Journal of Chemical Technology and Metallurgy, 58, 2, 2023, 376-384

FATE OF ORGANIC POLLUTANTS DURING COMBUSTION IN COAL-FIRED POWER PLANTS

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Received 25 July 2022
Accepted 30 September 2022

ABSTRACT

Thermoelectric power plants (TPPs) closure in Bulgaria will not automatically solve problems of combustion wastes management. Presently, in their majority, fly ashes (FAs) and slags are considered as potential environmental pollutants, especially due to the presence of toxic metals and polycyclic aromatic hydrocarbons (PAHs). Except of PAHs, minor consideration has been given to the environmental risks of organic constituents, preserved, or transformed during or after combustion. The scope of this study is: (i) to carry out a comprehensive analysis of the main biomarkers in the extractable organic matter (EOM) from Bobov Dol TPP feed coal blend and FAs from the three electrostatic precipitator (ESP) rows; (ii) to assess potential pollutants in the FA organic extractable portion.

The GC-MS data have pointed out that in combustion wastes many coal biomarkers were still capable of identification. After combustion, the biomarker assemblage generally has kept its signature as hydrocarbons from all samples were strongly dominated by diterpenoids (> 50 rel. % of the total identified species). However, some peculiarities were distinguished. Namely, n-alkanes yields, and distributions were affected by combustion as the total amounts have augmented and their distributions were shifted to the lighter homologues. The feed coal blend PAHs set was featureless, as only phenantrene (Phe) and perylene (Per) were detected. PAHs amounts in FAs were even lower, in the ESP rows only Phe was registered. The total PAHs amounts were compared to the norms for soils fixed by the Bulgarian legislation and magnitudes determined were below the PAHs backgrounds for soils.

The results highlight the role of coal extractable organic matter on the content and composition of organic pollutants in TPP combustion waste. Hence, beside elemental analyses (i.e., sulfur) of coal blends, monitoring for organic species may help to reduce potential environmental risks from FAs disposal.

Keywords*: combustion wastes, fly ash, hydrocarbons, PAHs, biomarker assemblage.*

INTRODUCTION

The National Energy and Climate Plan 2021-2030 in Bulgaria, due to the new "green deal" in Europe, previews reduction in the energy portion from coal-fired thermoelectric power plants (TPPs). However, their shutting down will not automatically solve the problems of combustion wastes management. Presently, in their majority, the TPPs wastes are considered as potential environmental pollutants. On the other hand, some studies have pointed out that they could be used as a feedstock for value-added materials [1]. Fly ashes (FAs) minerals and toxic metals in Bulgarian TPPs combustion wastes are well documented [2, 3], while the organic components are somewhat neglected. It is explained by the low amounts of organic matter and necessity of multi-step analytical protocol. The successful analysis requires sophisticated equipment for identification and quantification of compounds in trace amounts and interdisciplinary knowledge. However, previous studies have shown preservation of organic compounds, as well as interaction and adsorption of emissions on FA combustion wastes [4 - 7]. Therefore, their potential environmental risks (i.e., from polycyclic aromatic hydrocarbons (PAHs)) also depend on the sources and maturity of coal used in TPPs [8, 9].

A suite of recent studies addressed the composition of biomarkers in FAs by applying geochemical proxies, i. e. PAHs [7 - 10]. The aims of the present investigation are: (i) to carry out a comprehensive analysis of the main coal biomarkers, i.e., *n*-alkanes, di- and triterpenoids, hopanes, PAHs, etc., in Bobov Dol TPP feed coal blend and FAs from the TPP three consecutive electrostatic precipitator (ESP) rows; (ii) to assess potential pollutants in the FA extractable organic matter, paying attention mainly on PAHs.

EXPERIMENTAL

Samples

Bobov Dol TPP with its total capacity of 630 MW and three units burns Neogene lignites and Paleogene subbituminous coals from several Bulgarian coal deposits (Table 1). FAs samples were collected next to ESP rows at 138°C. The temperature difference between consecutive ESP rows was 3 - 4°C. All data were valid for the moment of the sampling.

Analytical methods

The proximate analysis was carried out as follows: analytical moisture (W^a) according to ISO 1015:1975 [26], ash content (A^d) according to ISO 602:2015 [27] and volatile matter (VM^{daf}) according to ISO 20360:2020 [28]. The ultimate analysis, i.e., carbon (C %) and hydrogen (H %) determination was performed on a LECO-CHN-4000 instrument. The total organic carbon (TOC) was determined by using Eltra Helios C/S analyzer. The samples were preliminary pre-treated with H_3PO_4. The measurements were duplicated, and the analytical error is less than 5 %. All samples bulk characteristics are gathered in Table 2.

