

## POLYCYCLIC AROMATIC HYDROCARBONS AND OTHER ORGANIC COMPOUNDS IN ASHES FROM BIOMASS COMBUSTION

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### ABSTRACT

Power generation from biomass is a substantial source of ashes, the extent of which depends on the type of biomass fuel and technology of combustion being used. The current study focuses on comparison of ashes with a special emphasis on hazardous organic compounds, particularly the polycyclic aromatic hydrocarbons (PAHs) fraction, present in ash. The reason is that ashes from combustion of wood or straw are considered as fertilizers in agricultural soils. Ash samples were therefore collected from power plants in the Czech Republic coming from combustion of wood chips, sawdust, bark and straw. The organic fraction was separated by extraction, the final determination of PAHs was performed by GC-UV. The total concentration of PAHs was found to be in the range 15-733 µg/kg. These compounds are formed during the pyrolysis stage of the combustion process by the secondary aromatization reactions in char at temperatures above 400 °C. The created PAHs are bound in the porous unburned carbon. For a more detailed qualitative analysis of other organic compounds the GC-MS was used. Higher and branched aliphatic hydrocarbons, ketones, amides and phthalates in the sample with the highest unburned carbon content were found.

**KEYWORDS:** biomass combustion, ash, PAHs, unburned carbon

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### INTRODUCTION

Industrial ashes are usually characterized by the inorganic components, physical features and unburned carbon. The organic compounds possibly present are not usually addressed. However, in the case of ashes from biomass combustion it is necessary to know not only the inorganic but also the organic harmful substances. The reason is that assessment the possibilities to utilize these ashes in agriculture is needed in the Czech Republic.

Combustion of wood chips or straw yields ashes of various compositions, given by a) the physical diversity of the incinerated material, b) the difference of the inorganic components present and, particularly, c) the type and operational conditions of the incinerator. These ashes are possible to be used either directly or after modification as fertilizer, already because they often contain a distinct share of potassium and calcium (e.g. 10-30 wt.% K<sub>2</sub>O and 17-56 wt.% CaO (Khan et al., 2009; Demirbas, 2005)). Since they are entirely realistically considered as the base of soil-friendly fertilizers (Hanzlíček and Perná, 2011), it is necessary to ascertain the contents of harmful substances in the ashes in question. A significant group of harmful substances are polycyclic aromatic hydrocarbons. These compounds are created by secondary aromatization reactions in char in the pyrolysis phase of incomplete biomass combustion at temperatures higher than 400 °C (Fisher et al., 2002). In the case of wood and straw, the composition of

incinerated mixture does not have a fundamental impact on the creation of PAHs, because the content of macromolecular components and the elemental composition are approximately the same with all woody plants. On average, the ultimate analysis values are 50 wt.% C, 6 wt.% H, 44 wt.% O and 0.1 wt.% N for hard woods and 53 wt.% C, 6 wt.% H, 41 wt.% O and 0.2 wt.% N for soft woods; for bark, the values given are 53-55 % C, 6 % H, 39-42 % O and 0.1-0.2 % N (dry ash free basis) (Ragland et al., 1991; Inari et al., 2009). Further, the elemental composition of straw is 48-50 % C, 6 % H, 42-45 % O and 0.2-0.5 % N (dry ash free basis). Consequently, an amount of PAHs, their composition, distribution between the particle and gas phases and distribution between the fly and bottom ashes are given predominantly by the type of incinerator and the process conditions (Mastral and Callén, 2000; Lu et al., 2009).

Recently, PAHs in ashes from different biofuels and municipal solid waste incineration were analyzed (Johansson and van Bavel, 2003). The sum of the 16 US EPA PAHs was found to vary from 140 µg/kg up to more than 77 mg/kg. Other authors (Zhao et al., 2008) reported the mean ΣPAH levels in the waste ashes varied widely from 4.16 mg/kg to 198.92 mg/kg. The mean amounts of carcinogenic PAHs ranged from 0.74 to 96.77 mg/kg.

Further, the Swedish EPA has developed generic guidelines for PAHs in soils. For sensitive land use

the limits are set to 0.3 mg/kg for carcinogenic PAHs and 20 mg/kg for non-carcinogenic US-EPA PAHs. For less sensitive land use with ground water protection, the limit was set to 7 and 40 mg/kg, respectively (Johansson and van Bavel, 2003). Other work by Johansson and van Bavel, 2003a, states that the average value for the total amount of PAHs in soil samples from cities in Sweden was 0.56 mg/kg. For carcinogenic PAHs the average value was 0.32 mg/kg.

According to Czech legislation on the use of auxiliary matters on agricultural soil (sediments, ashes etc.), the limit content of  $\Sigma$ PAHs is 6 mg/kg (Ministry of Agriculture of the Czech Republic, 2009). Thus, the considered ashes were examined from this aspect. The aim of this work was a) identify and determine the PAHs which could enter the soil with the biomass ashes, b) explain their formation during wood and straw combustion, and c) estimate the utility of ashes containing PAHs as fertilizers. For this purpose, samples from power plants with wood chips, sawdust, bark and straw as fuels were used.

## EXPERIMENTAL

Analyses of the PAHs were conducted using the GC-UV and GC-MS methods. The actual analyses were preceded by extractions. Moreover, unburned carbon in ashes was determined and surface measurements were carried out.

