Geochemical Features of Unburned Coal Particles in Fly Ashes from Thermal Power Plants in Bulgaria

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Abstract. Coal combustion in thermal power plants generates huge amounts of solid wastes, including fly ash (FA). The essays of its conversion into value-added products continuously increase. The aim of the study was: (i) to depict organic compounds (if any) present in industrial coal-derived FAs from four thermal power plants (TPPs) in Bulgaria; (ii) to assess the relationship of the compounds present with the feed coals using biomarker proxies; (iii) and, to appreciate biomarkers changes in distribution pattern caused by combustion. Average samples of FAs and samples from electrostatic precipitators of four TPPs feed by different rank coals were analyzed. The study was scheduled in comparison with parent feed coals. The yields of extractable organic matter (EOM) expressed in rel. % were low and comparable, ~ 0.01%, but normalized to total organic carbon (TOC) depicted some differences. For lower rank coals FAs yields were higher, in the range 10-20 mg/g TOC, all dominated by polar components and an order of magnitude lower for higher rank coal FAs, < 2 mg/g TOC, with considerable portions of neutral compounds. After extensive fractionation of EOM from unburned coal particles in neutral fractions of FAs short chain n-alkanes (nC15-nC19) prevalence was distinguished. The feature was assigned to high temperature of combustion and thermal destruction of long-chain homologues (nC27-nC31). The distribution signatures for low rank coals kept some characteristics of parent coals while in the case of bituminous coal longer homologues were almost absent. The changes in n-alkanes distributions were rank depended and an attempt for explanation by FA particles porosity was done. For organic compounds registered in EOM of coal-derived FAs two provenances are supposed. The first group comes from the feed coals and the second one is formed in combustion processes or has changed distributions under the thermal treatment. Insofar as n-alkanes distribution signature was altered in combustion the origin should rather be assigned to the second group of components.

1. Introduction
Coal combustion supplies 48% of the electricity generated in Bulgaria, with combustion of 35.2 Mt coal and annual production of 10.4 Mt solid wastes. Regardless of the European Union policy promoting the use of energy from renewable sources (Directive, 2018), until 2030, coal will remain one of the main energy sources in six EU countries, i.e. Poland, Germany, Czech Republic, Bulgaria, Romania and Greece (Directive, 2010).

In thermal power plants (TPPs) the large scale of coal mineral fraction is collected in cyclones (fly ash, FA) to be stored in waste dumps. In Bulgaria FA disposal has become a burden on the environment and the economy and the interest of conversion of FA into value-added products has
increased [1]. Presently, the world average coal FA utilization is about 25%. Since coal-derived FA is applied to many aims such as building industry, or landfilling it is important to know more details about their technological features and especially for their geochemical characteristics [2].

Unburned carbon (UC) in FAs is an indicator of inefficiencies in the combustion process, and an excessive proportion of UC in the FA means a significant loss of energy in power production [3]. High amounts of UC may also be an obstacle to utilization or beneficial use of FA, particularly in cement and concrete industries where FA characteristics are strictly defined and respected [4]. Nowadays, due to some promising UC properties, there is a strong tendency towards finding feasible utilization of this material, e.g., for preparation of cheap adsorbents, graphite-like materials, fillers, etc. [3-5]. The content of UC in FA is in the range 2-12%, but in some cases it can be > 20% and even up to 57% [6]. A number of factors influence the amount of UC in FA, among which are the nature of coal (e.g., rank, particle size, moisture, maceral and mineral compositions, calorific value, and volatile matter) and the technological parameters of each TPP.

Few attempts to characterize UC in FA in view assessment the possible impact of organic matter on human health and the environment were done [7]. There is a paucity of knowledge for the organic matter composition of the coal-derived UC in FA. This scarcity has inspired our interest on the topic and determined the objective of the present study: (i) to depict organic compounds present (if any) in industrial coal-derived FAs from four TPPs in Bulgaria feed by different rank coals; (ii) to assess by biomarker proxies the relationship between the presence of organic compounds in UC with the feed coal; (iii) and, to appreciate biomarkers changes in distribution pattern caused by combustion.

