Chemical Composition of Biochar from Combustion in Local Heating

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Abstract

Chemical composition of biochar from combustion in household heating was analyzed by pyrolysis gas chromatography with mass spectrometry detector. Various types of wooden briquettes used as a fuel are compared on the basis of concentrations of organic compounds identified in pyrolysates from biochar. Anhydrosaccharides, retene and chrysene can be used as organic markers. The retene/(retene + chrysene) ratio has the same range of values in biochar and in PM particles in the atmosphere. This ratio can be utilized for identification of burned biomass from the sample of biochar.

Keywords: biochar, biomass, combustion, organic markers, anhydrosaccharides, retene, py-GC/MS

Introduction

Combustion of biomass in domestic burners is considered to be the main source of pollution at the local and regional levels in Europe [1, 2]. Incomplete combustion of biomass contributes to an increase in occurrence of small particles measuring less than 10 µm (PM10–PM2.5) in the atmosphere [3]. Constituents of PM10 particles in the atmosphere also include soot defined as a mass of impure carbon particles resulting from the incomplete combustion of hydrocarbons. It is more properly restricted to the product of the gas-phase combustion process, but it is commonly extended to include the residual pyrolysed fuel particles that may become airborne during pyrolysis and that are more properly identified as chars (charcoal and in the case of biomass combustion – biochar).

Carbonaceous particles are resistant to decomposition. They become part of all environmental components (soil, sediments, water, atmosphere etc.) by means of atmospheric deposition or during utilization of energy by-products. Thus they negatively influence physico-chemical, chemical, biological and other processes in the environment [4]. Carbonaceous particles produced by incomplete combustion contain not only very toxic, carcinogenic and mutagenic substances (e.g. aromatic hydrocarbons, pyrolytic aromatic hydrocarbons, dibenzofurans, phenols etc.), but also substances without acute toxicity. Their "danger" is formed by interactions in the environment which result in the origin of toxic compounds with high reactivity. Boilers and stoves with manual loading of fuel (biomass) emit high amounts of PM particles with high content of organic compounds [3]. The low efficiency of combustion results in increased formation of tar substances (condensation products) and soot.

Boilers of Emission Class 2 according to the standard EN 303-5 (1999, 2012) with limit for solid contaminating substances of 180 mg/m3 currently belong to the most widespread combustion devices in households of the Moravian-Silesian Region (the Czech Republic) which has a high level of air pollution within Central Europe. This article is focused on an analysis of residues from combustion of various kinds of biomass in boilers of Emissions Class 2 (Viadrus) with manual loading. The residues are formed by condensed products which are deposited on the walls of the combustion chamber due to incomplete combustion.

The aim of the article is to identify the biofuel (for boilers of Emissions Class 2) which has the lowest production of hazardous organic compounds, and also to verify the validity of ratios or organic markers used for identification of PM10 sources in ambient concentrations and in biochar sampled in flue gas pipes.

Methods of analysis

The following materials were used for this study: briquettes manufactured from the conifer