*Preparation of the extract.* The ash acquired from power plants was extracted such that 20 ml of a hexane-acetone solution (7:3) was added to 10 g of a dry sample with a grain size below 0.2 mm; the mix created was extracted by ultrasound for 30 minutes (Marvin et al., 1992; Sun et al., 2006) and subsequently shaken for 30 minutes on a shaker. Demineralized water was then added in the amount precisely needed for the separation of acetone. After preliminary analyses of both phases by the GC-UV method, the acquired n-hexane part of the extract was used for further analyses, because PAHs were not found in the water-acetone phase. The extract was not further purified. As needed, the extract was concentrated by a gentle stream of nitrogen.

*PAHs analyses.* For quantitative analyses, the gas chromatography with ultraviolet detection (GC-UV) was selected, which enables the compounds class analysis (Mostecký, 1984; Lagesson-Andrasko et al., 1998; Lagesson et al., 2000; Hatzinikolaou et al., 2006). The basis of the identification and determination of the aromatic and other organic compounds by GC-UV is that ultraviolet spectra of organic compounds in the gas phase are very well defined (Lagesson-Andrasko and Lagesson, 2005). Under appropriate conditions, the aromatics and PAHs could be monitored in the areas of UV wavelengths ~188-203 nm (single aromatic rings), ~210-229 nm (double aromatic rings) and ~240-259 nm (polyaromatics) (Lagesson et al., 2000). The class analysis of these hydrocarbons may be therefore

successfully conducted in the mixture. Also further compounds, e.g. aliphatic hydrocarbons, ketones, aldehydes and others may be identified and determined. It is important that the agreement of the reference and analyzed spectra is very good even in very different concentrations. Further, the effect of the temperature of the detector on the shape of the UV spectrum is negligible.

Analyses were conducted on a gas chromatograph with an ultraviolet detector Chrom G11 UV, Labio, a.s., Prague. The UV detector was a Quant UV spectrometer working after construction adjustments in the area 155-310 nm. (Short wavelengths in the range 155-190 nm are very important for the utilization of UV spectrometry in connection with gas chromatography, because a significant part of the absorption maxima is in the area of wavelengths shorter than 190 nm.) The spectrometer operating software was Specsoft HS, which was used for activation, treatment and evaluation of the UV data. This program was also used to display the spectra and acquired chromatographs.

Separation of substances took place on a stainless packed column (240 cm x 2 mm) with a 3 % OV-1 fixed stationary phase on 100/120 Supelcoport (Supelco), thermally stable to 280 °C. The column was heated by electrical current. The GC oven was heated from 40 °C (2 min) to 260 °C (10 min) at a rate 20 °C/min. The temperature of UV detector was 260 °C. It did not have a perceptible influence on analytic results and was selected only considering the prevention of its contamination by condensation of separated compounds. The flow rate of carrier gas, ultra-clean nitrogen, was 50 ml/min. Peaks areas and PAHs contents were evaluated by Clarity Data Apex program. In acquired chromatograms the UV spectrum of the separated compound/s was acquired for each chromatographic peak. The identification was conducted following (Lagesson et al., 2000; Lagesson-Andrasko and Lagesson, 2005). The calibration was conducted with naphthalene, acenaphthylene, phenanthrene, fluoranthene and pyrene standards (Aldrich Chemical Comp., Inc.). By GC-UV the PAHs from naphthalenes to pyrenes as a prevailing lighter fraction of PAHs were identified and quantified.

For a detailed analysis of the compounds of two extracts selected, the GC-MS method was used. The samples were adjusted using n-pentane (Mandalakis et al., 2004) to the volume of 1 ml and analyzed by GC-MS using a Thermo Scientific Trace Ultra DSQ II instrument equipped with a capillary column with a DB 5 fixed stationary phase (30 m x 0.25 mm x 25  $\mu$ m film). The GC oven was heated from 35 °C (2 min) to 300 °C (5 min) at a rate of 8 °C/min. The sampling was carried out in the splitless mode at a temperature of 250 °C, with helium as the carrier gas. The mass spectra were recorded at EI 70 eV from 40 to 600 amu. The identification of the compounds

**Table 1** Investigated ashes from incinerated wood chips and straw.

Ash No.	Incinerated material	Ash type	Ash Color	Extract designation
1	straw and alfalfa	fly	black	1-H
2	wood chips (forest)	bottom	black	2-H
3	wood chips	fly	gray-brown	3-H
4	wood chips, sawdust, bark	fly	brown	4-H
5	wood chips	fly	light brown	5-H

**Table 2** Mesoporous characteristics, unburned carbon and polycyclic aromatic hydrocarbons in ashes from the biomass combustion.

Ash No.	$S_{BET}$ (m <sup>2</sup> /g)	$V_{BET}$ (mm <sup>3</sup> /g)	Helium density (g/cm <sup>3</sup> )	Unburned carbon (wt.%)	ΣPAHs (μg/kg)
1	5.06	6.73	2.34	14.54	6161
2	7.96	-	-	9.23	733
3	2.28	-	-	2.15	249
4	2.77	5.15	2.78	0.46	148
5	1.02	-	-	0.17	15

was based on a comparison of the spectra with the NIST mass spectral library. Further, benzo(a,e)pyrenes as heavier fraction of PAHs were quantified by GC-MS through a benzo(a)pyrene standard.

