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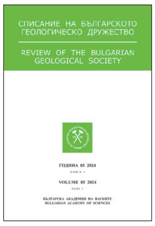

Pyrolysis of Maritsa Iztok lignite lithotypes: geochemical implication

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Пиролиз на литотипи от Източномаришки лигнити: геохимичен анализ

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Резюме. Пиролиз, при който газовете за анализ са свързани „off-line“ с апарат за термодесорбционна газова хроматография-масспектрометрия (TD-GC/MS), е използван за определяне на качествен/количествен състав на органичните функционалности в продуктите от термично разграждане на литотипи от Източномаришки лигнити в интервала 250–900 °C. Цел на изследването е да се определят органичните летливи съединения и да се направи опит те да се обвържат към градивните елементи на лигноцелулозната биомаса на въглеобразуващата растителност. Общите количества на анализираните органични вещества в пиролизатите в mg/g TOC са 58,14 за липтен, 21–37 за хумокларен и ксилен, а най-ниски стойности са определени за хумовитрен – 12. Незрелостта на пробите рефлектира в изобилие от феноли, метоксифеноли (само гуаяколови структури) и фурани. В най-голямо количество те присъстват в ксилена и съставят 68% от анализираните вещества. Идентифицирани са и продукти от разграждане на въглехидрати, в т.ч. фуралдехиди, 2-циклопентен-1-они и др. В пиролизатите на литотипове са установени и въглищни биомаркери (*n*-алкени/*n*-алкани, сески-, дитерпеноиди, полярни дитерпеноиди, хопени/хопани и др.).

Ключови думи: пиролиз, лигнитни литотипи, органични летливи вещества, въглищни биомаркери.

Abstract. Pyrolysis coupled “off-line” with thermal desorption gas chromatography–mass spectrometry (TD-GC/MS) instrument for flue gas analysis is used to specify qualitatively/quantitatively organic functionalities in “Maritsa-Iztok” lignite lithotypes thermal decomposed in the range 250–900 °C. The aim of the study is to specify organic volatiles and to assign identified components to the lignocellulose biomass building blocks of coal forming vegetation. In pyrolysates the total amounts of the analyzed organics, expressed in mg/g TOC, amount up to 58.14 for liptain, 21–37 for humoclarain and xylain, and the lowest values are determined for humovitrain, 12. The samples immaturity reflects in high diversity of phenols, methoxy phenols (only guaiacyl structures), furans, etc. maximizing at xylain lithotype, 68% of the total analyzed amount. Carbohydrate degradation products, i.e. furaldehydes, 2-cyclopenten-1-ones, etc. are identified as well. In lithotypes studied, coal biomarkers as *n*-alkene/*n*-alkanes, sesqui-, di-, polar diterpenoids and hopenes/hopanes, are present in different proportions.

Keywords: Pyrolysis, lignite lithotypes, organic volatiles, coal biomarkers.

Inroduction

There are several analytical techniques giving information for the structures of coal organic matter (OM) building blocks. Classical alkaline CuO oxidation at 170–200 °C identifies lignin structures preserved in coal OM. Our experience (Stefanova et al., 2004) for oxidative degradation of Maritsa Iztok (MI) lignite lithotypes gave proof for lignin monomers presence with strong dominance of vanillyl phenols

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(guaiacyl structures). Further, coumaric and ferulic acids in the products of CuO oxidation implied to non-woody tissue contribution to lignite lithotypes OM structuring. Another powerful technique for structural study of natural biopolymers and geomolecules is the analytical pyrolysis coupled with GC-MS (Pyr-GC/MS). Therein, the conventional pyrolysis (Curie-point pyrolysis at 510 °C) was improved by flash heating of the sample in the presence of tetramethylammonium hydroxide (TMAH) and method is known as "thermochemolysis". It is applied to biopolymers, fossils, i.e. peatified woods, lignins, humic substances, coals, asphaltenes, kerogen of petroleum source rocks, oil shales, etc. The study of MI lignite lithotypes by thermochemolysis (Stefanova, 2005) confirmed the high contribution of Gymnosperms to coal-forming community and total lack of syringic units (Angiosperms). The modest participation of Gramineae in lithotypes OM was proved by the low amount of coumaryl structures. Pyrolysate peculiarity was the high presence of linear polysulphides in the volatiles.

Coal lithotypes have fairly distinct maceral compositions originating from various combinations of plant vegetation which evolve different coalification paths. MI lithotypes were intensively investigated over the years in the frames of projects and theses in a search for methods for lignite OM structural investigation. HV as relatively "more" homogeneous representative of the coal received special attention. In the present study by pyrolytic destruction we keep the strategy and try to get knowledge on the main structural elements of lignite OM.