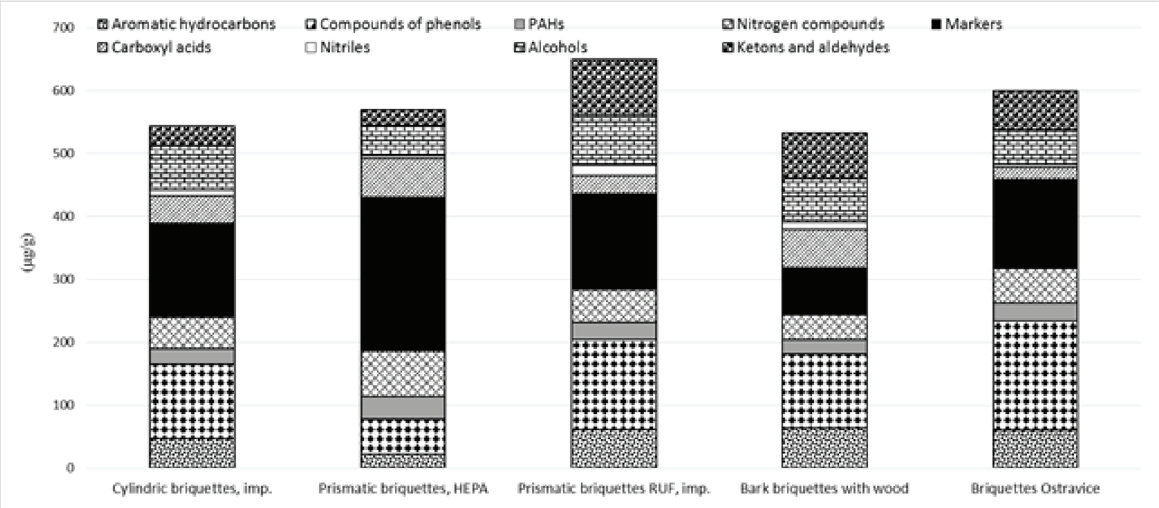

Fig.1. Sums of selected organic substances in biochar from various kind of briquettes and hard wood

Rys. 1. Sumy wybranych substancji organicznych w biowęglu z różnego typu brykietów i drewna

wood of local origin (prismatic briquettes – produced by HEPA), pure wooden chips and saw dust from soft wood (spruce) without binders and admixtures (briquettes Ostravice, imported cylindrical briquettes and prismatic RUF briquettes (Slovenia), and hard wood (local source from the Moravian-Silesian Region, Lesy CR – State Forest Enterprise) co-combusted with conifer bark briquettes (local manufacturer). After combustion of fuel, biochar was sampled and analysed by means of pyrolysis gas chromatography with mass spectrometry detection (Py-GC/MS).

Results

The Following groups of compounds were identified in pyrolysates from biochar obtained by combustion of conifers and co-combustion of hard wood and conifer briquettes: aromatic hydrocarbons, phenols, polycyclic aromatic hydrocarbons, alkanes, alkenes, alkines, alkadienes, pyrans, furans, carboxyl acids, aldehydes and ketones, anhydrosaccharides, alcohols, nitrogen compounds, alkanoates, compounds containing sulphur, sterols and their alteration products. Substantial differences in chemical composition of soot were observed for hard wood in comparison with conifer briquettes. Soot from conifer briquettes are distinguished by presence of methyldehydroabietate, dehydroabietic acid, 7-oxodehydrabietic acid, methyldehydroabietic acid and retene.

Residues from combustion of hard wood contain prevalently acids oleana-2,12-dien-18-ic, ursana-2,12-dien-18-ic, syringic acid, triterpenoides (lupeol etc.) and their alteration products, and unique derivates of syringol. The difference found for residues of soot from conifers and hard-wood trees correspond to the organic composition which was also identified for PM particles in aerosols.

Concentrations of organic compounds contained in pyrolysate were evaluated for aromatic hydrocarbons, polyaromatic hydrocarbons, phenols, aldehydes and ketones, nitrogen compounds, alkenes, alkanes, furans, pyrans, carboxyl acids. The lowest concentration of aromatic hydrocarbons (22.1 µg/mg) was determined in biochar from combustion of briquettes HEPA (CZ). Other briquettes from local sources in the Czech Republic (Ostravice) had concentration of aromatic hydrocarbons 57.6 µg/mg. Imported briquettes had concentrations of aromatic hydrocarbons in the range from 47 to 61 µg/mg. Concentrations of compounds from the group of phenols, which are thermal degradation products of lignin, range from 55.9 (HEPA) to 174.8 µg/mg in the samples of residues of local briquettes (Ostravice briquettes). For the imported briquettes, concentrations of compounds from the group of phenols were in the range from 118 to 143 µg/mg. The differences in concentrations of phenols in biochar are caused by combustion of different kinds of trees or bushes contained in briquettes.