*Determination of unburned carbon.* With regard to the evaluation of the methods of determining the unburned carbon in ashes (Bartoňová et al., 2008), unburned carbon was determined as the total organic carbon (TOC, wt.%) after the removal of the carbonates by their decomposition using HCl (1:1) and heating to 80 °C. For determination, a Flash 1112 EA microanalyzer (Thermo Finnigan, Rodano) was used.

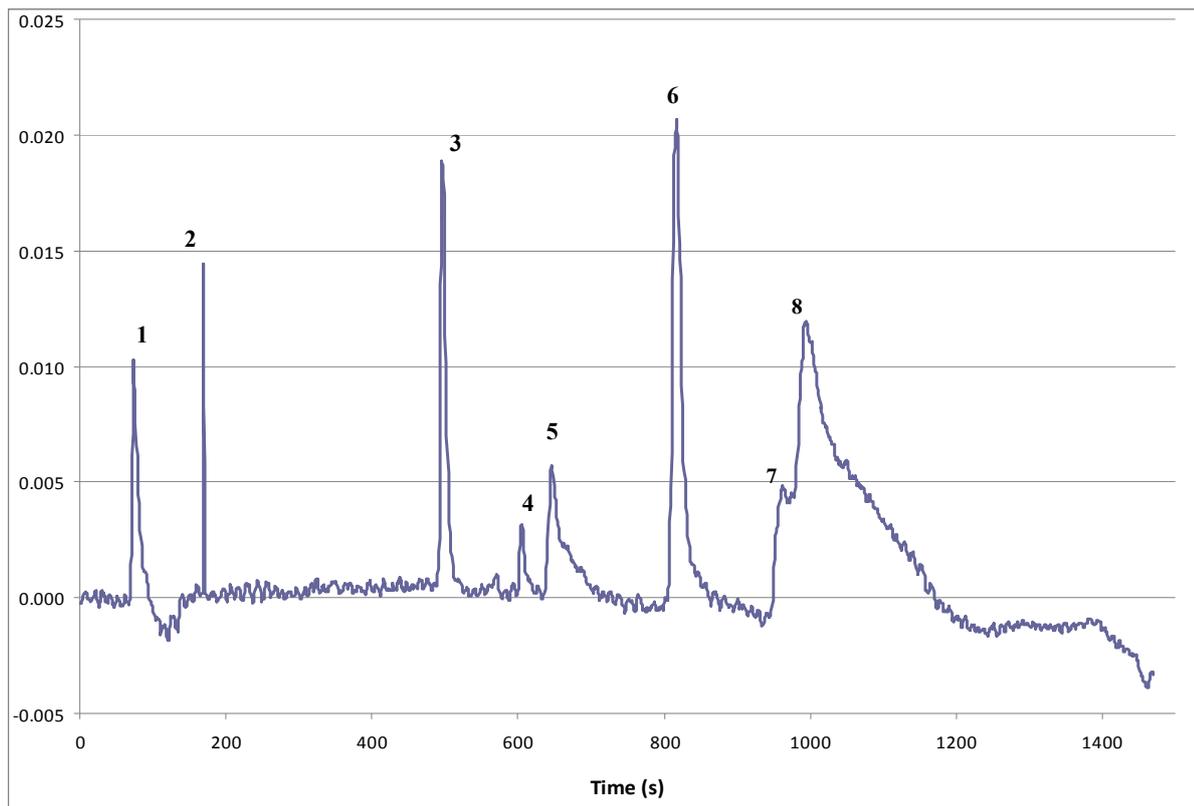
*Surface measurements of ashes.* The inner surface area  $S_{BET}$  and volume  $V_{BET}$  of those pores having radii > 1 nm were calculated from a N<sub>2</sub> adsorption isotherm at -197 °C using the Sorptomatic 1990 Carlo Erba instrument (Přikryl and Weishauptová, 2010). The adsorption isotherms were evaluated by the BET equation (Brunauer et al., 1938). The accuracy of this volumetric determination  $S_{BET}$  in the range of 1-8 m<sup>2</sup>/g was +/-10 %. Simultaneously, a helium density of chosen ash samples was determined.

## RESULTS AND DISCUSSION

PAHs analyses results. Ashes from wood chips and straw burning from five power plants in the Czech Republic operated in the South Bohemian, Pilsen and Olomouc regions were investigated. A list of the samples analyzed is provided in Table 1. The ashes were formed under various operational conditions and contained different amounts of unburned carbon, had different inner surface area  $S_{BET}$  (see below), and

