, *], Manuel Schwabl [a], Magdalena Kistler [b], Irene Sedlmayer [a], Norbert Kienzl [a], Alexander Weissinger [a], Christoph Schmidl [a], Walter Haslinger [a], Anne Kasper-Giebl [b]

[a] BIOENERGY 2020+ GmbH, Inffeldgasse 21b, 8010 Graz, Austria
[b] Institute of Chemical Technologies and Analytics, Vienna University of Technology, Getreidemarkt 9, 1060 Vienna, Austria

ARTICLE INFO

Article history:
Received 9 September 2016
Received in revised form
10 May 2017
Accepted 11 May 2017
Available online xxx

Keywords:
Automatic biomass boiler
Benzo(a)pyrene
Polycyclic aromatic hydrocarbons
Total solid particles
Emission

ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are emitted during incomplete combustion of organic materials and are particularly harmful to human health. As a representative of PAHs, Benzo(a)pyrene (BaP) is restricted by the European Union to an annual average value of 1 ng m^{-3} in ambient air. This threshold is significantly exceeded during the heating season in various regions. Residential wood combustion furnaces are considered to be a major source for BaP pollution.

In this research, a compact sampling method for BaP measurements was validated. Afterwards, the method was used to assess emissions from modern automatic wood boilers, in order to obtain a detailed knowledge of BaP emissions from residential wood combustion furnaces.

It was demonstrated that, for a wide range of BaP concentrations, sampling from the hot flue gas of residential wood combustors can be carried out effectively over a simple quartz filter, after proper dilution with cold purified air. Highest BaP emissions from the investigated boilers occurred during start, with a mean concentration value of 6.3 μg m-3. All values refer to standard conditions (273.15 °C, 100 kPa) and to an O_2 volume fraction of 13% in the dry flue gas. The lowest concentrations occurred during full load operation (mean value 73 ng m-3 at STP). It was found that, amongst all flue gas compounds analysed, elemental carbon is the parameter most closely related to BaP. This work demonstrates, at optimal operating conditions, modern automatic wood boilers have potentially lowest BaP emission concentrations amongst residential wood combustion furnaces.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are formed during incomplete combustion or pyrolysis of organic materials. Because of the widespread natural and anthropogenic emission sources they are found ubiquitously in the environment [1–3]. Anthropogenic sources, and in particular biomass and coal combustion, are recognized as one of the major sources of PAH emissions [3–7].

Several hundreds of substances, which contain at least two connected benzene rings in the chemical structure [8], are classified as PAHs. Although the biological properties of most PAHs are not investigated, the toxicity of several representatives of PAHs is well known and thus they are considered harmful pollutants [2,7–10].

Benzo(a)pyrene (BaP) is the most widely investigated representative of PAHs as well as one of the most toxic compounds in this group. Therefore, BaP is commonly defined as the guiding substance among the PAHs [1,8,11–13]. Although the suitability of BaP as guiding substance is still under discussion [14], there are clear indications that BaP is an appropriate representative for PAH emissions [13]. For instance Kelz et al. [15] analysed the emissions of various biomass heating systems and found a good correlation of BaP and the total genotoxic PAHs.

Since 2013, in the European Union, the limit value for BaP concentration in the ambient air is set to a yearly average value of

* Corresponding author. BIOENERGY 2020+ GmbH, Inffeldgasse 21b, 8010 Graz, Austria.
E-mail address: franziska.klauser@bioenergy2020.eu (F. Klauser).

http://dx.doi.org/10.1016/j.biombioe.2017.05.004
0961-9534/

1 ng m^{-3} [16]. Several reports show that in some regions, even where industry and traffic have a minor impact, this threshold is exceeded regularly [6,9,10]. As a matter of fact, the highest BaP concentrations are found in the winter season and in rural areas where traffic and industry play a minor role and where biomass heating systems are commonly used [6,9,10,17,18]. As previously mentioned, this is taken as a proof that biomass combustion for heating purposes contributes significantly to BaP pollution.

In times of climate change and increased efforts to reduce CO_2 emissions, the energetic use of biomass as a renewable source has an important role. In 2014, in the European Union 17.7% of the total energy demand for heating and cooling was provided by renewable resources. In particular, the shares in Sweden, Austria, Italy, Germany and Netherlands were 68.1, 32.6, 18.6, 12.2 and 5.2% respectively, indicating higher shares in countries with higher forest cover [19]. The importance of biomass for heating is particularly evident in Germany and Austria, where about 90% of the heat demand is covered by biomass [20,21]. For example in Austria the number of biomass heating systems in households (exclusive district heating) increased from 641 000 in 2003/04 to 740 000 in 2011/12. However, the stock of biomass heating systems comprises systems of different technological standard and are operated with different biomass fuels [20]. It is thus of high importance to differentiate biomass heating concepts with high particulate matter and PAH emissions from those with low emissions and high efficiency. So far, several investigations about BaP or PAH emissions from biomass combustion systems were conducted [15,22–27]. However, these investigations focus more on log wood stoves rather than on boilers. A detailed differentiation of BaP emissions for different boiler classes or rather the investigation of the boilers' operation phases was not conducted yet. Therefore, a detailed investigation of PAH emissions from biomass combustion systems is required in order to characterize modern automatic biomass boilers concerning their BaP emission behaviour.