The extractable organic matter (EOM) compositions of feed coal blend and FAs were determined using a protocol, developed during a previous study on Bulgarian coals of different rank [8]. Briefly, samples (*ca:* 5 g) were extracted by DCM for 1 h at 75°C and a pressure of 75 bar in a Dionex ASE 200 instrument. Asphaltenes were precipitated and the hexane-soluble portion (maltenes) were separated into saturated hydrocarbons (I fr.), aromatics (II fr.) and polars (NSO) by a Köhnen-Willsch medium-pressure liquid chromatography (MPLC) instrument [11]. The first two fractions were analyzed by gas chromatography-mass spectrometry (GC-MS).

Samples were analysed by a Trace-GC equipped with a DB-5MS silica capillary column (30 m, 0.25 mm i.d., 0.25 µm film thickness) and coupled to a Finnigan MAT GCQ mass spectrometer. Oven temperature was programmed from 70°C to 300°C with steps of 4°C min^{-1}, followed by an isothermal period of 15 min. Helium was used as a carrier gas. The device was set in EI mode with a scan rate of 50 - 650 Daltons (0.7 s scan^{-1}). Identification

Table 1. Stratigraphic age, reflection index and Rock Eval data of coals blended for combustion in Bobov Dol TPP.

Coal deposit	Stratigraphic age	Ro, %	Rock Eval data				
			TOC	S_1	S_2	T_{max}	HI
			wt.%	mg HC/g		°C	mg HC/g TOC
Chukurovo	Late Miocene	0.20	47.0	10.0	140.0	366	218.0
Stanianci	Late Miocene	0.20	44.4	3.9	63.3	415	142.6
Beli Breg	Late Miocene	0.22	49.3	n.d.	n.d.	360	161.0
Oranovo-Simitli	Late Miocene	0.34	56.0	0.7	45.5	409	81.2
Bobov Dol	Late Oligocene-Early Miocene	0.43	63.1	3.4	75.2	410	119.0
Pernik	Late Oligocene-Early Miocene	0.46	54.2	1.6	114.1	410	211.0
Bourgas	Late Eocene	0.43	54.4	2.9	130.6	421	240.1

n.d. - no data

Table 2. Feed coal blend and FAs bulk characteristics, yields of extractable organic matmer (EOM) and fractional compositions.

Sm.	ESP	TOC	Proximate analyses, %			Ultimate analyses, % ^{daf}					Yield of EOM		Fractional composition of EOM, %			
	Row	[%]	W^a	A^{daf}	VM $_{daf}$	C	H	N	S	$O^{diff.}$	mg kg^{-1}	mg/gTOC	I fr. (Ali).	II fr.(Arom.)	NSO	Asph.
Feed coal blend		31.1	22.6	34.2	14.6	44.0	7.4	1.1	2.3	45.2	8.60	27.67	6.1	4.5	56.3	33.1
Fly ash	1	1.4	0.1	99.0	-	0.7	0	0	0.5	< 0.01	0.05	3.62	28.6	9.4	36.0	26.0
	2	0.9	0.1	99.0	-	0.6	0	0	0.8	< 0.01	0.14	15.64	26.1	2.4	54.6	16.9
	3	0.7	0.1	99.1	-	0.6	0	0	1.0	< 0.01	0.07	10.20	25.7	6.5	49.9	17.9

was based on retention time and comparison of MS with published data. Absolute concentrations were determined by inner standard application (deuterated *n*-C_{24} alkane for the saturated hydrocarbon fractions, and 1,1'-binaphthyl for the aromatics).

RESULTS AND DISCUSSION

Coal biomarkers in feed coal blend and in FAs samples

In EOM of the samples, the sums of NSO+asphaltenes predominate the fractional compositions, a proof for the presence of polar constituents (Table 2). Aromatic hydrocarbons are present in lowest amounts. An increase in the proportion of saturated hydrocarbons after combustion is recognizable, from 6.1 % to 25 - 28 % (Table 2).

Published data have pointed out that many coal biomarkers could survive combustion [6]. In EOM of the FAs *n*-alkanes, terpenoids, hopanes, etc. were identified and quantified, all-in comparison with feed coal blend organic extract (Tables 3 and 4). Combustion has influenced the yield and *n*-alkanes composition. The distribution curves for FAs samples demonstrated well expressed shifts to the shorter-chain members (Fig. 1). Respectively, the rel. % of the long-chain alkanes has dropped to 32 % at the expense of the shorter homologues, from 3 % to 20 % for FAs (Table 3). Differences in *n*-alkanes composition are also reflected in the calculated geochemical indices (i.e. Carbon Preference Index (CPI) = $[(C_{25}\text{-}C_{33})_{odd}/(C_{24}\text{-}C_{32})_{even} + (C_{25}\text{-}C_{33})_{odd}/(C_{26}\text{-}C_{34})_{even}]/2$). High CPI of 3.87 was obtained for the feed coal blend, whereas CPI of FAs samples ranged from 1.31 to 2.05 (Table 3). The values proved enrichment in "even" numbered homologues in FAs comparing to the feed coal blend. The changes during combustion are also reflected by the ratio of short-long-chain alkanes (0.05 for the feed coal blend and 0.45 - 0.63 for FAs). The highest S/L value was obtained for FAs of the last ESP row, 0.63 (Table 3).