contained different amounts of PAHs as GC-UV analyses showed. A typical GC-UV chromatogram of n-hexane extract is shown in Figure 1. Besides PAHs and toluene, aliphatic ketones were identified according to characteristic absorption triplet at 183-200 nm in UV spectra of peaks 1 and 2 (Lagesson et al., 2000). PAHs were found in all of the ashes, even in those whose content of unburned carbon was very low (Nos. 3-5, Table 2). It is known that in the course of the combustion of lignocelluloses the PAHs are created, but the question is how at the high temperatures of combustion these hydrocarbons remain in the resultant ash. It is likely that they are preserved in the porous system of the unburned carbon, which is a typical component of ash, because the process parameters of the combustion are never set ideally. The amount of unburned carbon in the ashes and their inner surface area  $S_{BET}$  were therefore monitored as well. If this inner surface area grew with the amount of unburned carbon and at the same time with the unburned carbon also the PAHs content increased, it would probably mean that these hydrocarbons are preserved in the porous system of the unburned carbon. The results are summarized in Table 2. As expected, in considered samples the PAHs from naphthalenes to pyrenes were prevailing. But also benzo(a,e)pyrenes were identified by GS-MS in samples Nos. 1-3. Because of their hazardous potential, these compounds were quantified by GS-MS. Samples Nos. 1, 2, and 3 contained 382, 30, and 20 μg/kg benzo(a,e)pyrenes, resp. These quantities are included in ΣPAHs in Table 2.

It can be seen that ashes with higher content of PAHs and unburned carbon (Nos. 1 and 2) also had greater surface areas  $S_{BET}$  in comparison with the other



**Fig. 1** GC-UV chromatogram of n-hexane extract 1-H from ash No. 1 (Table 1) at wavelength 260 nm. Peaks: 1 – n-hexane and aliphatic ketone, 2 – toluene and aliphatic ketone, 3 – naphthalene/naphthalenes, 4 – acenaphthylene, 5 – phenanthrene/phenanthrenes, 6 – fluoranthene/fluoranthenes, 7, 8 – pyrenes.

ashes with a lower content of the considered compounds (Nos. 3-5) and, further, that the PAHs content increased with the unburned carbon. It could mean that at least a part of the created PAHs had been preserved in the porous system of the unburned carbon, but it is necessary to take into account also other data.

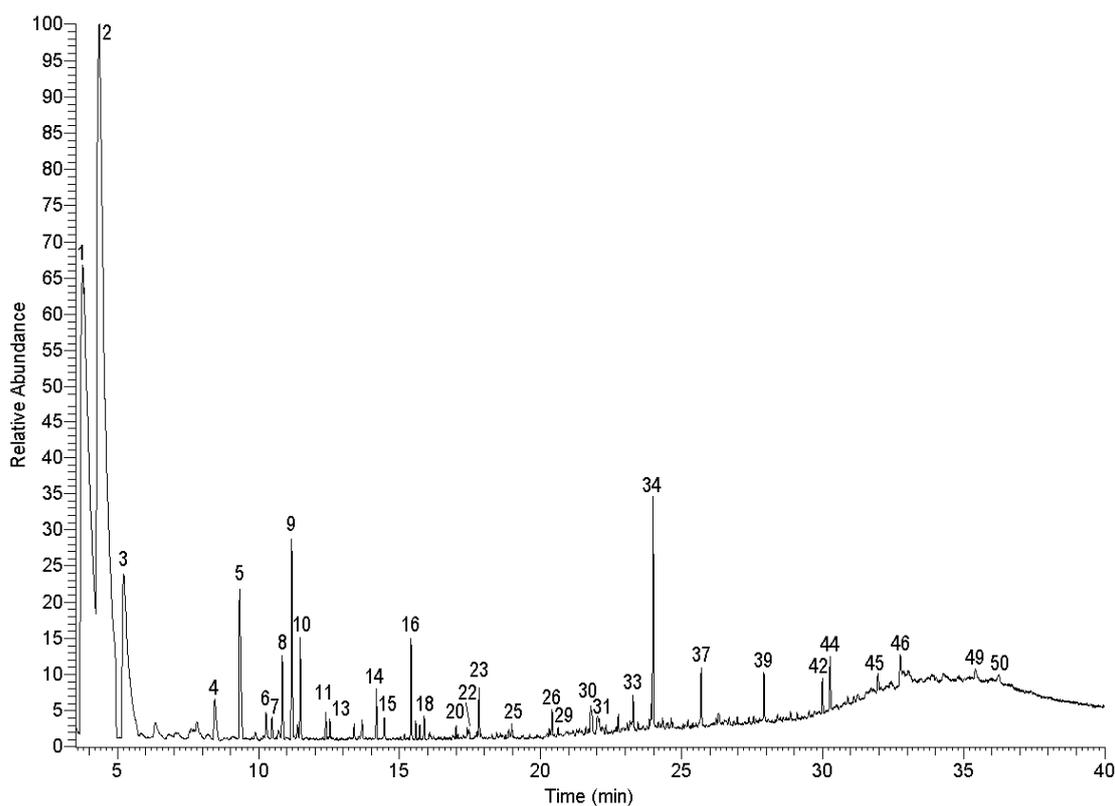
*Formation of unburned carbon.* Wood and straw are lignocelluloses comprised of cellulose, hemicelluloses and aromatic lignin. It arises already from this composition that in the course of pyrolysis and incomplete combustion of the pyrolysis products not only aromatic and PAHs can be created, but that they can be created simultaneously with the carbon porous system formation. The reason is that an important product, primary char, at temperatures above 400 °C succumbs to the aromatization process, and chars are always porous. The char created is later imperfectly incinerated, so that unburned carbon is formed as a component of the ash.