Comparison of concentrations of polycyclic aromatic hydrocarbons (PAHs) nitrogen compounds and general organic markers was performed for biochar from combustion of briquettes. Combustion of imported briquettes (Slovenia) produced by 7.2% less of PAHs, by 20.4% less of nitrogen compounds, by 10.7% less of carboxyl acids, by 36.2 less of alkenes, by 41.5% less of compounds with content of furansand pyrans, and by 21.8%

less of general organic markers in comparison with average concentrations for local briquettes. On the contrary, imported briquettes produced 3 times more of nitriles, by 46.8% more of alcohols, by 38.5% more of aldehydes and ketones, and by approximately 32.6% more of aromatic hydrocarbons in comparison with average concentrations for local briquettes. Sums of individual concentrations are compared in Fig. 1. The remaining organic compounds (alkanes, furans, pyrans, alkenes, alkines, alkadiens) have the same concentration range for all tested briquettes.

Conjoint co-combustion of conifer bark briquettes with hard wood (local sources in the Czech Republic) produces approximately 3 times more alkanes, 1.5 times more carboxyl acids and 5 times more alkanes in comparison with combustion of briquettes produced from conifers of local sources. The source of increased concentrations of alkanes and carboxyl acids, particularly alkane carboxyl acids, can be the presence of the tree bark with high content of lipids and cuticular waxes which protect trees against negative influences (weather, evaporation of waters, freezing, parasites etc.). Alkanes and carboxyl acids are components of cuticular lipids and waxes [5]. The increased concentration of alkenes are formed by combustion, where alkenes originate by thermal change from n-alkanoles or n-alkanes [6]. Co-combustion of wood and briquettes from conifers produces by 1/3 less of nitrogen compounds, by 67% less of pyrans and furans, by 26.3% less of PAHs, and by 36.3 more of aromatic hydrocarbons compared with combustion of conifer briquettes alone. Concentrations of the remaining substances (phenols, alkadiens, anhydrosaccharides, alcohols, nitriles, alkanoates, organic markers) in biochar from co-combustion of wood and briquettes have the same concentration range as biochar from combustion of conifer briquettes.

Pyrolysates of residues were analysed with the aim to determine occurrence of unit organic markers from biomass combustion. Organic markers are unique compounds which make it possible to characterize and identify burned fuel. Combustion of biomass produces (during thermal decomposition of cellulose and hemicellulose) the specific markers - anhydrosaccharides (levoglucosan, manosan, and galactosan). Organic markers vaporize directly into smoke by processes which are similar to volatilization of water vapour or stripping [5]. Consequently, they condense on particles formed earlier. Organic markers from biomass combustion, particularly their diagnostic ratios are utilized for identification of pollution sources in PM-particles [7, 8].

Diagnostic ratios of organic markers – anhydrosaccharides and polycyclic aromatic hydrocarbons in biochar were calculated in this study and consequently compared with values of diagnostic ratios which are applied for PM particles in ambient concentrations. The diagnostic ratio of anhydrosaccharides L/M (levoglucosan/manosan) varies for biochar from combustion of wooden briquettes from conifers in the range from 2.46 to 5.92. The value of L/M ratio for co-combustion of conifer briquettes with hard wood is 3.53. The L/M ratio for identification of PM particles in aerosols originated from combustion of conifer briquettes has value around 2.5 [9].

Concentrations of retene and chrysene in biochar were used for calculation of the ratio retene/(retene+chrysene). Retene and chrysene belong to the group of polycyclic hydrocarbons. From experiments with combustion of wood of conifers and deciduous trees, it was determined that retene (methylisopropyl phenanthrene or 1-methyl-7isopropyl phenanthrene, C18H18) is produced in high concentration during combustion of wood of conifers. Retene originates by decomposition of specific diterpenoids during combustion of wood. The presence of retene in ambient concentration indicates combustion of conifers [7]. Values of the ratio retene/(retene + chrysene) for analysed biochar vary from 0.75 to 1. This range of the ratio values is very close to the value reported for emissions of PM particles in aerosols, where the value of the ratio varies from 0.83 to 1 [7, 8].

