Journal of Analytical and Applied Pyrolysis 119 (2016) 24–30

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Strategies for producing biochars with minimum PAH contamination

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ARTICLE INFO

Article history:
Received 14 January 2016
Received in revised form 7 March 2016
Accepted 12 April 2016
Available online 22 April 2016

Keywords:
Biochar
Pyrolysis
PAH
Pyrolysis temperature
Carrier gas
Feedstock

ABSTRACT

With the aim to develop initial recommendations for production of biochars with minimal contamination with polycyclic aromatic hydrocarbons (PAHs), we analysed a systematic set of 46 biochars produced under highly controlled pyrolysis conditions. The effects of the highest treatment temperature (HTT), residence time, carrier gas flow and typical feedstocks (wheat/oilseed rape straw pellets (WSP), softwood pellets (SWP)) on 16 US EPA PAH concentration in biochar were investigated. Overall, the PAH concentrations ranged between 1.2 and 100 mg kg^{-1}. On average, straw-derived biochar contained 5.8 times higher PAH concentrations than softwood-derived biochar. In a batch pyrolysis reactor, increasing carrier gas flow significantly decreased PAH concentrations in biochar. In case of straw, the concentrations dropped from 43.1 mg kg^{-1} in the absence of carrier gas to 3.5 mg kg^{-1} with a carrier gas flow of 0.67 L min^{-1}, whilst for woody biomass PAHs concentrations declined from 7.4 mg kg^{-1} to 1.5 mg kg^{-1} with the same change of carrier gas flow. In the temperature range of 350–650 °C the HTT did not have any significant effect on PAH content in biochars, irrespective of feedstock type, however, in biochars produced at 750 °C the PAH concentrations were significantly higher. After detailed investigation it was deduced that this intensification in PAH contamination at high temperatures was most likely down to the specifics of the unit design of the continuous pyrolysis reactor used. Overall, it was concluded that besides PAH formation, vaporisation determines the PAH concentration in biochar. The fact that both of these mechanisms intensify with pyrolysis temperature (one increasing and the other one decreasing the PAH concentration in biochar) could explain why no consistent trend in PAH content in biochar with temperature has been found in the literature.

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1. Introduction

Biochar is the solid product of thermochemical conversion of biomass under an atmosphere with reduced content of free oxygen or its complete absence, i.e. pyrolysis and gasification [1]. During such conversion, biomass undergoes extensive devolatilisation and develops a solid carbonized matrix [2]. This is accompanied by formation of polycyclic aromatic hydrocarbons (PAHs), an important class of organic contaminants, associated with environmental problems [3]. PAHs can have acute adverse effects on human health, plants and the wider ecosystem with some displaying carcinogenic, mutagenic and teratogenic effects [4].

PAHs are defined as aromatic structures that consist of two or more linked carbon rings and only contain the elements carbon and hydrogen [3]. PAHs are formed during incomplete combustion of any type of biomass and biomass-derived material. Thus, PAHs are present in the environment naturally through forest fires and volcanic eruptions, with UK rural soils containing a mean PAH concentration of 2.2 mg kg^{-1} [5]. However, human actions increase PAH concentrations locally and the average PAH concentrations in UK urban soils were reported to be 14.2 mg kg^{-1} [5]. In soil they are known to accumulate as they are difficult to degrade, associate with organic matter and have low water solubility (half-life of PAHs of more than 3 rings >20 to hundreds of days) [4].

There are two main pathways by which PAHs are known to form: at lower conversion temperatures Diels-Alder reactions take place which involve dehydrogenation, polymerization, cyclization and aromatization of hydrocarbons to form PAHs [6–8]. At temperatures above 400–500 °C, the alternative is a pyrosynthetic pathway consisting of demethylation, demethoxylation and dehydroxylation of lignin, cellulose and hemicellulose to form phenol, alkyl-phenols and BTEX. This is followed by deoxygenation/dehydrogenation, connecting single compounds

Abbreviations: HTT, highest treatment temperature; I.D., inner diameter.

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http://dx.doi.org/10.1016/j.jaap.2016.04.001
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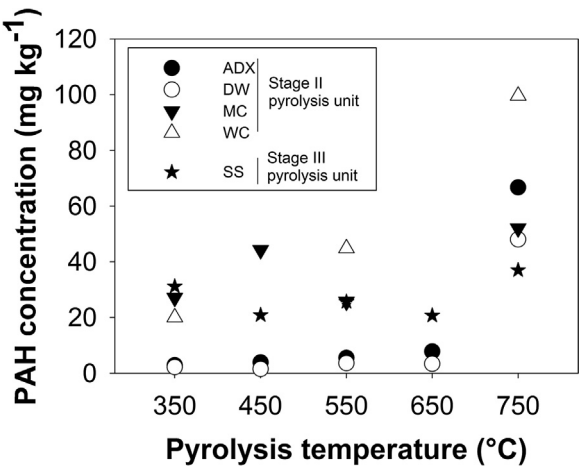

Fig. 1. Effect of pyrolysis temperature on 16 US EPA PAH concentration in biochar (mg kg^{-1}). The biochars were produced from 4 different feedstocks in Stage II pyrolysis unit (ADX, *Arundo donax*; DW, demolition wood; MC, miscanthus chips; WC, willow chips) and 1 feedstock in Stage III pyrolysis unit (SS, sewage sludge). For all the feedstocks combined, the PAH concentration in the biochars produced at 750 °C is significantly different to all the other HTTs (one-way ANOVA).

and condensing these into larger compounds which end up as polyaromatic networks (PAHs or pyrolytic carbon) [6,7,9,10].