Already the color of the ash indicates the presence of unburned carbon. In the case of ashes from wood or straw, the color of the ash reflected the content of unburned carbon. Black ashes (Nos. 1 and 2, Table 1), as expected, had the highest unburned carbon content (determined as TOC), the greatest

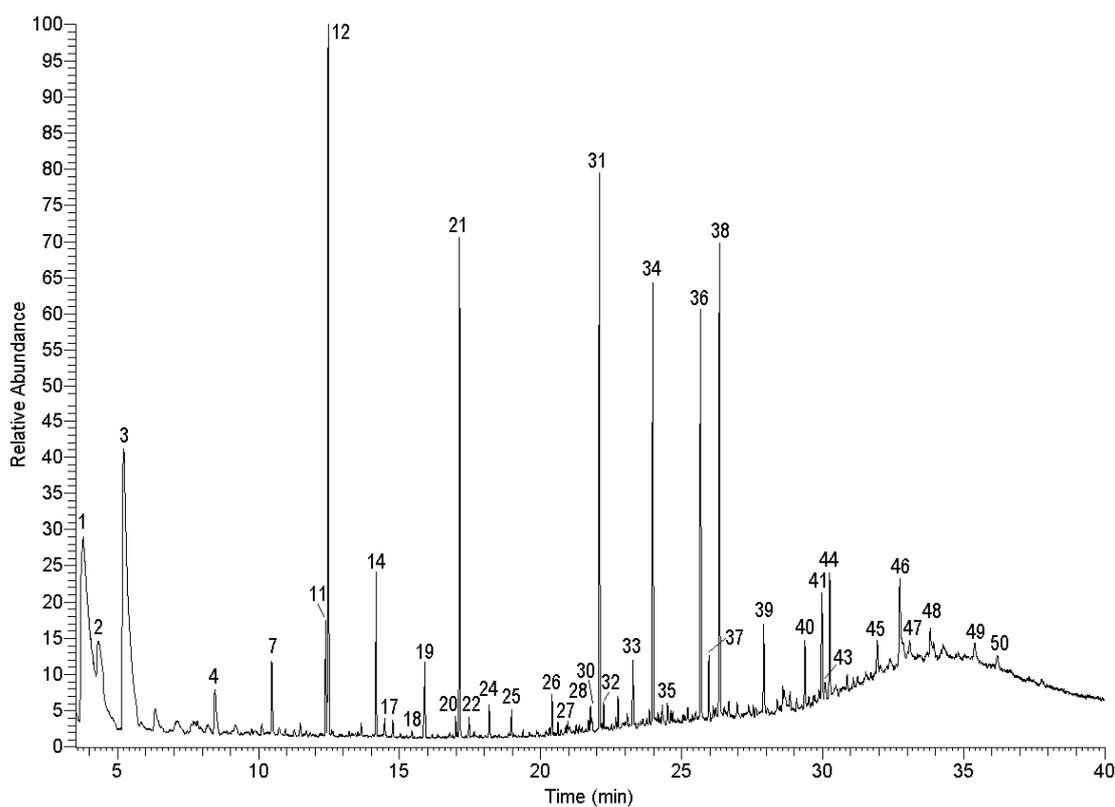
inner surface area  $S_{BET}$  and relatively high PAHs content (Table 2). In the grey-brown and brown colored ashes (Nos. 3-5, Table 1), a lower to distinctly lower content PAHs was found, just like the inner surface area  $S_{BET}$  and unburned carbon content (determined as TOC) (Table 2). Nevertheless, also these ashes contained the monitored PAHs, which means that also under the conditions of effective combustion these compounds are created and preserved in the mass of the ash. In order to explain this phenomenon, the n-hexane extracts of two selected ashes were investigated.

*Formation and preservation of PAHs.* Two contrasting ashes Nos. 1 and 4 (Tables 1 and 2) with a different unburned carbon content, mesoporous characteristics and PAHs content were further examined. The GC-MS method was used for a detailed identification and determination of the individual components. The chromatograms made are shown in Figures 2 and 3; the results are summarized in Table 3.

It is evident already from Table 2 that ash No. 1 contained substantially more unburned carbon in comparison with ash No. 4 and also had greater  $S_{BET}$ . This is reflected in the results presented in Table 3. The extract from ash No. 1 (1-H) contained higher and