EOM biomarker assemblages expressed in rel. %, have visualised the fact that the highest changes occurred in the *n*-alkanes abundance (Fig. 2). Due to combustion their relative portions have increased by more than 20 rel. % and reached up to a third of the total FAs EOM identified. In addition, the *n*-alkanes distribution was strongly affected by combustion. The *n*-alkanes

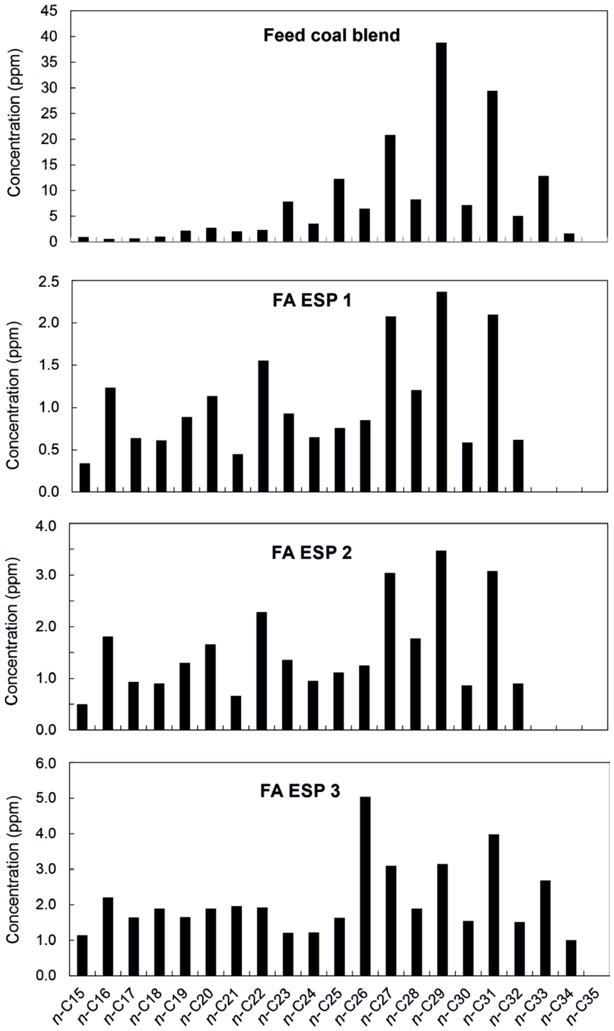

Fig. 1. *n*-Alkanes distributions according to the number of carbon atoms in the chain.

patterns of EOM from feed coal blend samples were dominated by long-chain homologues (*n*-C_{27} to *n*-C_{31}, maximizing at *n*-C_{29} or *n*-C_{31} [12]. Such distribution pattern is characteristic for terrigenous organic matter (Type III kerogen). Respectively, the rel. % of the long-chain homologues in the feed coal blend was high (63 %, Table 3).

All tracked coal biomarkers series are given in Table 4, including compounds typical for low rank coals: sesqui-, di-, triterpenoids, hopanoids, etc. Saturated and monounsaturated sesquiterpenoids (i.e., C_{14}, C_{15} compounds) related to the cadinene, eudesmane and drimane types were identified. Aromatic sesquiterpenoids were dominated by curcumene, cuparene, cadalene/isocadalene structures. The strong dominance of diterpenoids, especially of 16α(H)-phyllocladane and simonellite in the hydrocarbon fractions is well documented for Neogene coals from the Balkan Peninsula [13 - 17]. Hopane distribution with the presence of ββ-hopane stereo isomers, dominance at H_{31}αβ R epimer over H_{31}αβ S one is characteristic for the immature coals, used for feed coal mixture preparation. Triterpenois, des-A-triterpenois, and their aromatized derivatives are biomarkers for angiosperm vegetation in coal forming organic matter. All coal biomarkers and their sources are well known and described in the specialized literature (see above cited and references therein).