2. Material and Methods
In Bulgaria for power generation, different rank feed coals are used: lignites for Maritsa East-2 (ME-2) and Maritsa East-3 (ME-3) TPPs, subbituminous coal for Republika TPP and bituminous coals from Russia for Russe TPP (table 1). All sampled TPPs are supplied by electrostatic precipitators (ESP) which represent a filtration device for FA particles removal from combustion flue gases using the force of an induced electrostatic charge minimally impeding the flow of gases through the unit. Each ESP contains a row of vertically orientated large flat metal plates typically situated 1-18 cm apart, depending on the application. The air or gas stream flows horizontally through the spaces between the wires, and then passes through the stack of plates [8].

Coal-derived FAs from four TPPs in Bulgaria were under study, i.e. different ESP rows of TPPs Republika and Russe were sampled. For Maritsa East (ME) lignite coals, resp. ME-2 and ME-3, average samples were prepared.

| TPP     | Proximate analyses | Ultimate analyses | Sulphur distribution |
|---------|--------------------|-------------------|----------------------|
|         | A_d (v)            | C                | Pyritic Sulphatic Organic |
| ME-2    | 24.0               | 42.4             | 2.1 1.1 0.7           |
| ME-3    | 29.0               | 40.5             | 2.7 1.2 1.0           |
| Republika | 58.0              | 55.8             | 0.8 0.3 0.1           |
| Russe   | 18.1               | 90.2             | 0.1 0.6 0.2           |

The molecular compositions of feed coals and FAs hydrocarbons were determined by a protocol developed previously in the study of biomarker assemblages and PAHs in different rank Bulgarian coals [9]. Briefly, sample (ca: 5 g) was extracted by DCM for 1 h at 75 °C and a pressure of 75 bar in a Dionex ASR 200 instrument. Asphaltenes were precipitated and hexane-soluble organic compounds
(maltenes) were sub-divided into saturated (I fr.) and aromatic (II fr.) hydrocarbons and polar (NOS) components using a Willsch MPLC (medium pressure liquid chromatography) instrument. Herein first fractions with saturated hydrocarbons were analyzed by a gas chromatography-mass spectrometer (GC-MS) Finnigan MAT GCQ, equipped with a DB-5MS silica capillary column (30 m x 0.25 mm x 0.25μm), 70-300 °C with steps of 4 °C/min, followed by an isothermal period of 15 min. The device was set in El mode with a scan rate of 50-650 Daltons (0.7 s/scan). The biomarkers absolute concentrations were determined using inner standard deuterated nC24. Results were normalized to μg/gTOC and calculated in μg/kg FA.

3. Results and Discussions

In table 2 are present feed coals extractable organic matter (EOM) characteristics, i.e. yields and maltenes fractional compositions.

| Coal rank* | Basin In | TPP Provenance | TOC % | EOM Yield mg/gTOC | Fractional composition, % | I fr | II fr | III fr | Asph. |
|------------|----------|-----------------|-------|-------------------|--------------------------|------|------|-------|-------|
| L Thracian, | BG       | ME-2            | 42.71 | 143.75            | 6.14                     | 1.52 | 0.45 | 23.26 | 74.77 |
|            |          | ME-3            | 53.06 | 175.90            | 9.33                     | 1.21 | 0.30 | 33.81 | 64.67 |
| SB Pernik, BG | Republica |                | 25.46 | 22.11             | 0.56                     | 18.23 | 14.65 | 57.02 | 10.10 |
| B Kuznetz, RU |              |                | 78.51 | 1.13              | 0.09                     | 7.58 | 21.57 | 59.48 | 17.49 |

* L - lignite; SB - subbituminous; B – bituminous; TOC – Total Organic Carbon

Table 3 gives FAs bulk characteristics, including ultimate, proximate analyses. Eltra Helios C/S analyzer was used for total organic carbon (TOC) determination. Before measurements, samples were decarbonized by concentrated H3PO4.