**Fig. 2** TIC GC-MS chromatogram of n-hexane extract 4-H from ash No. 4. Identified compounds are in Table 3.



**Fig. 3** TIC GC-MS chromatogram of n-hexane extract 1-H from ash No. 1. Identified compounds are in Table 3.

**Table 3** Compounds identified by GS-MS in extracts 1-H and 4-H.

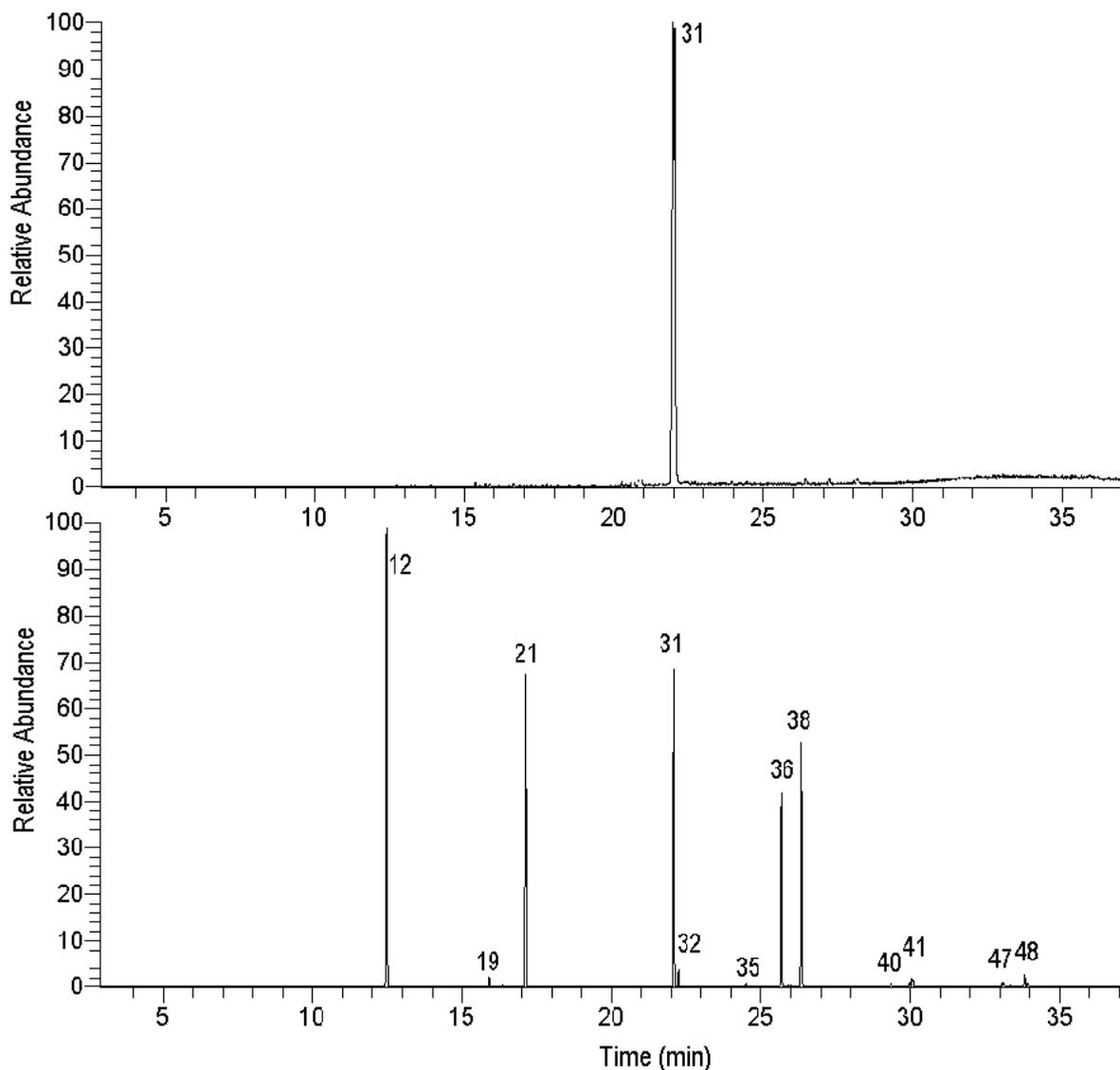
Identified compound	Rel. %	
	4-H	1-H
1 Toluene	17.55	18.24
2 4-Methyl-3-penten-2-one (mesityl oxide)	55.83	4.21
3 4-Hydroxy-4-methyl-2-pentanone (diacetone alc.)	9.44	21.75
4 Decane	1.21	1.3
5 3,5-Dimethyl-2-pyrazolin-1-carboxamide	2.58	-
6 2-Hydroxy-3,5,5-trimethylcyclohex-2-enone	0.32	-
7 Undecane	0.61	0.96
8 2,6-Dimethyl-2,5-heptadien-4-one	0.92	-
9 3,5,5-Trimethyl-2-cyclohex-2-enone	2.15	-
10 2,6-Dimethyl-6-nitro-2-hepten-4-one	0.89	-
11 Dodecane	0.71	1.13
12 Naphthalene	-	8.55
13 2-Methyl-4-octenal	0.26	-
14 Tridecane	0.94	1.56
15 2-Methyl-5-(1-methylethenyl)-2-cyclohexen-1-one	0.21	-
16 5,5,8a-Trimethyldecalin-1-one	0.73	-
17 Methylnaphthalenes	-	0.41
18 Tetradecane	0.2	0.22
19 Biphenyl	-	0.57
20 Cedrane	0.1	0.19
21 Acenaphthylene	-	5
22 Pentadecane	0.07	0.23
23 2,3-Dihydro-3,4,7-trimethyl-1H-inden-1-one	0.38	-
24 Dibenzofuran	-	0.38
25 Hexadecane	0.09	0.27
26 Heptadecane	0.19	0.45
27 2,6-Diisopropyl-naphthalenes	-	0.33
28 Dibenzothiophene	-	0.14
29 Branched alkane	0.06	-
30 Octadecane	0.09	0.3
31 Phenanthrene	0.07	5.91
32 Anthracene	-	0.35
33 Branched alkane	0.27	0.78
34 Dibutyl phthalate	1.78	4.95
35 Phenyl-naphthalene	-	0.29
36 Fluoranthene	-	5.13
37 Branched alkane	0.44	0.71
38 Pyrene	-	5.62
39 Branched alkane	0.38	1.06
40 Benzo(a)anthracene	-	0.93
41 Cyclopenta(cd)pyrene	-	1.52
42 Branched alkane	0.31	-
43 Chrysene	-	0.27
44 Unspecified phthalate	0.42	1.54
45 Branched alkane	0.16	0.63
46 13-Docosenamamide	0.35	1.31
47 Benzo(k+b)fluoranthenes	-	0.98
48 Benzo(e+a)pyrenes	-	0.67
49 17a,21b(H)-30-Norhopane	0.12	0.7
50 17a,21b(H)-Hopane	0.17	0.48