The past decades are marked by increased activities in developing pyrolytic pathways to produce biofuels and bio-based chemicals from lignocellulose biomass. Pyrolysis is a key stage in thermochemical conversion processes, i.e. coal combustion and gasification. On-line monitoring of the evolution of the intermediate products and the qualitative/quantitative measurement of the pyrolysis products shed light to the ongoing processes during thermal destruction of the feed material and give information for the combustibles. Thus, encouraged by the high informative potential of pyrolysis the aim of the study was formulated as: (i) to get data for the main constituents of coal-precursor vegetation and to appreciate changes in their structures during coalification; (ii) to compare results from different techniques for coal OM analysis. Finally, comments on advantages and pitfalls of the applied techniques based on own experience were done.

Material and methods

Maritsa Iztok (MI) lignite coal field of Late Miocene-Pliocene Age is located in SE Bulgaria (Fig. 1). The lignite is described by the following maceral composition, in %: Huminite, 92; Liptinite, 6; Inertinite, 2 (Šiškov, 1997). Bulgarian standard, BDS-1979, divides Neogene coals lithotypes into: (i) homogeneous, xylain (X) and humovitrain (HV); (ii) heterogeneousones. liptain (L) and humoclarain (HK). Xylain, HV and HK are the basic lithotypes of MI lignite with a strong dominance of HK (≥ 50%), followed by X (11–30%), HV (7–12%), and L (3–8%). The content of fusain/semifusain is negligible, < 1% (Šiškov, 1997). Samples under study were kindly supplied from the collection of the Department of Geology, Paleontology and Fossil Fuels at Sofia University "St. Kliment Ohridski" as "average" samples representative for the MI lithotypes. They were optically defined by MPT 2 Opton device. Data for proximate analysis, i.e. ash (A), moisture (M), volatile matter (VM), fixed carbon (C_{fix}), elemental analysis (C, H, N, S) are given by Markova et al. (2002) and for Rock-Eval data by Stefanova et al. (2004).

Fig. 1. Plan of Mini Maritsa Iztik EAD (https://no.wikipedia.org/wiki/Maritsa_Iztok#/media/Fil:Maritsa_Iztok.jpg).

Фиг. 1. План на Мини Марица Изток ЕАД (https://no.wikipedia.org/wiki/Maritsa_Iztok#/media/Fil:Maritsa_Iztok.jpg).

Initially, laboratory equipment for pyrolysis was constructed to study sulphur in solid materials (incl. coal) and gases were potentiometrically analyzed (Yperman et al., 1999). Later on, it was modified for “off-line” application and adapted to trap volatiles for GC-MS analysis (Stefanova et al., 2005). Briefly, *ca.* 40 mg sample and 20 mg fumed silica are placed in the quartz reactor heated under a 100 ml/min N_2 flow. A linear temperature program of 10 °C/min from ambient temperature up to 900 °C is applied. The outlet of the reactor is connected to a sequence of two ice-cooled tubes containing Tenax (Sigma-Aldrich), a porous polymer of 2,6-diphenyl-p-phenylene oxide, as adsorbent. Volatiles are trapped in two separated temperature ranges selected based on the maxima in the MI lithotypes kinetograms (Stefanova et al., 2005). Two ranges were used: 250–500 °C (tube 1) and 500–900 °C (tube 2). Tubes were separately desorbed and analyzed by thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) instrument using He as carrier gas at 85 kPa and the following conditions: a) Unity thermal desorber (Marks): primary desorption 20 min at 275 °C; Cold trap at –10 °C, heated at maximum heating rate up to 320 °C, hold time 15 min; flow path temperature 200 °C; b) Trace GC Ultra-Gas chromatography (Thermo Instruments): capillary column 30 m ZB 5-MS x 0.25 mm x 0.25 μm Phenomenex; temperature program: 3 min at 30 °C, 30–100 °C (8 °C/min), 100–310 °C (12 °C/min), hold time 5 min at 310 °C; c) DSQ-Mass spectrometer (Thermo Instruments): EI spectra; Ionization energy: 70 eV; Scan range: *m/z* 33 – 480 a.u. in 0.4 s. Deuterated thiophene, Th-d_4, 3 μg, is used as a standard. Each sample is run after Th-d_4 standard. NIST library spectra was used for peak identification. Homologous series were MS tracked by single ion monitoring (SIM). Amounts of compounds in pyrolysate were normalized in μg/g lithotype.