The total amounts of EOM and contents of different biomarker series are several folds higher in the feed coal

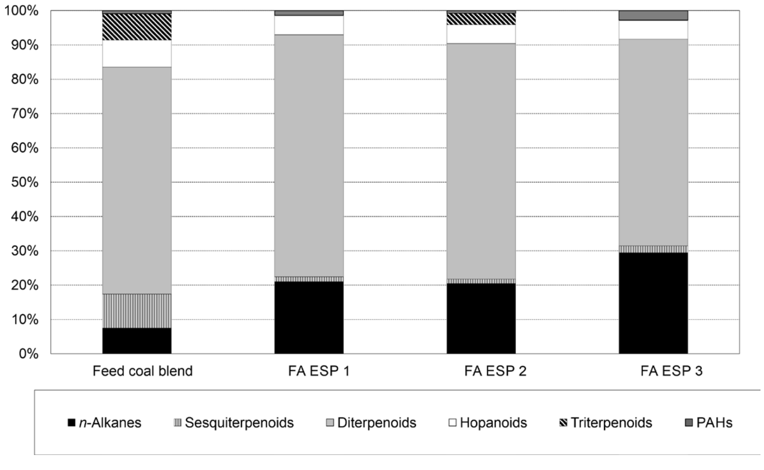

Fig. 2. Biomarker assemblages of feed coal blend and FAs from the three consecutive rows of the ESP, in rel. %.

Table 3. *n*-Alkanes content and distribution of Bobov Dol TPP feed coal blend and FAs from the consecutive ESP rows.

Sm.	ESP row	Content			n-Alkanes distribution, %			Ratios	
		mg/gTOC	mg kg^{-1}	ppm	Short-	Mid-	Long-	CPI	Short/Long
					n-C_{15}-n-C_{19}	n-C_{20}-n-C_{25}	n-C_{27}-n-C_{31}		(S/L)
Feed coal blend		166.7	51.8	48.0	3	17	63	3.87	0.05
Fly ash	1			19.0	20	23	44	2.05	0.45
	2			27.8	20	23	44	2.05	0.45
	3			42.2	20	19	32	1.31	0.63

blend comparing to the FAs extract (Table 4). As was already discussed above, combustion has increased the total amounts of *n*-alkanes and has modified the distribution by a shift to short chain homologues (Fig. 1). Generally, other series have kept their proportions (Table 4). Namely, in the total EOM samples (Fig. 2): (i) diterpenoid coal biomarkers remained the dominant components, from 66 rel. % for the feed coal blend to 60 - 71 rel. % for the FAs; (ii) sesquiterpenoids were present in low amounts and dropped from 10 rel. % in the feed coal blend to 1 - 2 rel. % in the FAs samples; (iii) triterpenoids changed from 8 rel. % to 3 rel. %; (iv) proportions of PAHs have slightly increased from 1 rel. % to 3 rel. %; (v) considerable changes in the proportions of hopanes were not registered (8 rel. % for the feed coal blend and 5 - 6 rel. % for the FAs samples). Generally, the distribution pattern of hopanes was preserved. However, the dominance of H_{31}aβ R was replaced by H_{29}ββ in the FA sample from the ESP 3 row (Table 4). Moreover, hop-17(21)-ene content has considerable decreased in all FAs samples. In brief, hopanes were found in comparable portions in the studied samples but the remarked changes reflect modification in their stereochemistry induced by combustion.

PAHs in feed coal blend and in FAs samples

Coal burning is a proven anthropogenic source for PAHs in the environment [18 - 20]. PAHs generated during fossil fuels combustion in TPPs is divided into two main categories: emitted through the feed coal organic matter volatilization and produced during combustion by complex pyrochemical synthesis. The formation and emission of PAHs is a complex physico-chemical process that has received considerable attention due to its environmental impact. Emissions and toxicity effects of PAHs formed during coal combustion have analyzed and proposed several PAHs formation mechanisms [21].

In Bulgaria there are some limited studies on PAHs in FAs from combustion in TPPs [22, 23]. Recently, a thorough study on the PAHs in FAs from combustion in Bulgarian TPPs was published [9]. In the current study, a complex mixture of coals from different deposits, used in the Bobov Dol TPP, was investigated. A further focus of the research was to outline changes in PAHs composition in FAs in combination with coal biomarkers.