branched aliphatic hydrocarbons, toluene, mesityl oxide, and significant amounts of diacetone alcohol, phthalates and PAHs. On the other hand, the extract from ash No.4 (4-H) contained from the PAHs only phenanthrene, but many more aliphatic ketones, with the dominant compound being mesityl oxide. Amounts of higher and branched aliphatic hydrocarbons, toluene and phthalates were comparable in the two extracts. The difference found in the number and amount of PAHs is proven by Figure 4 (a single ionic monitoring).

It can be explained such that the own combustion of lignocelluloses is preceded by their pyrolysis, in which volatile combustible matter is created from the polysaccharides and polyphenols while formed aromatics, aliphatic ketones, higher and branched aliphatic hydrocarbons, and phthalates remain into char; through further aromatization of the char the PAHs are formed. In the subsequent imperfect oxidation of the volatile matter, CO<sub>2</sub>, CO, NO<sub>2</sub>, hydrocarbons (methane, benzene, toluene and others) are created; also particulate matter is formed. Simultaneously, also through imperfect oxidation, unburned carbon is created in the char. In the porous texture of the unburned carbon, a certain proportions of the PAHs, aliphatic ketones, higher and branched aliphatic hydrocarbons and phthalates are preserved. According to the conditions of the pyrolysis and combustion, more or less unburned carbon is created and more or fewer PAHs are formed, but they are always formed. In accordance with that, the amounts of these hydrocarbons in the resultant ash then differ. Also the amounts of aliphatic ketones differ. It seems that the key factors of mentioned compounds formation are the conditions of pyrolysis – heating rate and residence time while the key factor of unburned carbon creation is the conditions of combustion.

*Pyrolysis stage of combustion.* Besides cellulose, wood and straw have hemicelluloses as polysaccharides with various building units, namely monosaccharides with low polymerization abilities, e.g. glucomannan and glucuronoxylan. Hemicelluloses form a cementing layer between the cellulose macromolecules, and lignin binds to them. Lignin differs greatly from cellulose and hemicelluloses, because it is a macromolecular substance of an aromatic nature, whose base is a hydroxyl phenyl propyl unit with a hydroxyl and methoxyl functional group. Approximately 70 % of the wood complex is formed by the polysaccharide part, 25-27 % by the aromatic part and 3-5 % by the accompanying components (resins, terpenes, fatty acids, alcohols, proteins and inorganic compounds) (Sjostrom, 1993).

From this recapitulation of the chemical description it is clear that the oxidation of the wood/straw components must be preceded by their pyrolysis, providing in the primary step (200-400 °C) smaller molecules forming a volatile matter, further



**Fig. 4** SIM GC-MS chromatograms ( $m/z=166+178+202+228+252+276+278$ ) of PAHs in n-hexane extracts 4-H (upper) and 1-H (below) from ashes Nos.4. and 1. Identified PAHs are listed in Table 3.

oxidizable. In the primary pyrolysis, methane, aldehydes, ketones, organic acids, alcohols and phenols are created as the main volatile products capable of cracking and/or oxidation in the subsequent phase of combustion process (Liu et al., 2009). Polysaccharides and lignin are pyrolyzed in different ways. As their volatile products, wood polysaccharides form anhydrosugars, furans, aldehydes, ketones and carboxylic acids. Contrary, the volatiles from lignin mainly consist of low molecular aromatic compounds with 4-hydroxyl-3-methoxyphenyl units (guaiacyl units). In more detail, cellulose/hemicellulose-derived pyrolysis products are levoglucosan,  $C_2$ - $C_3$  carbonyls, furans and formic and acetic acids. Lignin-derived pyrolysis products are guaiacols, further, catechols and *o*-cresols, further, phenol and *p*-cresol, and formic and acetic acids

(Hosoya et al., 2009). Under incomplete combustion conditions, mainly water, CO, CO<sub>2</sub>, H<sub>2</sub>, and light hydrocarbons are created from these volatiles.

