#### Fuel 102 (2012) 333-344

Contents lists available at SciVerse ScienceDirect

## Fuel

journal homepage: www.elsevier.com/locate/fuel

# Biomarker compounds in ash from coal combustion in domestic furnaces (Upper Silesia Coal Basin, Poland)

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#### HIGHLIGHTS

- ▶ We investigate organic compounds in coal ash from domestic furnaces.
- ▶ Two types of organic compounds in ash extracts: from source coal and heat-originated.
- ▶ Biomarkers show recognizable distributions of source bituminous coal.
- ▶ Some biomarkers distributions are partially affected by heat.
- Temperature and oxygen level influence biomarker distributions.

#### ARTICLE INFO

Article history: Received 6 April 2011 Received in revised form 5 July 2012 Accepted 5 July 2012 Available online 20 July 2012

Keywords: Coal combustion Coal ash Coal waste Gas chromatography-mass spectrometry Biomarkers

### ABSTRACT

Organic compounds occurring in coal ash of known mineralogy were investigated. Ash came from two domestic furnaces using bituminous coal from the Upper Silesia Coal Basin. Dichloromethane extracts of ash were analyzed with gas chromatography–mass spectrometry (GC–MS) for biomarkers from fuel and formed during combustion. Distributions of aliphatic hydrocarbons, aromatic and polar compounds were researched. Results were compared with those found for power plant coal ash, coal wastes which underwent self-heating and source bituminous coal. It was found that geochemical features of plant coal ash organic matter reflects mainly geochemistry of source bituminous coal. Several groups of biomarkers such as as *n*-alkanes, steranes and pentacyclic triterpanes show distributions recognizable as coal-deriving what enables to identify source fuel. Values of most biomarker and aromatic hydrocarbon parameters show minor changes due to heat of the combustion process. The most advanced changes are found in distributions of alkylnaphthalenes, pristane, phytane and lighter *n*-alkanes reflected by values of Pr/Ph, Pr/*n*-C<sub>17</sub> and Ph/*n*-C<sub>18</sub> ratios. Much less extensive changes are seen in distributions of pentacyclic triterpanes which make them the most useful biomarker group for source fuel characterisation. Most of biomarkers are probably present in coal ash in unburnt coal particles occurring in ash due to low temperature in domestic furnaces favoring organic matter preservation.

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#### 1. Introduction

Due to it its abundant world's reserves coal is still the primary energy/heat source in the world [1]. Coal combustion generates a great amount of ash showing adsorbing properties. It has been estimated that the worldwide production of coal ash from only coalfired power plants exceeds  $550 \times 10^6$  tones/year [2]. While in power plants the large part of coal mineral fraction is collected in cyclones (fly ash) to be stored in waste dumps or reused in building industry, in combustion for domestic purposes finer fractions of ash are emitted to the atmosphere or dumped out without any control. Due to its adsorbing properties coal ash can contain organic compounds deriving from parent coal or formed in burning process, e.g. [3]. While relatively low amounts of carbon in fly ash from coal-fired power plants has been found [4,5], ash from domestic combustion contain higher amounts of it due to generally lower temperatures of combustion and more limited access of air to fuel [6–8].

To evaluate the possible impacts of coal ash organic matter on human health and the environment it is important to characterize its chemical composition. Many attempts have been made to link the various type of carbon in fly ash with parent coal properties, such as rank and maceral composition [9,10]. Liptinite is completely burnt during combustion without leaving any char particles whereas vitrinite and inertinite form isotropic and anisotropic carbon [5]. Vitrinite char is a reactive component of coal, forming large angular particles, mostly volatilized during





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combustion. Inertinite macerals, being natural chars, burn lessreadily than the vitrinite particles and form isotropic particles. Low rank coals tend to produce isotropic char whereas higher rank bituminous coals anisotropic coke with various granular optical textures [9–14].

