



The assessment of maturation changes of humic coal organic matter – Insights from closed-system pyrolysis experiments



Nikola Vuković^a, Dragana Životić^a, João Graciano Mendonça Filho^b, Tamara Kravić-Stevović^c, Mária Hámor-Vidó^d, Joalice de Oliveira Mendonça^b, Ksenija Stojanović^{e,*}

^a University of Belgrade, Faculty of Mining and Geology, Đušina 7, 11000 Belgrade, Serbia

^b Federal University of Rio de Janeiro, Institute of Geosciences, Department of Geology, Av. Athos da Silveira, 274, 21949-900 Rio de Janeiro, Brazil

^c University of Belgrade, Faculty of Medicine, Institute of Histology and Embryology, Višegradska 26, 11000 Belgrade, Serbia

^d Geological and Geophysical Institute of Hungary, Stefánia str. 14, 1143 Budapest, P.O. Box 106, Hungary

^e University of Belgrade, Faculty of Chemistry, Studentski trg 12-16, 11000 Belgrade, Serbia

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ABSTRACT

The artificial maturation changes of the humic coal organic matter (OM) from late diagenesis to the semianthracite stage of coalification were investigated using the closed-system pyrolysis. Two extracted coal samples, a subbituminous coal 26C (with a random vitrinite reflectance $R_r = 0.42\%$) and a high volatile bituminous coal 30C ($R_r = 0.56\%$), were pyrolysed during 4 h at two different temperatures, 250 °C and 400 °C.

The applied petrographic and organic geochemical analyses showed that the humic coal OM is sensitive to the artificial thermal stress. A good correlation between the changes in petrographic characteristics and the derived liquid products was observed.

The contents of all vitrinite macerals, as well as total vitrinite, increased during the thermal maturation. The abundance of liptinite macerals decreased during the maturation and they practically disappeared after 4 h of the pyrolysis at 400 °C. The total inertinite contents increased after the pyrolysis at 250 °C, yet to be decreased after the pyrolysis at 400 °C. The content of organic carbon increased from coals to the solid residues at 400 °C, whereas the contents of total hydrogen and sulphur decreased. The yields of gases, liquid products and solid residues at respective temperatures were very similar for both coals, regardless of the rank. As expected, the pyrolysis at 400 °C gave higher gas and liquid yields than at 250 °C.

Regarding the liquid pyrolysates, more pronounced changes were observed in the distribution of aromatic compounds than in saturated biomarkers. The distributions of the aromatics indicate that apart from cracking and isomerisation (the formation of thermodynamically more stable isomers), the reactions of dehydrocyclization, condensation (the formation of more stable conjugated systems) and aromatization, as well as reactions involving H_2S , elemental sulphur and reactive phenyl radicals released during the pyrolysis, also play an important role. It was shown that bentonitic clay plays a more important role in the subsequent aromatization of the OM than the initial maturity of the coal OM.

n-Alkane parameters were useful at lower maturities (up to $\sim 0.75\%$ R_r), whereas sterane, naphthalene and phenanthrene maturity ratios are applicable at higher maturities ($>0.75\%$ R_r). Hopane parameters showed variable sensitivities over the investigated maturity range (0.5–1.8% R_r). The most sensitive maturity parameters in the wide range of the humic OM maturity (0.5–1.8% R_r) are vitrinite reflectance, phenyl/naphthalene ratio, methylchrysene index 2 and a parameter proposed in this study, based on the distribution of methylfluorenes (MF): $(2- + 3-MF) / (1- + 4-MF)$. Generally, maturity parameters based solely on the isomerisation reactions of alkylaromatics, which do not include alkylation/dealkylation processes, are more appropriate for the humic OM, particularly at higher maturities.

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1. Introduction

The maturation changes of an immature sample can be experimentally simulated by the substitution of low temperature and long residence time natural processes with short duration procedures operated at higher temperatures, generally between 250 and 550 °C, using different pyrolytic techniques (Behar et al., 1992, 1997; Budinova et al., 2014;

* Corresponding author.