| TPP | ESP row | Proximate analysis | Ultimate analysis |
|-----|---------|--------------------|-------------------|
| ME-2| avr*    | Moisturea 0.9       | Carbon 0.9        |
|     |         | Ashd 97.8          | Hydrogen 0.2      |
| ME-3| avr*    | 3.6                | 1.36              |
|     |         | 94.0               | 1.6              |
|     |         | 3.75               | 0.9              |
|     |         | 1.31               | 0.2              |
| Republika | I | 0.3                | 0.4               |
|     |         | 98.6               | 0.68              |
|     |         | 1.31               | 0.6              |
|     |         | 0.6               | 0.5              |
|     |         | 0.5              | 0.1              |
| Indonesia, | II | 0.2                | 0.3               |
|     |         | 82.4               | 0.9               |
|     |         | 18.14              | 17.1              |
|     |         | 14.7              | 1.0              |
|     |         | 0.2              | 0.1              |
|     |         | 66.75              | 61.9              |
|     |         | 0.2              | 0.2              |

* - average sample;

In table 4 are summarized data for EOM of FAs, i.e. yields expressed in wt. %, normalized in mg/gTOC, and extracts fractional compositions. All first fractions were GC-MS analyzed and by SIM m/z 57 tracking n-alkanes were depicted.

In distributions of n-alkanes according to the length of the carbon chain in them they were divided into short-, mid-, and long-chain homologues. Geochemical indices, i.e. Carbon Preference Index (CPI), ratio of regular isoprenoids (Pr/Ph), ratio of short vs. long homologues (Short/Long) are calculated (table 5).
Table 4. Characteristics of EOM of fly ashes.

| TPP     | ESP row | Yield mg/gTOC | wt.% | I fr. | II fr. | III fr. | Asph. |
|---------|---------|---------------|------|-------|--------|---------|-------|
| ME-2    | avr.    | 8.88          | 0.0121 | 7.8   | 1.0    | 83.4   | 7.8   |
| ME-3    | avr.    | 2.74          | 0.0103 | 35.7  | 11.9   | 51.2   | 1.2   |
| Republika | I  | 7.27          | 0.0088 | 5.4   | 9.5    | 70.3   | 14.8  |
|         | II      | 15.05         | 0.0102 | 25.8  | 11.8   | 42.4   | 20.0  |
|         | III     | 19.87         | 0.0117 | 13.1  | 1.0    | 77.8   | 8.1   |
| Russe   | I       | 0.8           | 0.0145 | 21.8  | 1.8    | 59.8   | 16.6  |
|         | II      | 1.91          | 0.0308 | 37.9  | 1.5    | 45.7   | 14.9  |
|         | III     | 0.23          | 0.0154 | 28.0  | 0.6    | 55.0   | 16.4  |

3.1. Content of unburned carbon in FAs studied

According to the literature data, content of UC in FA is in the range 2-12%, but in some cases it can be >20% and even up to 57% [6]. The implementation of modern low-NOx burners additionally increases the UC level in FA. Different methods for UC determination are used: loss-on-ignition (LOI), thermogravimetry and a broad range of analytical approached reviewed by Bartoňová [4] and Xing et al. [10]. The feasible determination of UC in FA is of utmost importance for further application.

In our study a hint for UB content in FA offers the relationship TOC vs. C content (table 3, Figure 1) where a strong correlation ($R^2=0.9991$) was estimated. Values for the UB contents in FAs from ME and Republika TPPs are in acceptable ranges (aforesaid) while the magnitudes measured for Russe TPP are beyond the above cited limits. Taking in consideration the magnitudes determined by two independent analyses we are inclined to appraise the data as reliable. Inasmuch as the aim of the study is to appreciate organic matter present in FA the proxy to evaluate UC levels in FA fulfills us at least as a rough estimate.

Figure 1. Cross-plot TOC vs. C content for coal-derived fly ashes

The class of FA effects UC distribution in ESP rows. Fundamental FAs characteristics distinguish class F (for higher rank coals) and class C (for lower rank coals). In class F UC particles tend to be enriched in the later rows of ESP, an affirmation valid for Russe TPP (table 3). Therein FA from the ESP row III contains UC with TOC 66.75%, (table 2). This is very high amount of UC in FA but on the other hand, the characteristic makes the waste product promising as a precursor for “value-added” material. For example, by subsequent one-step activation, it can serve as a feedstock for activated carbon preparation.
3.2. Biomarker assemblage in EOM
Many biomarkers from the feed coals survive combustion processes [7]. They were recognized in EOM of the FAs, i.e. hydrocarbons, terpenoids, hopanes, etc. In our study data for the last two compound classes’ are not considered, in as much as in all EOM biomarker assemblages aliphatic hydrocarbons strongly predominated, particularly \( n \)-alkanes (Figure 2). Their amounts in FAs depend on the rank of feed coals - higher for lignites and lower for bituminous coal (table 5).