Resistant organic matter (ROM) was determined in biochar in order to characterize the part of organic matter which is not decomposed even at increased temperatures and has a high resistivity. ROM is an important carrier of black carbon. The amount of produced ROM was evaluated for individual residues on the basis of occurrence of specific markers which include compounds from the following groups: benzonitrile, benzene, toluene, naphthalene, (iso)quinoline, dibenzofurans, biphenyls, benzofurans, alkylnaphthalenes. These compounds are thermostable residues which reflect the highly condensed structure of BC (black carbon) and they are unequivocal indicators of black carbon [10]. ROM in biochar from combustion of local briquettes from conifers varies in the range from 33.9 (Ostravice) to 34.3% (HEPA). ROM in biochar for briquettes from Slovenia has slightly higher content of 31.1%. ROM content in biochar from co-combustion of conifer briquettes and hard wood is the lowest – 28.2%. The determined values of ROM in biochar from combustion of briquettes produced from conifers and from co-combustion of conifer briquettes and hard wood correspond to the range of values reported by Song et al. (2010) [11].

The determination of content of black carbon in biochar was performed by means of degree of dealkylation B/T (benzene/toluene) which allows estimation of the carbonization degree. The B/T ratio values for biochar from combustion of briquettes vary in the range from 0.53 to 0.654. The B/T ratio value for biochar from co-combustion of conifer briquettes and wood is 0.59. It is a general rule that higher values of B/T ratio are connected with higher production of benzene which represents a dominant product in carbonized component [12]. All determined values B/T ratio correspond to the values of biomass reported by Fabbri et al. (2012) [13].

Conclusions

Biofuels can be ranked on the basis of the chemical composition of biochar (with attention paid to toxic and carcinogenic substances), and the amount of resistant organic matter. Conjoint co-combustion of bark briquettes with wood (local source of fuel) belong to the most advantageous biofuels. The lower position belongs to the important cylindrical briquettes (Slovenia) and to the local conifer briquettes (Ostravice). The highest concentrations of PAHs and other dangerous organic compounds in biochar were found during combustion of local briquettes HEPA and the imported prismatic briquettes RUF from Slovenia. Analysis of specific markers (retene, chrysene and anhydrosaccharides) in biochar and calculation of diagnostic ration retene/(retene + chrysene) and levoglucosan/manosan (L/M) have shown that values of L/M ratio are not in accordance with values of L/M ratio for PM particles in the atmosphere. From this it follows that L/M ratio cannot be utilized for identification of burned fuel in biochar. The retene/(retene + chrysene) ratio has the same range of values in biochar and in PM particles in the atmosphere. This ratio can be utilized for identification of burned biomass from the sample of biochar.

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Skład chemiczny biowęgla ze spalania w ogrzewaniu lokalnym

Skład chemiczny biowęgla ze spalania podczas ogrzewania gospodarstw domowych był analizowany za pomocą chromatografii gazowej pirolizy z użyciem masowego detektora spektrometrycznego. Różne typy drewnianych brykietów zastosowanych jako paliwo zostały porównane na podstawie stężeń związków organicznych rozpoznanych w produktach pirolizy z biowęgla. Anhydrosacharydy, reten oraz chryzen były zastosowane jako znaczniki organiczne. Stosunek reten/(reten + chryzen) ma ten sam zakres wartości dla biowęgla, jak i dla ziaren pyłu zawieszonego PM w atmosferze. Wskaźnik ten może zostać zastosowany do identyfikacji spalonej biomasy z próbki biowęgla.

Słowa klucze: biowęgiel, biomasa, spalanie, znaczniki organiczne, anhydrosacharydy, reten, py-GC/MS