E-mail addresses: vukovic.nik@gmail.com (N. Vuković), dragana.zivotic@rgf.bg.ac.rs (D. Životić), graciano@geologia.ufir.br (J.G. Mendonça Filho), tamarakravic@med.bg.ac.rs (T. Kravić-Stevović), vido.maria@mfgi.hu (M. Hámor-Vidó), ksenija@chem.bg.ac.rs, xenasyu@yahoo.com (K. Stojanović).

Monthieux et al., 1985; Parsi et al., 2007). At these temperatures, reactions are rapid enough to monitor the changes within an acceptable time. Certainly, it is important to bear in mind that there is no ideal pyrolysis, as the conditions during these simulations are different from the natural ones (Yoshioka and Ishiwatari, 2002). Numerous methods are used to characterize the changes in structure and composition of the sedimentary organic matter (OM) during natural and artificial maturation.

Random vitrinite reflectance (R_r) is a widely accepted thermal stress parameter, used to describe effects of temperature and time on the thermal maturity of the sedimentary OM. In the literature, reference values of R_r corresponding to early, peak (maximum) and late oil window were proposed (Kostić, 2010; Peters et al., 2005). However, these values are considered empirical, because the increase in vitrinite reflectance and the generation of hydrocarbons (HC) from kerogen are processes with different mechanisms.

The analysis of the extractable organic matter (bitumen) has been proved to be a promising tool for the reconstruction of the sedimentary environment, as well as of the precursor biomass and its transformation during diagenesis and catagenesis. Concerning the bitumen analysis, the maturation changes are most often followed by the changes in the distribution of biomarkers (*n*-alkanes, hopanes, steranes, etc.; Peters et al., 2005 and references therein) and aromatic compounds (alkylated naphthalenes, phenanthrenes, dibenzothiophenes, chrysenes, aromatic steroids, etc.; Dzou et al., 1995; Li et al., 2012a; Radke, 1987). Moreover, in addition to commonly used methylated aromatics, maturity indices based on phenylated aromatics and binaphthyls were also reported (Li et al., 2012b; Marynowski et al., 2001, 2002; Rospondek et al., 2009). Most of proposed maturity parameters are based on the reactions of isomerisation, aromatization and cracking. In order to correlate vitrinite reflectance with some of the maturity parameters, several equations have been proposed (e.g. Dzou et al., 1995; Radke and Welte, 1983; Radke et al., 1984, 1986; Sofer et al., 1993).

However, there is no ideal maturity index, because most of them – in addition to maturity – may depend on the source and depositional environment of the OM, lithology (i.e. mineral catalytic activity), weathering, and in the case of oils also on the length of the migration path and secondary processes in the reservoir rocks (Peters et al., 2005). Moreover, some parameters demonstrated sensitivity to the thermal stress only in a certain range of maturity, and are non-useful at lower and higher maturities. Therefore, a reliable evaluation of the OM maturation changes and the applicability of maturity parameters on the investigated suite of samples require a simultaneous consideration of a great number of maturity indicators (George et al., 1998; Peters et al., 2005).

In this study, the changes of humic coal organic matter during the artificial maturation were investigated using different approaches. Vitrinite reflectance, maceral and elemental compositions were determined on the coal samples and the solid residues after pyrolysis. Simultaneously, bitumen isolated from the coal samples and the liquid products of pyrolysis were analysed using gas chromatography–mass spectrometry technique (GC–MS). A subbituminous coal 26C and a high volatile bituminous coal 30C from the Bogovina Basin were used as substrates. These coals contain a relatively immature OM (vitrinite reflectance 0.42% and 0.56%, respectively), which allows us to follow the maturation changes in the wide range from late diagenesis to the semianthracite stage of coalification. Moreover, these samples were chosen because previous analyses showed that they contain considerable amounts of liptinites for humic coals (up to 16.1 vol.%; Ercegovac et al., 2006; Životić et al., 2010), whereas the secondary maceral exsudatinitite (that is indicative for the generation of immature hydrocarbons, which probably originate from resins and waxes of higher plants – generally gymnosperms) was also observed in the case of 26C coal (Životić et al., 2010).