The separations of EOM \( n \)-alkanes from all feed coal samples were prevailed by long-chain homologues, \( nC_{27-29} \), maximizing at \( nC_{29} \) or \( nC_{31} \) (Figure 2). Such distribution pattern is typical for terrigenous organic matter (Type III kerogen). Respectively, the rel. % of long-chain homologues in all feed coals is very high, 45-78% (table 5). Combustion strongly affected the \( n \)-alkanes separation mode. Distribution curves in Figure 2 for FAs samples visualize well-expressed shift to shorter-chain \( n \)-alkanes members, especially for bituminous coal maximising at \( nC_{18} \). The rel. % of long-chain alkanes dropped to 1-3% (TPP Russe). The separations reflect also in the calculated geochemical indices: CPI and ratio short/long homologues. CPI considerable decreased for TPP Russe and TPP ME-2 samples and was less influenced for the other samples (table 5). Appreciable changes in \( n \)-alkanes distributions were proved by the ratio short/long members. For all samples a shift to shorter homologues was registered, highly expressed for TPP Russe samples (bituminous feed coal) where value \( >> 1 \) for all ESP rows were calculated.

In all EOMs regular isoprenoids are represented by pristane (Pr) and phytane (Ph), both in low amounts. There are some controversial changes - increase for TPP Russe and decrease for TPP Republika samples but regular increase with ESP rows. Herein samples from ME lignites are not commented as they are extremely immature (Ro,%=0.2), and isoprenoids are still “bound” to the kerogen organic matter. Respectively, calculated Pr/Ph ratios are not informative.

| Coal   | TPP | ESP row | Content µg/gTOC | \( n \)-Alkanes distribution, % | Geochemical indices |
|--------|-----|---------|-----------------|-------------------------------|---------------------|
|        |     |         |                 | Short- \((nC_{15}-nC_{19})\) | Mid- \((nC_{21}-nC_{25})\) | Long- \((nC_{27}-nC_{31})\) | CPI | Pr/Ph | Short/Long |
| L*     | ME-2 avr. | 162 | 4 | 22 | 74 | 3.36 | 0.28 | 0.05 |
|        | ME-3 avr. | 26.85 | 40 | 26 | 34 | 1.84 | 0.7 | 1.18 |
| L      | ME-2 avr. | 69 | 3 | 19 | 78 | 3.38 | 1.45 | 0.03 |
|        | ME-3 avr. | 24.31 | 16 | 26 | 58 | 3.34 | 0.92 | 0.28 |
| SB     | 141 | 5 | 25 | 70 | 1.57 | 1.37 | 0.07 |
| Republika | I | 9.7 | 38 | 16 | 46 | 2.38 | 0.86 | 0.83 |
|        | II | 96.76 | 55 | 27 | 18 | 1.76 | 0.98 | 3.06 |
|        | III | 70.76 | 32 | 36 | 32 | 2.04 | 0.66 | 1.00 |
| B      | 4 | 15 | 40 | 45 | 2.11 | 0.71 | 0.33 |
| Russe  | I | 32.39 | 72 | 26 | 2 | 0.64 | 1.19 | \( >> 1 \) |
|        | II | 7.51 | 64 | 35 | 1 | 0.56 | 0.97 | \( >> 1 \) |
|        | III | 1.92 | 53 | 44 | 3 | 0.47 | 0.85 | \( >> 1 \) |

* - feed coals marked in grey;
CPI – Carbon Preference Index = \[\Sigma(nC_{23+nC_{31}})_{\text{even}}+(nC_{25+nC_{33}})_{\text{odd}}]/2[\Sigma(nC_{24+nC_{32}})_{\text{even}}];
Figure 2. Profiles of $n$-alkane distributions in EOM of feed coals (in blue) and FAs (in red).
3.3. An essay to correlate FAs porosity with n-alkanes distribution
Determination of specific surface area (SSA) and porosity of UC in FA is of great importance for further utilization of the waste material from energy production. Significant parameters affecting SSA are coal rank, maceral composition and morphology. With respect to porosity, there is generally accepted consensus that most FA carbons are predominantly of mesoporous nature with some contribution of micropores [11]. It was reported that the porosity and SSA generally increased as the volatile increased, i.e. from high rank coal to low rank coal.

