Organic Compounds in Pyrolytic Carbon

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Abstract

The content of organic compounds in char affects its ecotoxicity. The chemical composition of pyrolysis carbon was studied in carbon prepared by torrefaction of spruce wood and pyrolysis of wood pellets, tyres and TetraPak. Organic compounds present in biochar and char were investigated with respect to assessment of suitability for agricultural applications. Char and biochar samples were analysed by method of pyrolysis gas chromatography with mass spectrometric detection. The identified compounds were aromatic hydrocarbons, polycyclic aromatic hydrocarbons, furans, benzofurans, substances containing phenol, benzepolycarboxyl acids, and substances of biogenic origin (fragments of cellulose, hemicellulose, protein, etc.). Relatively higher concentrations of compound fragments from biocomponents are associated with biochar from wood pellets. Organic compounds which are potentially toxic and carcinogenic for living organisms (PAHs, benzofurans and aromatic hydrocarbons) have higher concetrations in char from synthetic materials (scarp tyres, TetraPak) compared with biochar.

Keywords: biochar, char, pyrolysis, polyaromatic hydrocarbons, BTEX, styrene

Introduction

Pyrolysis is among the most important thermochemical technologies that enable conversion of various materials (biomass, wood, herbs, etc.) and waste to chemicals and energy-related substances that are used as fuel. Pyrolysis processes produce three main products – gas, liquid and pyrolytic carbon (char). The amount and nature of output products is influenced by the composition of feed material and pyrolysis conditions (Elyounssi et al, 2010). An important product of pyrolysis is char, which can be used in various industrial applications, e.g., as a precursor for the production of activated carbon for water purification, as catalyst support or for the capture of CO_2, etc. Char is defined as a solid material that occurs in the early stages of thermal decomposition of carbonaceous material such as coal, biomass or synthetic materials (Elmquist et al., 2004), when light gaseous components and tar in an atmosphere without oxygen are removed. Char has characteristics of the chemical and morphological composition of an input fuel (Fernandes et al., 2003). Char, which is produced by pyrolysis of biomass is referred to as biochar.

Biochar is resistant to biological decay, it contains recalcitrant organic carbon (OC), which helps in global warming mitigation. Incorporation of biochar into soil can be used as soil conditioner to enhance soil fertility mainly due to its high sorptive capacity for water and nutrients. The application of biochar to the soil increased its pH, CEC, level of highly stable OC and nutrient content (Hossain et al., 2010). Besides recalcitrant organic matter, char also contains resistant organic matter. Resistant organic matter is matter which is not subject to biological degradation, it is difficult to decompose at elevated temperatures – the decomposition temperature of ROM (Resistant Organic Matter) is 475–650°C (De la Rosa Arranz et al., 2009), sometimes it is reported to be up to 750°C (Kaal et al., 2009). Resistant organic matter comprises carbon black (pyrogenic carbon) and common toxic and carcinogenic substances, e.g. polycyclic aromatic hydrocarbons, benzonitrile, benzene, and its compounds, dibenzofurans, etc. (Kaal et al., 2009). Sorption of aromatic compounds to black carbon is 10 to 1,000 times stronger than to nonpyrogenic organic matter (Cornelissen and Gustafsson, 2004).

There is still very little information on what happens to the material sorbed in soils, its behaviour and impact on other components of the ecosystem. The behaviour of black carbon (BC) in the soil environment depends on a large array of intrinsic BC properties (e.g. feedstock characteristics, charring temperature, duration, moisture content, pH, composition and activity of the microbial population, parent material), which are only superficially understood (Braadbaart et al., 2009). One of the key parameters (Kaal et al., 2012) in predicting BC degradation/preservation in soil is the degree of thermal alteration (charring intensity). Typically with increasing charring intensity, the carbon content, degree of condensation, specific surface area and sorption