Unfortunately, the PAHs information was rather limited as only phenanthrene (Phe) and perylene (Per) were quantified in the feed coal blend. In Fig. 3 are given 16 PAHs tracked by the United States Environmental Protection Agency (USEPA) [29], and the following PAHs are considered as carcinogenic (CPAHs): benzo[a]anthracene (B[a]A), chrysene (Ch), benzo[b]fluoranthene (B[b]Fl), benzo[k]fluoranthene (B[k]Fl), benzo[a]pyrene (B[a]P), indeno[1,2,3-cd]pyrene (In[1,2,3-cd]P), dibenzo[a,h]anthracene (DB[ah]A). None of them has been identified in the feed coal blend. Only 470 μg kg^{-1} of Phe and 2710 μg kg^{-1} Per, were quantified in the feed coal blend. In a previous study on *Taxodium* macrofossil from the Bobov Dol subbituminous coal Per was identified [24]. So, the result for its abundance matched very well to the high values for Per in Bobov Dol feed coal. Per (Fig. 4) is not in the list of USEPA classification for CPAHs. In the specialized literature it is measured as coal biomarkers and is used for correlation purposes to evaluate organic matter transformations. In the coal blend burnt in Bobov Dol TPP Per amounted up to 85 % of ΣPAHs. Respectively, calculation of parameter and ratios based on PAHs distribution for feed coal blend was

Table 4. Biomarker assemblages of Bobov Dol TPP feed coal blend and FAs from the consecutive ESP rows.

Series	Compound	Fraction	Feed coal blend		Fly ash		
			Content		ESP 1	ESP 2	ESP 3
			mg kg^{-1}	µg/g TOC	ppm		
Sesquiterpenoids							
	Cadinene	I	19.54	62.83	0.28	0.4	0.57
	Eudesmane	I	20.42	65.68	0.27	0.39	0.36
	Drimene	I	13.02	41.89	0.51	0.75	1.51
	Cuparene	II	1.57	5.05	0	0	0
	Curcumene	II	1.71	5.51	0	0	0
	Cadalene/Isocadalene	II	12.57	40.44	0.23	0.22	0.44
	Total		68.83	221.4	1.29	1.76	2.88
Diterpenoids							
	Norpimarane	I	19.11	61.47	1.27	1.86	0
	Beyerane	I	35.64	114.64	9.87	14.46	21.48
	Pimarane	I	51.75	166.46	18.95	27.77	40.87
	16β(H)-Phyllocladane	I	12.5	40.22	0.95	1.39	1.92
	Abietane	I	32.44	104.34	1.67	2.44	3.06
	16α(H)-Phyllocladane	I	122.1	392.66	4.58	6.71	10.81
	Norabietatriene	II	6.32	20.34	0.15	0.22	0.72
	Dehydroabietane	II	13.94	44.84	0.78	1.14	0.84
	Simonellite	II	140.3	451.41	2.85	4.18	5.78
	Retene	II	15.64	50.31	0.72	1.05	0.91
	Methyl retene	II	9.21	29.63	21.96	32.17	0
	Total		459	1476.32	63.75	93.39	86.39
Non-hopanoid triterpenoids							
	Des-A-Oleananes	I	1.56	5	0	2.1	0
	Des-A-Ursene	I	1.19	3.83	0	0	0
	Des-A-Lupane	I	3.18	10.22	0	0.56	0
	Oleanenes	I	10.25	27.14	0	0.96	0
	Ursene	I	3.45	11.1	0	0.84	0
	Aromatic Des-A-Triterpenoids	II	4.58	14.76	0.04	0.06	0.07
	Dinoroleanatetraene	II	8.96	28.8	0	0	0
	Dinorursatetraene	II	10.23	32.9	0	0	0
	Dinorlupatriene	II	5.13	16.5	0	0	0
	Triaromatic triterpenoids	II	2.3	7.39	0	0	0
	Tetraaromatic triterpenoids	II	4.04	13	0	0	0
	Total		54.87	170.64	0.04	4.52	0.07
Hopanoid triterpenoids							
	$H_{27}\beta$	I	1.67	5.38	1.05	1.54	0.71
	$H_{29}a\beta$	I	1.12	3.59	0.22	0.33	0.37
	$H_{30}a\beta$	I	0.87	2.81	0.49	0.72	1.43
	$H_{29}\beta\beta$	I	2.13	6.84	0.63	0.93	1.98
	$H_{31}a\beta$ S	I	1.4	4.5	0.32	0.47	0.8
	$H_{31}a\beta$ R	I	8.14	26.17	1.35	1.98	1.51
	$H_{30}\beta\beta$	I	0.79	2.54	0.33	0.48	0
	$H_{31}\beta\beta$ R	I	1.65	45.3	0.12	0.18	0
	Hop-17(21)-ene	I	25.01	79.04	0.55	0.8	1.08
	Total		42.78	176.17	5.06	7.43	7.88
PAHs							
	Phenanthrene	II	0.49	1.57	0	0	0.27
	Perylene	II	2.71	8.72	0	0	0
	Alkylphenanthrenes	II	0	0	1.24	1.06	3.4
	Alkylnaphthalenes	II	3.16	10.17	0	0	0.3
	Total		6.36	20.46	1.24	1.06	3.97