Results and discussion

The separation of non-condensable volatiles in X pyrolysate (250–500 °C region) is shown in Fig. 2 and in Fig. 3 for the volatiles in the high temperature region (500–900 °C). Data for the series of organic compounds identified in pyrolysates of MI lithotypes are grouped in series, i.e. aromatic compounds, oxygen containing compounds and the group of coal biomarkers plus sulphur containing compounds. The three sums are expressed in rel.% from the total analyzed amounts.

The total sums of the identified compounds in pyrolysate volatiles amount up to 58 mg/g TOC for L and are minimal for HV lithotype, 12 mg/g TOC. These values are comparable with the magnitude determined by pyrolysis for MI humic acids, 55.9 mg/g TOC published by Stefanova et al. (2016) but the distribution in chemical classes is different. At one hand, in lithotypes pyrolysates nitrogen containing compounds were not present; on the other hand, there was a high variety of S-containing compounds, i.e. linear and cyclic, with mixed structures containing O- plus S- and elemental sulphur, S_8. The novelty in the present study is that by the obtained data for sulphur distribution it is possible to assess roughly the contribution of each lithotype to the final sulphur content of the lignite OM. Minimal amount of sulphur, 0.5%, (only in cyclic form as thiophens and benzothiophens) was measured for HK, and maximal amount of 15.3% for HV (12.1% linear S-containing compounds, 3.2% sulphur in cyclic type). Values for L and X were comparable, 2.6–3.9%.

Coal biomarker assemblages, i.e. *n*-alkenes/*n*-alkanes doublets, regular isoprenoids, terpenoids, etc. were already published. (Stefanova et al., 1995; Bechtel et al., 2005). By the present data the high ability of the applied protocol to separate and identify compounds of high diversity and with high molecular masses was demonstrated. Hopenes, i.e. 22,29,30-trisnorhop-17(21)-ene, $C_{27}H_{44}$ with M^+ 368 and 30-Norhop-17,21-ene, $C_{29}H_{48}$, M^+ 396, were identified only in 500–900 °C HK pyrolysate.

Vanillyl phenols, i.e. 2-methoxy and methyl-2-methoxy phenols were highly abundant, up to 47 rel.% in X lithotype. Methoxy phenols were indicative for the presence of residues from lignin arranged in the lignite structural building blocks. Also, high content of phenol and its alkylated homologues is a clue for lignin rests coalification, namely, demethoxylation and subsequent phenolic structures rearrangement with cyclization. Identification only of vanillyl phenols (guaiacyl structures) is a proof for the dominance of Gymnosperm vegetation in the coal-forming palaeomire. These results totally confirm the data obtained by the other analytic techniques (Stefanova et al., 2004; Stefanova, 2005) but in the present study the data are quantitatively interpreted.