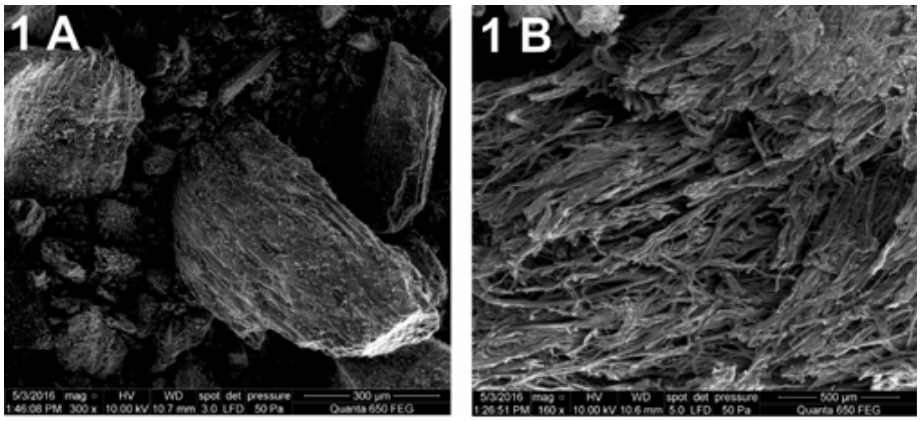

Fig. 1 Examples of pyrolytic products: A – biochar of wood, B – char of TetraPak from SEM microscope

Rys. 1 Przykład produktów pirolizy: A – karbonizat z drewna, B – karbonizat z TetraPaków – zdjęcia SEM

capacity of black carbon increase, while its susceptibility to degradation decreases. It is therefore evident that the degree of thermal alteration directly affects the chemical composition of char, and thus its properties for subsequent applications (agricultural, industrial).

In this article, we focused on finding the organic composition of char produced by pyrolysis at 600 ± 50°C) from the following materials: TetraPak packaging, wood, biomass and tyres. Char and biochar with a minimum content of toxic organic substances, which would be applicable for agricultural purposes were identified. The main criterion for agricultural applications of char was the content of PAHs.

Materials and methods

Char samples were obtained by pyrolysis of spruce wood pellets, shredded TetraPak carton packaging and discarded tyres at 600 ± 500°C at the pilot plant Pyromatic, ENET Centre, Technical University of Ostrava. The sample labelled "biomass" comes from torrefaction of spruce wood (temperature 360°C) at the pilot torrefaction unit Andritz ACB (Frohnleiten, Austria), which has a capacity of 1 ton of torrefied briquettes per hour.

Char and biochar samples were analysed by method of pyrolytic gas-chromatography with mass spectrometric detection (py-GC/MS). The residue samples (100 μg) were inserted into quartz tube sealed at both ends by quartz wool. The samples were analysed by analytical pyrolysis at temperatures of 650°C (the original temperature of the input material pyrolysis) and 750°C (the temperature for detection of labile biochar portion), time 10 s, temperature increase rate was 5 C/ms. The interface between the pyrolytic unit and the gas chromatograph was heated to the temperature of 285°C in order to prevent condensation of pyrolytic products. The pyrolysate was separated at the temperature of 650 and 750°C equally at the non-polar column HP 5 ms (60 m x 0.25 mm x 0.25 μm). Identification and quantification was carried out by standards and NIST library.

Results

In char, the following groups of substances were identified: aromatic hydrocarbons, carboxylic acids, ketones, aldehydes, polycyclic aromatic hydrocarbons, nitrogen compounds, furans, pyrans, phenols. In total, in char and biochar pyrolysates, 140 organic substances were identified. Attention was focused mainly on substances with potentially dangerous properties and substances and favourable for agricultural applications of char. Substances were selected using International Biochar Initiative (IBI, 2015) and the European Biochar Certificate (EBC2012, 2016). Microphotographs (Scanning Electron Microscope, SEM) of the char of TetraPak and biochar from wood, are shown in Figure 1.

A common characteristic of char (TetraPak, tyres) and biochar (spruce wood) is the presence of aromatic hydrocarbons from BTEX (benzene, toluene, xylenes, and ethylbenzene), methylated compounds of benzene and styrene. The presence of aromatic hydrocarbons, especially benzene in char indicates the presence of black carbon. The amount of aromatics in char increases with increasing temperature of thermal decomposition (Kaal et al., 2009). This was verified by raising the temperature during pyrolysis analysis from 650°C to 750°C, at which the greatest amount of aromatic compounds was released from char. In analytical pyrolysis, almost 60% of aromatic hydrocarbons released from TetraPak char at 750°C, in the case of char from tyres, the amount was 37.4%. The least amount of aromatic hydrocarbons released from biochar from wood pellets (10.25%) and torrefied spruce wood (23.62%). The quantity of aromatic compounds obtained from char at the analytical pyrolysis temperature of 650°C was significantly lower. Biochar from wood pellets contains 4.39% of aromatic hydrocarbons and biochar of torre-

fied spruce wood contains 1.78% of aromatic hydrocarbons. Char from tyres contains about 8% of aromatic hydrocarbons and char from TetraPak 7.5%.