Our previous studies on UC SSA of FA carbon are closely related to pore-size distribution and Hg capture [11,12]. It was concluded that even if SSA is structured predominantly by micropores, mesopores and macropores are important because they assure Hg species access to the active sites of FA carbon. In case of lignite UCs, it was pointed out that Hg is adsorbed on both micropores and mesopores, while preferable adsorption of Hg on bituminous coal UC is related mainly to micropores. May be the pattern is applicable to n-alkanes, as well. Respectively, Class C FA adsorbs both long- and short-chain in micropores and mesopores while Class F FA adsorbs only in micropores. This hypothesis should be verified rendering into account the hydrocarbons molecular dimensions. Retention mechanism of n-alkanes on/in FA particles and the role of UC are not well-defined. However, it seems acceptable and reinforced by zeolites presence in FA and their proven aptitude for n-alkanes absorption. Further research in this field is needed.

3.4. General discussion
The experimental protocol applied in the study has the target to isolate organic matter in a separate fraction and to search for individual compounds. Likewise, this approach is somewhat controversial to the well documented in the specialized literature traditional methods for organic matter bulk characterization of UC by petrography, i.e. maceral composition, optical texture and morphology, turbostratic structure of carbonaceous matrix, i.e. X-ray diffraction, HRTE microscopy, Raman spectroscopy, etc. However, at a certain extent, both approaches are complementary. Identification of individual compounds by componential analyses convincingly will confirm/deny structures assumed by the above listed bulk techniques. Functional groups estimate by componential analyses verifies and enriches the vision for active centres in the adsorbent, and will aid in the further surface modification. The knowledge for the EOM composition of coal-derived FA will help for better multi-component utilization of wastes and development new, green product streams to reduce the environmental threat.

3.5. Horizon for future studies
UC particles in coal-derived FA are of considerable environmental concern. They act as a sink for hydrophobic organic compounds, i.e. PAHs, explained by strong sorption capacity. UC from coal-derived FA can uptake not only Hg, but also some other toxic volatiles from the flue gas. This is an item for future studies, the role of UC in PAHs accumulation.

4. Conclusions
The present investigation provides a detailed emphasis on the effect of combustion on EOM composition. The thorough study by geochemical methods of FA from four TPPs in Bulgaria feed by different rank coals in comparison with initial coals and ESP rows samples has revealed the following peculiarities:

i) A rough estimate of UC amount in FA based on the strong correlation TOC vs. C content ($R^2 = 0.9991$) based on two different measurements, is proposed. Magnitudes determined for Class C FAs are reasonable, < 5 %, while for Class F FAs values are inadmissible, an indicator of inefficiencies in the combustion process.
ii) The yields of EOM expressed in rel. % are low and comparable, ~ 0.01%, but normalized to TOC depict some differences. For lower rank coals FA yields are higher, in the range 10-20 mg/g TOC, all dominated by polar components and an order of magnitude lower for higher rank coal FA, < 2 mg/g TOC, with considerable portion of neutral compounds.

iii) Content of n-alkanes in samples studied is comparable, >100 μg/gTOC. There is a tendency for decrease from the first to the last ESP rows for Russe TPP, and regular changes in homologous distributions - decrease in short-chain members, from 72% to 53%, at the expense of the mid-chain homologues, from 26% to 44%.

iv) Compounds registered in the EOM of coal-derived FA could have two origins. The first group comes from the feed coal and the second one is formed in combustion process or changes distribution under the thermal treatment. In all samples studied combustion resulted in n-alkanes distribution transformations. Coal organic matter thermal destruction affected linear hydrocarbons distribution, the relative portions of shorter chain homologues drastically increased and geochemical indices changed. The signatures for low rank coals keep some characteristics of parent coals while in the case of bituminous coal longer homologues are almost absent, 1-3 rel. %.

Future studies will target the relationship of UC in FAs with some toxic volatiles in the combustion flue gas starting with PAHs.

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