The varying temperature and oxygen contents in the combustion zone determine a degree of organic matter alteration and type of compounds emitted from fuel combusted. Low temperature of burning is common in domestic furnaces. As a result smoldering (<300 °C) prevails in them. This causes a release of organic compounds by volatilization/steam stripping effect from coal combusted [15]. The extent of the process is affected by coal moisture content related to coal rank. Apart from volatilization the primary chemical reactions under smoldering condition include water elimination, depolymerization and fragmentation of coal macromolecule. organic matter oxidation, and char formation.

Numerous organic compounds have been identified in smoke emissions from various fuels (biomass and fossil fuels), e.g. [4,15–18]. These compounds are related to organic components of the parent coal. Among them are biomarkers belonging to various groups of organic compounds, previously identified in the world's coals of different age, rank and maceral composition. These compounds such as *n*-alkanes, acyclic isoprenoids, sesquiterpenoids, diterpenoids, steranes, tri- and pentacyclic triterpanes can be applied as markers of a particular source of organic matter helping in its identification and assessment of its input to the environment, for example, [19–24].

#### 2. Bituminous coals of the Upper Silesia Coal Basin (Poland)

The majority of Polish resources of bituminous (hard) coals are located in Upper Carboniferous (Pennsylvanian) strata (Fig. 1). In this study, bituminous coal of the Upper Silesia Coal Basin (USCB), the most often fuel applied for both domestic and industrial purposes, is used as the source of coal ash investigated. Domestic and power plant coal ash contained unburnt remains of organic compounds. Their composition is compared here to that of the source USCB bituminous coal and to coal and smelting wastes as well.

The Upper Silesia Coal Basin is situated in the south-western part of Poland (Fig. 1). It was formed as a Variscan foredeep of the Moravo-Silesian fold zone [22,25]. The Upper Carboniferous coal-bearing succession, more than 8000 m thick, is a major part of the molasse infill. The lower paralic part of the sequence (Namurian A) consists of marine, shore, deltaic and fluvial deposits, whereas the upper part (Namurian B to Westphalian D) contains variable non-marine deposits [26]. The ranks of coals in the USCB are variable. They range from subbituminous to high volatile bituminous coals. Maceral composition is more uniform: humic coals rich in vitrinites dominate here with rare sapropelic coals. The ranks of coals and maceral group composition of the USCB coals from the Polish basins were investigated in numerous research, for instance [27-30], among many others. Generally, vitrinite reflectance values tend to decrease eastward the basin. In the western USCB part they are in the range from 0.45 to 2.00, in the central part of the basin Ro = 0.80-1, 1%, whereas coals in the easternmost part (the Upper Vistula Coal Basin) are of the lowest rank (Ro  $\sim$  0.50%).

In the last decade organic geochemistry of these bituminous coals was investigated [22,30–32]. Typical distributions of biomarkers such as n-alkanes, steranes, cyclic and acyclic isoprenoids were presented there. These research has shown that the organic matter contained in the coals and carbonaceous shales present in the same sequence was derived predominantly from higher plant (terrestrial) precursors, however depositional conditions and sources of organic matter changed sharply between deposition of the coals and the shales.

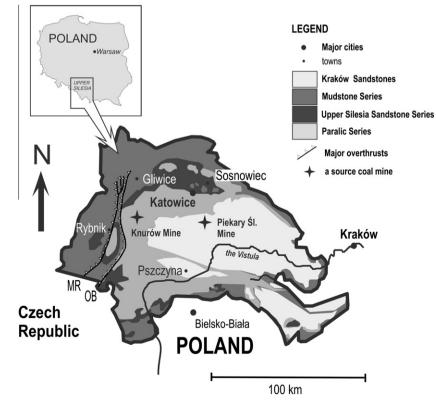


Fig. 1. Simplified geological map of the Upper Silesia Coal Basin (after [25,26]); MR-Michałkowice-Rybnik Overthrust, OB-Orłowa-Boguszowice Overthrust.

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