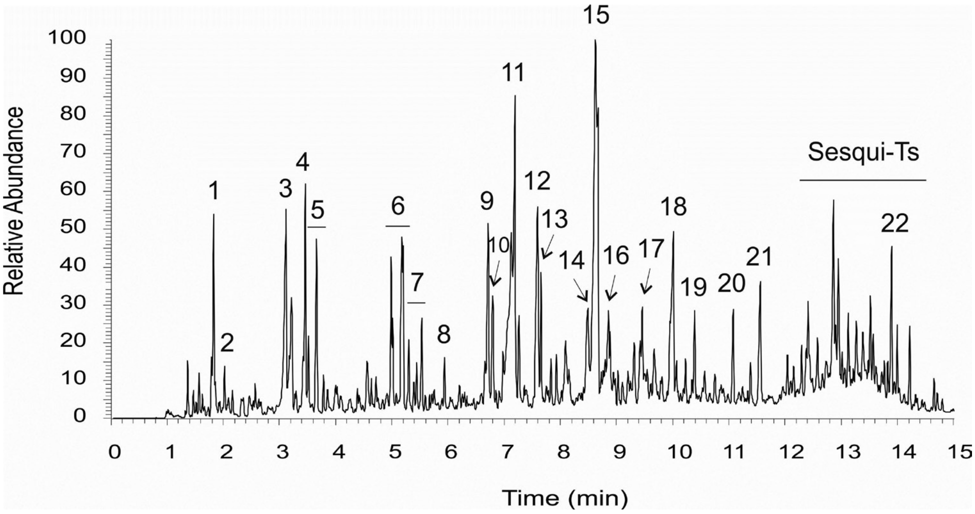

Fig. 2. Total Ion Chromatography (TIC) from Pyr-TD/GC-MS of xylain lithotype in the range 250–500 °C. Compound identification: 1, methyl cyclopentene; 2, benzene (Bz); 3, dimethyl disulphide; 4, methyl Bz; 5, methyl thiophene (Th); 6, dimethyl Bz; 7, dimethyl Th; 8, methoxy Bz; 9, trimethyl Bz; 10, dimethyl trisulphide; 11, phenol (Ph); 12, methyl methoxy Bz; 13, trimethyl Bz; 14, cresol; 15, guaiacol (G); 16, dimethyl methoxy Bz; 17, tetramethyl benzene; 18, methyl G; 19, dimethyl tetrasulphide; 20, dimethyl G; 21, vinyl G; 22, cuparene; Sesqui-Ts, sesquiterpenoids.

Фиг. 2. Обща йонна хроматограма от пиролиз с ТД/ГХ-МС анализ на ксилен в интервала 250–500 °С. Доказани съединения: 1 – метил циклопентен; 2 – бензен (Б); 3 – диметил дисулфид; 4 – метил Б; 5 – метил тиофен (Т); 6 – диметил Б; 7 – диметил Т; 8 – метокси Б; 9 – триметил Б; 10 – диметил трисулфид; 11 – фенол (Ф); 12 – метил метокси Б; 13 – триметил Б; 14 – крезол; 15 – гуайакол (Г); 16 – диметил метокси Б; 17 – тетраметил Б; 18 – метил Г; 19 – диметил тетрасулфид; 20 – диметил Г; 21 – винил Г; 22 – кипарене; Sesqui -Тс – сескитерпеноиди.

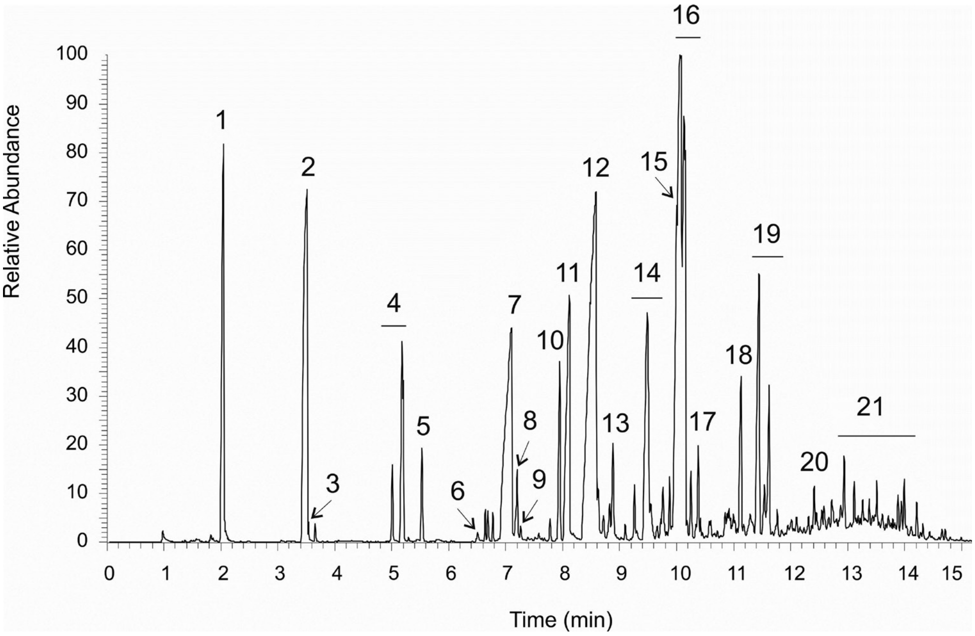

Fig. 3. Total Ion Chromatography (TIC) from Pyr-TD/GC-MS of xylain lithotype in the range 500 °C–900 °C. Compound identification: 1, benzene (Bz); 2, methyl Bz; 3, methyl thiophene (Th); 4, dimethyl Bz; 5, dimethyl Th; 6, methyl cyclopenten-1-one; 7, Phenol (Ph); 8, benzofuran (BzF); 9, dimethyl cyclopenten-1-one; 10, vinyl Bz; 11, cresol; 12, methyl Ph; 13, methyl BzF; 14, dimethyl Ph; 15, naphthalene (Naph); 16, methyl G; 17, dimethyl F; 18, dimethyl G; 19, methyl naph; 20, biphenyl; 21, dimethyl naph.