2. Samples and analytical methods

Two coal samples, a subbituminous (26C) and a high volatile bituminous (30C), were collected from two fresh working faces in

the underground mines of the Bogovina Basin. The intermontane Bogovina Basin is located in Serbia, 220 km south-east of Belgrade (43°53'33" N 21°56'50" E), and covers an area of about 70 km². It is a northeast–southwest elongated tectonic depression, with a maximum length of 25 km and a width of 2.5 km, which is divided into two fields: West and East. 30C sample was collected from the central part of the coal seam in the West field (the Upper Oligocene coal series ≈ 30–25 Ma; Životić et al., 2010) and 26C sample from the lower part of the main coal seam in the East field (Lower Miocene series ≈ 20–16 Ma). Petrographic and organic geochemical analyses were performed on the coal samples and the corresponding pyrolysis products obtained at 250 °C and 400 °C.

2.1. Petrographic analysis

For rank determination and maceral analysis, the coal samples were crushed to particles of up to 1 mm in size, mounted in epoxy resin and polished. The pyrolysis residues were also mounted in epoxy resin and polished. Maceral analysis was performed on a Leitz DMLP microscope under monochromatic and UV reflected light at 500 points (ISO 7404-3, 2009) in oil immersion. Macerals were identified after ICCP (1998), (2001) and Taylor et al. (1998) for the vitrinite, inertinite and liptinite maceral groups, respectively.

The reflectance measurements were performed under monochromatic light of 546 nm using a Leitz MPVII microscope and optical standards having reflectances of 0.589% and 1.699% in oil, following the procedures outlined by Taylor et al. (1998). The rank was determined by measuring the random reflectance on collotelinite B.

Confocal laser scanning microscopy (CLSM) was performed on a Leica SP2 inverted confocal microscope, with three lasers used for excitation: multiline Ar-ion (454.5–514.5 nm), green HeNe (543 nm) and red HeNe (633 nm). Confocal image stacks and k-series were acquired through an HCX PL APO oil-immersion objective (magnification 63×, numerical aperture 1.4), using Leica confocal software v. 2.61. The CLSM images were acquired as composite pseudocolour (RGB) images, where a false-colour palette is applied to three 8-bit signals of different primary colours.

2.2. Organic geochemical analysis

Elemental analysis was performed in order to determine the contents of total sulphur, nitrogen, hydrogen and organic carbon (C_{org}) in coals and the solid pyrolysis products. C_{org} was determined after the removal of carbonates with diluted hydrochloric acid (1:3, v:v). The samples were analysed using an Elementar Analysensysteme GmbH – Vario EL III CHNS/O Element Analyser.

Bitumen was extracted from the pulverized coal samples using Soxhlet extraction with dichloromethane/methanol azeotrope (15:2, v:v) during 72 h. Asphaltenes were separated from bitumen and the liquid pyrolysates (see below) by precipitation with *n*-heptane (mass ratio *n*-heptane:bitumen or liquid pyrolysate = 40:1).

The pyrolysis experiments were conducted on the extracted coal samples, which contained kerogen with native minerals. The initial masses of extracted samples were approximately 6 g. The pyrolyses were performed in an autoclave under a nitrogen atmosphere (the initial pressure at 25 °C was 6 bar), during 4 h at two different temperatures: 250 and 400 °C. Liquid pyrolysis products were extracted using chloroform, by combining thorough rinsing of the autoclave interior with hot solvent and Soxhlet extraction from the solid residue during 36 h. The liquid pyrolysates were further treated using the same methods applied for bitumen extracted from the coal samples (see above). Gaseous products were not analysed, although their formation was indicated by the pressure change in the autoclave.

Asphaltene-free bitumen and the liquid pyrolysates were separated into the saturated, aromatic and polar (NSO) fractions using column chromatography (adsorbents: SiO₂, 2.25 g and Al₂O₃, 1.65 g; eluents:

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