In all samples of char, styrene was detected. Styrene in biochar from spruce wood and pellets comes from thermal degradation of lignin, tannins and proteins (Galletti and Reeves, 1992), which was verified using the ratio E3/S (toluene/styrene) > 1 (Dignac et al., 2005). The values of the ratio E3/S for biochar from wood pellets and of torrefied spruce wood are 4.2 and 2.09. Styrene in char from tyres comes from the degradation of the original rubber (SBR – styrene butadiene rubber). The other rubber used in the production of tyres (BR – polybutadiene rubber, NR – natural rubber, IR-polyisoprene rubber) were identified in char using specific markers – 1-methyl-4-(1-methylethenyl)cyclohexene, isoprene, butadiene, 4-vinylcyclohexen, dipentene. Synthetic styrene origin of this char was confirmed by the diagnostic ratio E3/S < 1 (Dignac et al., 2005). The value of the ratio E3/S for char from tyres is 0.97. For char from TetraPak, styrene was detected in minor amounts (about 0.5%), this styrene comes from the degradation of the paper layer of the original TetraPak packaging.

Another important group of substances that have been identified in char are compounds containing phenol. Substances containing phenol were detected by analytical pyrolysis at 750°C, particularly in char from torrefaction (21.1%) and wood pellets (9.16%), where they are products of degradation of plant lignin (Galletti and Reeves, 1992). In these biochar characteristic fragments occur that identify the cleavage of the original matrix of lignin e.g. 2-methoxy-4-vinylphenol, 3-methoxy-5-methylphenol, eugenol, isoeugenol, vanillin, 2-methoxy-4-propylphenol, dimethylphenol, and methylphenoles. Using biochar analysis at the analytical pyrolysis temperature of 650°C, small amount of phenolic compounds was found – 6.7% of biochar from wood pellets and 18.9% of biochar from torrefied spruce. For char from tyres and TetraPak, substances containing phenol were not detected.

Biochar samples (from pellets and spruce wood) contain functional groups of substances – biogenic markers that make it possible to identify the type of pyrolysed fuel. These substances include substances from the group of – furans, pyrans, anhydrosaccharides, ketones and specific carboxylic acids. Anhydrosacharides are the result of thermal decomposition of cellulose (levoglucosan), hemicellulose (galactosan, manosan). Levoglucosan presence in biochar indicates uncharred material (Fabbri et al., 2012).

Decomposition products of celullose in biochar are represented by furanmethanol and cyclopentenone, 2-methylcyclopentenone (Saiz Jimenéz and De Leeuw, 1986). Biochar from wood pellets contains unique markers that make it possible to identify coniferous biomass – 7-oxodehydroabietic acid, methyldehydroabietic acid and retene. Furans (2-methylfuran, 2.5-dimethylfuran), furaldehydes, pyrans, furfural and 5-hydroxymethylfurfural in biochar pyrolysates identify original matrices of saccharides (Saiz Jimenéz and De Leeuw, 1986). The amount of fragments that characterize cellulose, hemicellulose and saccharides in biochar from wood pellets is 6.9% and for biochar of torrefied spruce wood, it is 4.23% at the analytical pyrolysis temperature of 750°C. At the temperature of 650°C, the amount of fragments characterizing cellulose, hemicellulose and saccharides in biochar from biomass is 8.74%, in biochar from torrefied wood it is 12.8%. This increase is the result of the effect of a lower temperature on the sample. The same phenomenon was observed when analysing char from peat samples (Kaal et al., 2009), where the increase in temperature leads to reduction of the fragments derived from the degradation of polysaccharides and an increase in aromatic hydrocarbons.

Benzofurans and methylbenzofurans are markers for the presence of black carbon in biochar (Kaal et al., 2009). Their occurrence is bound to charred fraction of black carbon (Fabbri et al., 2012). Benzofurans and methylbenzofurans were found only in biochar from wood pellets and torrefied spruce wood, since these compounds are present in fuels with a high content of cellulose and a high degree of aromaticity. Biochar from wood pellets (750°C) contains 1.06% of benzofurans and methylbenzofurans, while biochar of torrefied spruce wood contains 2.35%. The content of benzofurans (analytical pyrolysis at 650°C) in biochar from torrefied wood is 0.3% for biochar from wood pellets, it is 0.1%. The amount of benzofurans and methylated forms increases with the increasing temperature of thermal degradation.