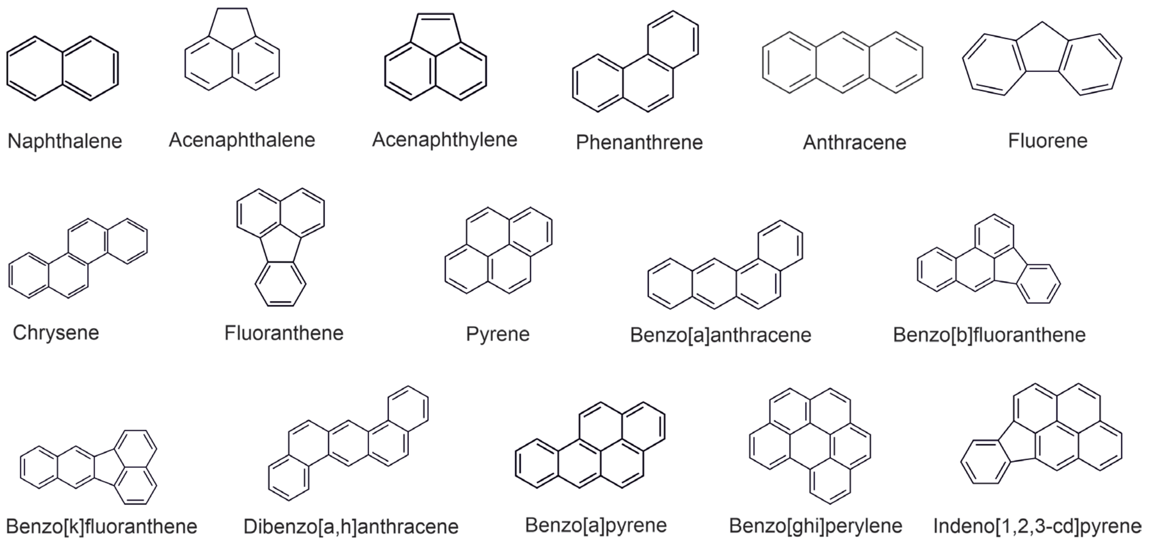

Fig. 3. Sixteen PAHs tracked by USEPA.

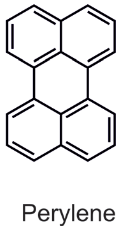

Fig. 4. Chemical structure of perylene.

meaningless. In such cases proposed to use geochemical proxies for other biomarkers to characterize the sample and to fill the information gap [25].

The contents of PAHs in FAs were even lower, as in the ESP rows only Phe was registered at the appreciable amount of 0.28 μg/gTOC (normalized to FA: 2 $\mu g\ kg^{-1}$ FA). In ESP diagrams for PAHs in FAs, the contents of alkyl naphthalenes and alkyl phenanthrenes were added to the amounts of Phe (Table 4, Fig. 2). The portions of total PAHs in the analyzed mixtures have slightly augmented from 1 rel. % for the feed coal blend to 1 - 3 rel. %, the highest value found in FAs from the last ESP row (Fig. 2).

Due to missing promulgated regulation for PAHs in FAs their amounts were compared to soils. The total ΣPAHs were <<150 $\mu g\ kg^{-1}$ soil, fixed by the Bulgarian legislation [30]. Nevertheless, PAHs harmful effects on the environment must be estimated in tight combination with data for mineral components.

CONCLUSIONS

The present comparative study of feed coal blend and FAs from Bobov Dol TPP waste provided quantitative information about the EOM composition and changes in relative proportions of different homologue series during burning. Several groups of organic compounds were tracked, i.e., sesquiterpanes, diterpanes, triterpanes, hopanes and PAHs. The diterpenoids were dominant in all samples studied, mainly represented by cyclic hydrocarbons with beyerane, abietane and phyllocladane skeleton. Triterpanes were represented by structures typical for terrestrial vegetation, i.e., oleanane, ursane, and lupane types. Hopanes pattern was characterized by the presence of αβ and ββ hopane, from C_{27} to C_{31} and $C_{27:1}$. The predominance of ββ hopanes is characteristic for immature organic matter in coals. The hydrocarbons found in the FAs samples mimic the feed coal blend assemblage but in significantly lower concentrations.

Different origin was assigned to the identified compounds: for the feed coal blend - petrogenic origin, while for FAs, for compounds formed during combustion - pyrogenic origin and for some series petrogenic origin was possible. The first group is composed by coal biomarkers, specific for low rank coals. Apparently, they have survived combustion and kept the mode of distribution. A petrogenic origin was assigned to the identified sesqui-, di-, and triterpenoids. It is supposed that they were vaporized in the combustion chamber, volatilized, and adsorbed by the FAs particular matter. However, the strong similarity in the distribution of biomarkers series for feed coal blend and FAs (expressed in rel. %) provided evidence that coal organic matter has persisted combustion as unburned carbon. Often biomarker distributions are unchanged or slightly altered by the thermal treatment comparing to those of the feed coal blend. Hence, the similarities in distribution patterns for biomarkers series argue for petrogenic origin for sesqui-, di-, and triterpenoids identified in the FAs from combustion in Bobov Dol TPP.