Фиг. 3. Обща йонна хроматограма от пиролиз с ТД/ГХ-МС анализ на ксилен в интервала 500 °С–900 °С. Доказани съединения: 1 – бензен (Б); 2 – метил Б; 3 – метил тиофен (Т); 4 – диметил Б; 5 – диметил Т; 6 – метил циклопентен- 2-оне; 7 – фенол (Ф); 8 – бензофуран (БФ); 9 – диметил циклопентен- 2-оне; 10 – винил Б; 11 – крезол; 12 – метил Ф; 13 – метил БФ; 14 – диметил Ф; 15 – нафталенн (наф) ; 16 – метил Г; 17 – диметил Ф; 18 – диметил Г; 19 – метил наф; 20 – бифенил; 21 – диметил наф.

It is known that at the biochemical stage of coalification, hemicellulose is completely degraded, cellulose is considerably reduced and lignin-derived structures are selectively preserved. Hence, products of carbohydrates pyrolysis are expected in the pyrolysates. These compounds support the extant concept for coalification as a selective preservation of certain resistant plant components in the lignocellulose biomass and subsequent minor reorganization of the survived biopolymers. Actually, the data obtained denote some small portions of reworked carbohydrates incorporated in MI lithotypes, < 1 rel.%, and total absence in L lithotype. The primary polysaccharides in pyrolysates are associated with dianhydromonosaccharide fragments, whereas the secondary polysaccharides yield furan fragments. Therefore, furans and furaldehydes were considered as products for carbohydrates pyrolysis. There was about 2 rel.% of furans in HK pyrolysate, lower amount of 0.7 rel.% – in X pyrolysate, and a lack – in L pyrolysate. The maximal content of 2.5 rel.% was determined for HV sample. The diversity in content was assigned to the variety in the plant vegetation combinations taking part in the OM structuring.

Levoglucosan (anhydroglucosan) $C_6H_{10}O_5$, M^+ 162, is used as a biomarker to track flue gases for products of lignite combustion (Fabbri et al., 2008). Levoglucosan was not detected in the pyrograms though the careful spectra tracking. One possible explanation could be that carbohydrates were heavy microbial reworked while pyrolysis generated only furanic structures. So, limited amounts of 2-cyclopentenones, and furaldehyde in pyrolysates, were regarded as a proof for the participation of heavy reworked carbohydrates during coalification of the lignocellulose biomass.

One of the main series present in the pyrolysates was the one of the aromatic compounds, i.e. alkyl benzenes, C_6-C_{10} and polycyclic aromatic hydrocarbons (PAHs), 2–4 cyclics. They represent about a third of the total analyzed amount and more than a half for L sample. In the low temperature region, 250–500 °C, the distribution is dominated by toluene (Fig. 2) while in the 500–900 °C region benzene is the main aromatic compound (Fig. 3). Generally, alkyl aromatics are considered as a product of the humification of the primary lignocellulose vegetation.

Naphthalenes, anthracene, phenanthrene, biphenyls, acenaphthalenes, fluorenes, phenyl-naphthalene and their alkylated analogues were preferentially detected in the higher temperature region (Fig. 3). Pyrene was identified only in HK sample. Abundance of PAHs with higher degree of condensation was not expected, due to the parent coal immaturity.

Conclusions

The data obtained by Pyr-TD/GC-MS perfectly agree with results from the previously applied techniques for coal structural study. However, each used method has its pitfalls and advantages. Namely, classical alkaline CuO oxidation at 170–200 °C is a proven procedure for identification of preserved lignin structures in coal OM but is time-consuming. In addition, the microbially altered lignin monomers (catechols) are not analyzed as were oxidized to low molecular fatty acids. An adventure of Pyr-TD/GC-MS is that gives the total picture for the distribution of oxygen containing compounds in the mixture.

Other widely applied method for geochemical structural study is thermochemolysis. It has advantages over the conventional pyrolysis because assures simultaneous pyrolysis/methylation, avoids decarboxylation and produces high yields of esters and ethers as end products. Besides, it could be done separately (“off-line”) when pyrolytic unit coupling to the MS instrument is omitted. Thus it is possible to run experiments in a preparative mode with inner standard application and quantitative data interpretation. The method is well documented in the literature but is laborious and acquires experienced personal for reproducible results. In comparison, Pyr-TD/GC-MS is a faster method giving quantitative information for a broad range of chemical series, reproducible results and offers credible “finger print” for the analyzed sample. Its drawbacks are the necessity of TD/GC-MS equipment and impossibility to run experiments in preparative scale.

Finally, as a recommendation for future pyrolytic experiments in view to gain information only for the structure of the high molecular phase of the lignite OM, preliminary bitumen extraction or mild hydrolysis of the lithotypes are advisable.

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