Several approved measurement methods for PAHs exist [28–34]. As already mentioned, PAHs comprise a group of several hundreds of single substances with different thermodynamic behaviour. Thus, the sampling method needs to be capable to collect substances in gaseous as well as in solid state at a certain sampling temperature. This means that PAHs are collected in two [28–30,34] or even three [29,33] different samples, like filter, adsorber or impinger samples, which makes the sampling rather complex and the analysis costly. For this work the focus is set on the representative substance BaP. With a target on a single substance, the investigation of the thermodynamic behaviour may allow a simplification of the sampling procedure. A compact measurement method for application in different sites and an analysis with adequate costs contribute to a comprehensive investigation of the BaP emission behaviour of residential wood firings, as the modern automatic biomass boilers, that are analysed in the present study.

The objectives of this work are:

- The validation of a compact BaP measurement method for flue gas sampling from residential wood combustion furnaces.
- The determination of BaP concentration profiles of modern automatic biomass boilers during specific operating conditions
- The assessment of possible indicators or closely related parameters for BaP.

2. Materials and methods

2.1. Combustion technologies

In the first step of the work, the BaP sampling method is validated. For this part a logwood stove and a logwood boiler are used (Table 1). The furnaces are chosen according to the requirements of the validation approach, which is described in chapter 2.3.1. The 8 kW wood stove is selected because of the typically varying flue gas composition. This steel stove, partly covered with soap stones, has a primary and secondary air supply and weighs 331 kg. A 30 kW downdraught logwood boiler with lambda control, automatic ignition and a 150 L charging volume is used because of the opportunity to modulating air supply which results in varying combustion conditions. Thereby different flue gas qualities can be achieved.

For the second part of the work six different automatic biomass boilers are investigated in order to characterize the BaP emission behaviour of state-of-the-art biomass boilers. All tested boilers have automatic primary and secondary air supply. Boiler A (as named in Table 1) is a top-fed grate system operated with pellets. Boilers B to D are all horizontally fed boilers with different designs. At boiler B (15 kW) the fuel is charged with a screw stoker to a multi-segmental grate. Boiler C (50 kW) has a horizontally oriented burner in a horizontal, tube shaped combustion chamber. The fuel is charged into the combustion chamber with a rotary valve. Boiler D, a multifuel boiler (500 kW) has a step grate which is charged with screw stoker and can be operated with both, pellets (D1) and wood chips (D2, see Table 1). Boilers E (12 kW) and F (15 kW) are underfed systems where combustion takes place in retorts. Technical data are summarized in Table 1. The measurements are carried out in the laboratories of five different boiler manufacturers in Austria and Liechtenstein. At all testing facilities the boiler was integrated into a hydraulic heat uptake system. The flue gas pipe connection to the chimney has measurement sections for particulate and gaseous emissions following the requirements of EN 13284-1 [35] and VDI-2066-2 [36].

2.2. Fuels

For the validation tests beech wood logs of A1 quality according to ISO 17225-5 [37] are used (Table 3). For the boiler testing (boiler A - F) pellet fuels of A1 quality according to ISO 17225-2 [38] (Table 4) are applied. Boiler D was also tested with wood chips (D2; Table 1) with a moisture content of 18% (mass fraction; M25 according to ISO 17225-4 [39]) and a wood chip length of $\leq$30 mm (P16S according to [39]).

2.3. Experimental procedure

2.3.1. Validation tests

The work consists of two parts. In the first part the BaP sampling method which was adapted for the flue gas measurements of residential wood combustion furnaces is validated. The validity of the method is defined with the criterion that more than 90% (mass fraction) of the BaP can be collected on the quartz fibre filter. This means that, even at different flue gas qualities or rather varying flue gas quality within test runs, BaP must be predominantly in solid state to be sampled by a filter unit. It is thus required that at all BaP concentrations, the temperature, which is adjusted with the porous tube diluter (PTD), is below the current thermodynamic dew point. The share of gaseous BaP that remains in the diluted flue gas is determined by an adsorber unit downstream the filter (see Fig. 1). A vertically installed vessel containing Amberlite® XAD-2® (Sigma Aldrich) as adsorber is used for the separation of gaseous BaP. Dimensions of the resin bed are chosen according to ISO 11338-1 [29]. The validation is carried out in three steps.

Validation step 1: The particle/gas-phase partitioning of BaP in the flue gases from two different combustion systems (log wood stove, log wood boiler; Table 1) is assessed. Based upon thermodynamic calculations on the gas/particle phase partitioning of BaP,

Please cite this article in press as: F. Klauser, et al., Development of a compact technique to measure benzo(a)pyrene emissions from residential wood combustion, and subsequent testing in six modern wood boilers, Biomass and Bioenergy (2017), http://dx.doi.org/10.1016/j.biombioe.2017.05.004