Generally, hopanes in samples studied have preserved the distribution pattern. However, at the FA sample from ESP 3 row, the H_{31}aβ R dominance was replaced by H_{29}ββ. Also, the hop-17(21)-ene content decreases in all FAs studied. The identified changes in hopanes distribution between feed coal blend and FAs suggest modification in their stereochemistry induced by combustion.

Other coal biomarkers, i.e., *n*-alkanes, were seriously attained by combustion. Short chain *n*-alkanes have dominated the distributions of biomarkers in FAs studied. The fact was explained by carbon chain cleavage and thermal destruction of long-chain *n*-alkanes. Accordingly, a pyrogenic origin was assigned to *n*-alkanes.

USEPA PAHs distributions were featureless. Only Phe and Per were detected in feed coal blend. The contents of PAHs in FAs were lower, as in the ESP rows only Phe was identified at low amount of 0.28 μg/gTOC (2 μg kg^{-1} FA). The results are in agreement with previous observations of low concentrations of PAHs in FAs from low rank coals. Due to missing regulation for PAHs in FAs, their amounts were compared to soils. The total PAHs in FAs were several times less than 150 μg kg^{-1} soil, fixed by the Bulgarian legislation [30]. However, it is advisable to estimate PAHs harmful effects to the environment in combination with data for other toxic substances.

In conclusion, the study demonstrates the applicability of organic geochemistry for the assessment of complex organic pollutants in wastes from coal combustion in TPPs. As far as EOM biomarker assemblages keep the features of the feed coals, they could be successfully used in surveys for potential pollutants in the environment. Despite of low concentrations of potentially hazardous compounds, PAHs should be strictly monitored considering the huge FAs annual production, their accumulation, and possibilities for mobilization of harmful inorganic/organic compounds in different environmental areas.

Acknowledgements

The study was supported by the Bulgarian National Science Fund in the frame of the project КП-06-Н34/2019.

REFERENCES

1. J.S.J. Hargreaves, I. Palford, M. Balakrishman, V.S. Batza, Conversion of Large Scale Wastes into Value-added Products, 1st Ed. CRC Press, Boca Raton, 2013, 174 pp.
2. S. Vassilev, C. Vassileva, Mineralogy of combustion wastes from coal-fired power stations, Fuel Proc. Tech., 47, 1996, 261-280.
3. I. Kostova, D. Apostolova, S. Dai, Investigation of some mercury organic compounds in coal fly ash samples from Bulgarian and Greek thermoelectric power plants, C.R. Acad. Bulg. des Sciences, 68, 2015, 889-896.
4. W.H. Griest, L.B. Yeatts, J.B Laton, Recovery of polycyclic aromatic hydrocarbons sorbed on fly ash for quantitative determination, Anal. Chem., 52, 1980, 149-201.
5. M.L. Lee, D.W. Later, D.K. Rollins, D.J. Eatough, L.D. Hansen, Dimethyl and monomethyl sulfate: presence in coal fly ash and airborne particulate matter, Science, 207, 1980, 186-188.
6. M.J. Fabiańska, D. Smȯlka-Danielowska, Biomarker compounds in ash from coal combustion in domestic furnaces, Fuel, 102, 2012, 333-344.
7. D. Apostolova, A. Bechtel, I. Kostova, M. Stefanova, Biomarker assemblage of unburned coal particles in FAs from Bulgarian TPPs, Journal of Mining and Geological Sciences, 63, 2020, 203-206.
8. D. Apostolova, A. Bechtel, K. Markova, I. Kostova, Biomarker composition and PAHs characteristics of Bulgarian coals with different rank and origin, *C.R.* Acad. Bulg. des Sciences, 217, 2017, 243-252.
9. D. Apostolova, I. Kostova, A. Bechtel, M. Stefanova, PAHs in feed coals and fly ashes from coal-fired thermal power plants in Bulgaria, Int. J. Coal Geol., 243, 2021, 103782.
10. I. Kostova, D. Apostolova, M. Stefanova, Geochemical