Polycyclic aromatic hydrocarbons (PAHs) are produced by thermal decomposition (incineration, pyrolysis) of fuel. In char and biochar, the following PAHs were identified by analytical pyrolysis (temperature 650°C) according to the US EPA: naphthalene, acenaphthene, acenaphthylene, fluorene, anthracene, phenanthrene, pyrene, chrysene, fluoranthene, benzo(a) pyrene, benzo(ghi)perylene, benzo(k)fluoranthene, benzo(b)fluoranthene, chrysene, indeno(1,2,3-cd) pyrene, dibenzo(a,h)anthracene. In addition to that, dimethoxynaphthalenes, dimethylnapthalenes, methylated forms of fluorene and azaarenes (2.4-dimethylbenzo(h)quinoline, isoquinoline, 2.4- and 2.6-dimethylquinoline) we identified as well. The concentration of PAHs in biochar and char (at the analytical pyrolysis temperature of 750°C and 650°C) are given in Table

Tab. 1 The concentration of selected substances with the potential risk to human health in char and biochar in %

Tab. 1 Zawartość wybranych substancji niebezpiecznych dla człowieka w karbonizacie i biowęglu w %

Group of substances/char	Temperature	TetraPak	Tyres	Wood pellets	Spruce wood
Aromatic hydrocarbons	650 °C	7	8	4.39	1.78
	750 °C	59.7	37.4	10.25	23.62
Benzofurans and methylbenzofurans	650 °C	< DL	< DL	0.1	0.3
	750 °C	< DL	< DL	1.06	2.35
Polycyclic aromatic hydrocarbons according to the US EPA	650 °C	21.90	17.61	8.96	18
	750 °C	11.97	8.69	4.7	12.76
Polycyclic aromatic hydrocarbons	650 °C	219.0	176.1	89.6	
	750 °C	120.0	86.9	47.0	

1. From the table it is evident that biochar and char contains summarily the amounts of PAHs from 89.6 mg/kg (biochar from wood pellets) to 219 mg/kg (char from TetraPak). At higher temperature of the analysis (750°C), the amount of polycyclic hydrocarbons decreases for all char. At higher temperatures, in all char and biochar samples naphthalene dominates. Occurrence of naphthalene is bound to charred fraction of black carbon (Fabbri et al., 2012). The content of PAHs in individual types of char and biochar, according to the recommended evaluation methodology IBI (International Biochar Initiative) – Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil (USA) satisfies the range of 6–300 mg/kg for the concentration of PAHs in all samples. According to IBI, char with the above mentioned range for PAHs can be applied for agricultural purposes (IBI, 2015). According to the certificate and EBC recommendation (EBC2012, 2016) of biochar application on farmland, the tested types of char and biochar not qualifying for the content of hazardous PAHs. European legislation states the range in PAHs in biochar for agricultural applications from 4 mg/kg to 12 mg/kg.

Nitrogen compounds were identified mainly in biochar. The presence of nitrogen compounds in biochar pyrolysates is related to the chemical composition of the input fuel. Nitrogen compounds such as amides, amines, pyridines, pyrroles originate from the degradation of proteins and peptides. The amount of nitrogen compounds at a temperature of 650°C is about 7% for biochar from wood pellets and 3.59% for torrefied spruce wood. At a higher temperature of the analysis (750°C), the amount of nitrogen compounds decreases to 1.7% for wood pellets and 2.3% for torrefied spruce wood. The decrease in the quantity of nitrogenous substances is due to the temperature increase.

From the viewpoint of agricultural applications of char, it is appropriate that char contained nitrogen compounds. The amount of nitrogen compounds in char may affect the pyrolysis temperature, the temperature recommended is 400–500°C (Kaal et al., 2009). In this temperature range, it is assumed that a part of nitrogen is incorporated into the thermostable likely heterocyclic aromatics (amido nitrogen), where nitrogen becomes resistant to the temperature and will thus remain in the structure of char. This form of nitrogen can be utilized by microorganisms. Nitrogen that does not become a part of the heterocyclic components can be released when the temperature rises above 500°C.