Research effort regarding anthropogenic pollution with PAHs used to focus on reducing PAH emissions from fossil fuel and biomass combustion [3]. Studies that dealt with PAHs and pyrolysis mostly investigated PAH formation and concentrations in pyrolysis liquids/gases [6,9,11–13]. Recently, attention has shifted to PAH concentrations in pyrolysis solids because of the potential application of biochar to soil for soil improvement, soil remediation and carbon sequestration [8,14–19]. In order to avoid possible negative effects on soil ecosystems and to comply with environmental legislation, it is essential to produce biochars with low PAH concentrations. Biochar guideline values have been established which are based on current legislation. For example, the European Biochar Certificate (EBC) allows up to 12 mg kg^{-1} of 16 US EPA PAHs for basic grade and up to 4 mg kg^{-1} for premium grade biochar which was adopted from the Swiss Chemical Risk Reduction Act [20]. The International Biochar Initiative (IBI) guidelines use threshold values of 20 mg kg^{-1} and 6 mg kg^{-1} based on the Austrian Compost Ordinance [21].

The few systematic studies on dependence of PAH concentrations on pyrolysis conditions that exist, provide different perspectives and no overall trend is observed [8,14–19,22]. In Hale et al. [16], the effects of highest treatment temperature (HTT—maximum temperature material is exposed to), residence time and feedstock was investigated by analysing 59 biochars, however, due to the highly variable technologies used for biochar production only limited conclusions could be drawn. This shows the absolute need for a systematic study on the relationship of pyrolysis conditions and feedstock with PAHs in biochars produced from highly controlled, slow pyrolysis units.

Consequently, in this work the effects of two common feedstock types (wood and straw) and typical pyrolysis parameters (residence time, HTT and carrier gas flow rate) were investigated to determine their effect on total concentrations of 16 US EPA PAHs in resulting biochars. The overall objective was to provide recommendations to produce pyrolysis solids (biochar) with minimal PAH contamination based on a data set of biochars produced from highly controlled pyrolysis units.

2. Materials and methods

2.1. Feedstocks

For production of the 46 biochars, 7 feedstocks were used: (1) straw pellets (WSP) from 50/50 wheat: oilseed rape straw [23]; (2) softwood pellets (SWP) from 5/95 pine: spruce; (3) willow chips (WC) Koolfuel 40, supplied by Strawsons (Retford, UK); (4) miscanthus chips (MC) (*Miscanthus x giganteus*); (5) demolition wood (DW) and (6) *Arundo donax* (ADX) as described in Buss et al. [24]; and (7) sewage sludge (SS).

2.2. Biochar production

46 biochars were produced under highly controlled pyrolysis conditions using three different slow pyrolysis units that are located at the UK Biochar Research Centre (UKBRC). The smallest unit ("Stage I") is a fixed bed, batch, quartz tube reactor with an inner diameter (I.D.) of 50 mm and around 200 mm sample bed depth which is heated up by an infrared gold image furnace and can pyrolyse about 15–40 g per batch [25]. The second unit ("Stage II") typically processes 500 g h^{-1} and is a continuous pyrolysis unit with a furnace screw which is heated up by an electric split-tube furnace [24]. The pilot scale pyrolysis unit ("Stage III") has a rotary kiln and can process up to 50 kg h^{-1} of feedstock [26]. Production parameters, such as HTT (350–750 °C), residence time (10, 20, 40 min) and carrier gas flow (0, 0.33, 0.67 L min^{-1}) were varied. The carrier gas flows under standard conditions were 10 L min^{-1} for Stage III (I.D. 244 mm), 1 L min^{-1} for Stage II (I.D. 100 mm) and 0.3 L min^{-1} for Stage I (I.D. 50 mm). When inconsistencies during a pyrolysis run were detected, such as high pressure peaks, the biochars were discarded and the pyrolysis run was repeated ensuring comparative conditions between runs. An overview of all the biochars including production conditions and feedstocks can be found in Table S1.

2.2.1. Highest treatment temperature (HTT)

To be able to find overall trends of the influence of HTT on the total PAH concentration in biochar, different feedstocks were pyrolysed using two pyrolysis units in the typical temperature range used for biochar production (350–750 °C). Stage II pyrolysis unit was used to pyrolyse demolition wood and *A. donax* at 5 temperatures (350, 450, 550, 650, 750 °C), willow chips at 3 temperatures (350, 550, 750 °C) and miscanthus chips at 4 temperatures (350, 450, 550, 750 °C). Furthermore, sewage sludge was pyrolysed at 5 temperatures (350, 450, 550, 650, 750 °C) with the Stage III pyrolysis unit.

2.2.2. Carrier gas flow rate, HTT, feedstock, and residence time

The Stage I pyrolysis unit was used to pyrolyse straw pellets (WSP) and softwood pellets (SWP) at 2 HTTs (350, 650 °C), 2 residence times (10, 40 min) and 3 carrier gas flow rates (0, 0.33, 0.67 L min^{-1}). In total, 24 biochars were produced. The feedstocks and production conditions were chosen as typical feedstocks and production conditions for biochar production. More details on the production and on the feedstocks, such as elemental content (ultimate analysis) and biomass components, can be found in Crombie & Mašek [23].

2.3. PAH analysis

2.3.1. Sampling

To gain representative samples, first the container with the biochar was mixed and around 1/10 of the biochar was sampled (~10 g) from all areas of the container. The 10 g sample was ground with mortar and pestle and homogenized, transferred into a sample

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