features of unburned coal particles in fly ashes from thermal power plants in Bulgaria, IOP Conf. Ser. Earth Environ. Sci., 609 (012092), 2020, 1-9.
11. M. Radke, H. Willsch, D.H. Welte, Preparative hydrocarbon group type determination by automated medium pressure liquid chromatography, Anal. Chem., 52, 1980, 406-411.
12. I. Kostova, D. Apostolova, A. Bechtel, M. Stefanova, Biomarker assemblages of feed coal blend and fly ashes from Bobov dol TPP, Bulgaria, Abstract book 37th TSOP Annual meeting, 12-14. Sept. 2021, Sofia, Bulgaria, 2021, 101-103.
13. A. Bechtel, R.F. Sachsenhofer, A. Zdravkov, I. Kostova, R. Gratzer, Influence of floral assemblage, facies and diagenesis on petrography and organic geochemistry of the Eocene Bourgas coal and the Miocene Maritza-East lignite (Bulgaria), Org. Geochem., 36, 2005, 1498-1522.
14. M. Stefanova, K. Markova, S. Marinov, B.R.T. Simoneit, Molecular indicators for coal-forming vegetation of the Miocene Chukurovo lignite, Bulgaria, Fuel, 84, 2005, 1830-1838.
15. A. Zdravkov, A. Bechtel, R.F. Sachsenhofer, J. Kortenski, R. Gratzer, Vegetation differences and diagenetic changes between two Bulgarian lignite deposits - Insights from coal petrology and biomarker composition, Org. Geochem., 42, 2011, 237-254.
16. D. Mitrović, N. Đoković, D. Životić, A. Bechtel, A. Šajnović, K. Stojanović, Petrographical and organic geochemical study of the Kovin lignite deposit, Serbia, Int. J. Coal Geol., 168, 2016, 80-107.
17. C. Papanicolaou, J. Dehmer, M. Fowler, Petrological and organic geochemical characteristics of coal samples from Florina, Lava, Moschopotamos and Kalavryta coal fields, Greece, Int. J. Coal Geol., 44, 2020, 267-292.
18. A.M. Mastral, M.S. Callén, A review on polycyclic aromatic hydrocarbon (PAH) emissions from energy generation, Environ. Sci. Technol., 34, 2000, 3051–3057.
19. S.S Xu, W.X. Liu, S. Tao, Emission of polycyclic aromatic hydrocarbons in China, Environ. Sci. Technol., 40, 2006, 702-708.
20. R.W. Wang, J.M. Zhang, J.J. Liu, G.J. Liu, Levels and patterns of polycyclic aromatic hydrocarbons in coal-fired power plant bottom ash and fly ash from Huainan, China, Archives of Environmental Contamination and Toxicology, 65, 2013, 193-202.
21. G.J. Liu, Z.Y. Niu, D. van Niekerk, J. Xue, L.G. Zheng, Polycyclic aromatic hydrocarbons (PAHs) from coal combustion: emissions, analysis and toxicology, Reviews of Environmental Contamination and Toxicology, 192, 2008, 1-28.
22. M.S Callén, M.T de la Cruz, A.M Mastral, S. Marinov, R. Murillo, R., M. Stefanova, Hot gas cleaning in power stations by using electron beam technology. Influence on PAH emissions, Fuel Proc. Tech., 88, 2007, 251–258.
23. M. Stefanova, S.P. Marinov, L. Gonsalvesh, A. Mastral, M. Callén, P. Gadjanov, PAHs in fly ash from lignite combustion, Bull. Geol. Soc. Greece XXXX, 2007, 1499–1504.
24. M. Stefanova, D.A. Ivanov, B.R.T. Simoneit, Palaeoenvironmental application of Taxodium macrofossil biomarkers from the Bobov dol coal formation, Bulgaria, Int. J. Coal Geol., 120, 2013, 102-110.
25. M.J. Fabiańska, B. Kozielska, J. Konieczynski, Differences in the Occurrence of Polycyclic Aromatic Hydrocarbons and Geochemical Markers in the Dust Emitted from various Coal-Fired Boilers, Energy & Fuels, 31, 2017, 2585–2595.
26. ISO 1015:1975, 1975. Brown Coal and Lignite – Determination of Moisture Content - Direct Volumetric Method. International Organization for Standardization, Switzerland (3 pp).
27. ISO 602:2015, 2015. Coal - Determination of Mineral Matter. International Organization for Standardization, Switzerland (7 pp).
28. ISO 20360:2020, 2020. Brown Coals and Lignites – Determination of the Volatile Matter in the Analysis Sample: One Furnace Method. International Organization for Standardization, Switzerland (12 pp).
29. United States Environmental Protection Agency 1993: Provisional guidance for quantitative risk assessment of polycyclic aromatic hydrocarbons. EPA/600/R-93/089. USEPA, Washington, DC. https://cfpub.epa.gov/ncea/risk/www.epa.gov.
30. Regulation No. 3, 2008: On the standards for permissible content of harmful substances in soils, Official Gazette of the Republic of Bulgaria, 71, 1-6, (in Bulgarian).