Comparison of different types of char and biochar for potential agricultural applications was performed by evaluating the content of potentially harmful compounds contained in char and using substances derived from degradation of natural macro components that may be used as a source of nutrients in soil. Harmful substances were assessed using the International Biochar Initiative – Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil (IBI, 2015). The percentage of toxic, carcinogenic and therefore potentially hazardous substances in char and biochar is presented in Table 1.

The table shows that larger amounts of hazardous compounds is contained in char from TetraPak and tyres. Char and biochar prepared by technological pyrolysis in a temperature range from 600°C to 650°C contains higher amounts of organic compounds, especially PAHs that are further decomposed with increasing temperature. However, increasing the pyrolysis temperature (750°C) is not appropriate in terms of higher production of aromatic hydrocarbons, benzofurans (Table 1). Increase in the temperature (750°C) leads only to reduction of the concentrations of polycyclic aromatic hydrocarbons. In terms of improving sorption properties of soils, a very significant role is played by the content of fragments derived from the degradation of natural components such as hemicellulose, cellulose, saccharides, lignin, proteins, and peptides in char.

Unfortunately, these components were not identified in synthetic char prepared from tyres. Char from TetraPak contained them in minor amounts. They were identified in sufficient quantities only in biochar. The maximum number of fragments derived from degradation of natural components is associated with the initial temperature of the pyrolysis of the input material (650°C). The only exceptions are phenolic substances which are produced in a slightly higher amount at

750°C. Otherwise, increase in the temperature (750°C) produces fewer fragments derived from natural macro constituents. In terms of comparison of the natural components in each type of char it is clear that the largest amount of fragments is contained in char from wood pellets compared to biochar from the torrefaction of spruce wood.

Conclusions

In terms of comparison of the "residual organics" focusing on the fragments of the original bio-components in each type of biochar and char, it was found that sufficient quantity of these substances is contained only in biochar. Relatively higher concentrations of compounds fragments from bio components are associated with biochar from wood pellets. With respect to the assessment of potentially toxic and carcinogenic organic compounds for living organisms (PAHs, benzofurans and aromatic hydrocarbons), higher contents were found in char from synthetic materials (scrap tyres, TetraPak packaging) than with biochar. Char from TetraPak does not fulfil the conditions for concentrations of PAHs according to IBI (IBI, 2015), while all types of char and biochar do not meet the PAHs content according to EBC (EBC2012, 2016) (concentration of 16 PAHs < 6 mg/kg). An exception for the above mentioned substances is only represented by benzofurans and their methylated derivatives, which are produced only in biochar by thermal decomposition of the input biomass rich in cellulose and hemicellulose. In terms of an overall assessment – the assessment of toxic and potentially hazardous substances and fragments derived from natural substances that can be successfully used to improve soil quality, the most appropriate type of char according to IBI (IBI, 2015) is char from wood pellets, followed by char from torrefaction of spruce wood. There are very small differences between the content of potentially hazardous substances in char from tyres and TetraPak. Due to the absence of fragments that indicate the original bio components (lignin, cellulose, hemicellulose, etc.), these kinds char are not suitable for agricultural applications. According to EBC (EBC2012, 2016) none of analysed types of biochar and char is suitable for agricultural applications in terms of the amount of PAHs.

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Składniki organiczne w karbonizacie z pirolizy

Zawartość związków organicznych w stałej pozostałości po pirolizie wpływa na jej ekotoksyczność. Skład chemiczny karbonizatu po pirolizie zbadano w produktach toryfikacji drewna świerkowego, granulatu drzewnego, opon i opakowań typu TetraPak. Związki organiczne występujące w karbonizacie zostały zbadane pod katem zastosowania rolniczego. Próbki poddano analizie chromatograficznej metodą chromatografii gazowej z detekcją spektrometryczną masową. Zidentyfikowane związki to węglowodory aromatyczne, policykliczne węglowodory aromatyczne, furan, benzofuran, substancje zawierające fenol, kwasy benzepolikarboksylowe, substancje pochodzenia biogennego (fragmenty celulozy, hemicelulozy, białek i innych). Relatywnie wyższe stężenia biokomponentów są związane z karbonizatem z peletów. Związki organiczne, które są potencjalnie toksyczne i rakotwórcze dla organizmów żywych (WWA, benzofurany i węglowodory aromatyczne) mają wyższe stężenie w karbonizacie z materiałów syntetycznych (opony, Tetrapaki) w porównaniu z biowęglem.

Słowa kluczowe: węgiel, karbonizat, biowęgiel, piroliza, węglowodory poliaromatyczne, BTEX, styrene