Nevertheless, primary pyrolysis yields also a solid residue – primary char. Unlike the volatiles, this char is formed due to structural changes in polysaccharides and lignin. Changes in cellulose and hemicellulose are caused mainly by the loss of aliphatic components and the formation of aromatic components; lignin shows a slight increase in aromatic carbon throughout the heating as there is formation of aromatic carbon from aliphatic carbon and practically no decomposition of the aromatic components (Rutherford et al., 2005). These changes begin at relatively low temperatures, e.g. around 250 °C (Baldock and Smernik, 2002; Czimeczik et al., 2002). Similarly, coal originated from wood/plant

substances under very mild thermal conditions (Straka and Náhunková, 2009). During the secondary pyrolysis of the created char (above 400 °C) an aromatization process continues and PAHs structures are formed. The secondary char created through secondary pyrolysis is further incompletely oxidized, but with the creation of unburned carbon with adsorbed PAHs.

*Combustion of biomass.* Regarding the work (Khan et al., 2009), combustion process takes place in several stages, which partially overlap:

- heating of wood or straw to 200 °C – drying and thermal activation of lignocellulose,
- primary pyrolysis – the release of volatile combustible matter in the interval of 200-400 °C and the creation of primary char,
- incomplete combustion of volatile matter and particulate matter formation,
- secondary pyrolysis – an aromatization process in primary char at >400 °C to form secondary char with PAHs,
- incomplete combustion of secondary char and the formation of ash with the unburned carbon with PAHs.

A significant property of wood and straw for the combustion itself is the distinct proportion of volatile matter (65-85 %, dry basis (Jenkins et al., 1998), typically 75 % (Khan et al., 2009)), which is released between 200 and 400 °C during the primary pyrolysis of lignocellulose as a mixture of combustible gases. Another combustible gas is created at temperatures above 400 °C during the aromatization reactions in char and contains predominantly CO, CH<sub>4</sub> and hydrogen. These combustible gases then along with the air supplied under the grate of the incinerator are subjected to primary combustion. During that, however, not all of the combustible components are burned, because under operational conditions there is not usually enough oxygen or a sufficiently high temperature for that. If there is insufficient oxygen, complete combustion cannot occur and particulate matter is created. On the other hand, if too much air is driven under the grate, the flame cools too much and part of the volatile combustible material is discharged again in the form of particulate matter. The amount of this substance substantially decreases if the combustion chamber is reasonably heat-insulated and secondary air mixes in the flame at a certain distance above the grate, which allows the final burning of the as-yet unburned gases by secondary combustion.

Unburned carbon as a component of the ash is created during the imperfect combustion of secondary char as an unburned porous share of this char. Since secondary char contains also PAHs, which are easily adsorbed on the carbonaceous sorbents (Yang et al., 2006) including unburned carbon (Bartoňová, 2010), a part of them is preserved in the porous system of the unburned carbon. Proof of this is the finding that the

content of PAHs in ash increased with the unburned carbon content (Table 2) and, further, that the inner surface area  $S_{BET}$  in ashes with a relatively higher unburned carbon content (Nos.1 and 2 – 14.5 and 9.2 %, resp.) was greater than in the other ashes with low unburned carbon. It can thus be said that the PAHs created are bound in the porous system of the unburned carbon. This conclusion agrees with the finding (Cornelissen et al., 2006). (Similarly, above-mentioned particulate matter is capable of adsorbing aromates with 5 and 6 aromatic rings (Mastral and Callén, 2000)).

*Surface properties of ashes.* With the contrasting ashes Nos. 1 and 4, the volume of the pores  $V_{BET}$  was comparable, but ash No. 4 had a smaller inner surface area  $S_{BET}$  (Table 2). That means that the distribution of the mesopores of this ash (with very low unburned carbon) was as against ash No. 1 (with a high unburned carbon) shifted towards pores of a greater diameter. At the same time, the helium density of ash No. 4 was perceptibly higher than that of ash No. 1. That means that the consequence of the lower unburned carbon content is, as expected, a higher true density of the ash and a reduction of the mesoporous system.

*Use of ashes as fertilizer.* The content of PAHs found in ashes Nos.2-5 was in a range 15-733 µg/kg, but in ash No. 1 an amount 6161 µg/kg was found, i.e. more than 6 mg/kg. This ash also had high unburned carbon content, 14.54 %. From the above-mentioned regulations of Czech legislation (Ministry of Agriculture of the Czech Republic, 2009) it follows that the limit content of ΣPAHs in substances improving soil is 6 mg/kg. This limit value also applies to ashes or fertilizers prepared from ashes, because these are auxiliary substances improving agricultural soil. Probably, if the unburned carbon content in ash is less than approximately 9 %, the PAHs content is distinctly lower than the mentioned limit, because it is in a range 0.015-0.733 mg/kg. It can be concluded that ashes from the combustion of wood and straw could be considered as fertilizers but that it is necessary to monitor them and always determine the unburned carbon content in the given ash. If it is greater than 9 %, it is necessary to modify the ash or prepare from it a fertilizer with a content of PAHs corresponding to the mentioned limit.

## CONCLUSION

The content of polycyclic aromatic hydrocarbons in five ashes from various power plants in the Czech Republic was monitored. Their concentration in ashes was low, 15-733 µg/kg with unburned carbon content 9 % and below 9 %. If however the unburned carbon content in the ash increased to 14.5 %, the ΣPAHs increased very distinctly, above 6 mg/kg. It was found that the created PAHs are bound in the porous system of the unburned carbon. It can be suggested that ashes from combustion of wood and straw with unburned

carbon content less than 9 % can be considered as fertilizers.

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