PECHORA BASIN COALS ORGANIC GEOCHEMISTRY AND HYPERCOAL PRODUCTION

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The limited use of coals of Pechora coal basin (PCB) is primarily related to a high ash content, reaching 50 %, resulting in a low calorific value of the coal, technological problems of combustion, high harmful emissions, a large volume of fine solid wastes. At present the production of ashless coals, so called "hypercoals" is the easiest methodically technology related to the thermal treatment of initial coal by an organic solvent (Takanohashi et al., 1996, Koyano et al., 2011).

The aim of this study is to find the possibility of production of ashless extracts from Early Permian coals from Inta field, to reveal the connection of structure of laboratory hypercoals with the structure of the initial coal, as well as clarification of the composition of the initial organic matter and conditions of formation of organic mass of coals from PCB Inta field by organic geochemistry.

The considered coals are related to Lower Permian Inta coal field located in the south-western part of PCB (Protsko, Medvedeva 2014).

Chloroform bitumen was extracted from the initial coals, which was fractionated into aromatic and aliphatic fractions and studied by gas chromatography and chromatography-mass spectrometry. Then the initial coal samples were enriched in a solvent with density 1.6 g/cm3. The resulting light fraction was dried and treated with N-methylpyrrolidone (NMP). A mixture of coal and NMP a day later was boiled under reflux for 2 hours, filtered on a Buchner funnel under vacuum through a paper filter, washed by a hot NMP and the resulting solution was evaporated. After distilling of solvent, the obtained precipitate of ashless coal was dried in an oven at 230 °C. The light fraction residue was washed with hot water from the residual solvent and dried in an oven at 140 °C after isolation of hypercoal. The analysis of the obtained extracts and initial coals was carried out with 13C NMR spectroscopy in a solid state (spectrometer BRUKER AVANCE II-500, operating frequency at ^{13}C – 125.77 MHz), and the elemental composition was also determined.

The presence of high concentrations of C29 steranes, C27-C29 n-alkanes in bitumen indicates a significant contribution of terrigenous vegetation into initial biomass, for a number of samples the presence of high concentrations of C23-C25 n-alkanes can be a sign of the contribution of aquatic vegetation into initial biomass.

The maturity indicators show a low degree of thermal maturity of coals organic matter. Thus, 20S/20S+R ratio of C29 steranes composition is less than 0.1 in all samples; a high concentration of biological ββ diastereomers of hopane hydrocarbons and 22S/22S + R ratio, less than 0.2, support this conclusion. Among pentacyclic terpanes we also found their unsaturated analogues - neohop-13(18)-enes with C29 and C30 composition (Bushnev et al, 2016.). Among major components of bitumen aromatic fraction we determined simonellite, dehydroabiethane, retene, metylretene representing products of abietic acid transformation (Tewari et al, 2017.), and also cadalene, which precursor is bicyclic sesquiterpene - cadinene.

The predominance of simonellite (m/z = 237, M = 252) and dehydroabiethane (m/z = 255, M = 270) over retene (m/z = 219, M = 234) confirms low maturity of the coals (Tewari et al., 2017). Methylnaphthalenes, metyl substituted phenanthrene, dibenzofuran, pyrene are contained in subordinate concentrations. An exception is one of the samples, where methyl-, ethylnaphthalenes and also methyl- and ethyl derivatives of phenanthrene are dominant components of the fraction.

The vitrinite reflectance (Ro) in Inta coal mines are 0.6-0.67 % (Protsko, Medvedeva, 2014), which correspond to the onset of mesocatagenesis or coal stage, and biomarker data suggest lignite stage of OM transformation or its protocatagenesis.

The processing of the initial coal by N-methylpyrrolidone resulted in the extract yield from 11 to 31 %. Similar yields were obtained by NMP processing of coals from PCB Vorgashor and Vorkuta fields with more mature OM.

The H/C atomic ratio, obtained in the course of the elemental analysis of the studied extracts, testifies to the dominant role of aromatic components in their structure. The composition of the extracts is also marked by an increased content of nitrogen that can be explained by the direct influence of used solvent (Takanohashi et al., 1996). The latter is confirmed by CP/MAS 13C NMR spectroscopy of the hypercoals, where in area of 165 - 167 ppm spectra a signal is clearly recorded, which is characteristic of carbon in carboxyl groups and cyclic amides, which can also testify to favor of N-methylpyrrolidone. Variations of intensity of this signal can be related to nitrogen content in the studied samples. This signal is absent in the initial coal spectra. For the initial coals (IC) we received absolutely similar 13C NMR spectra, testifying to a similar structure of coal OM chemical structure. The result of processing of the initial coals by N-methylpyrrolidone is an extract, which chemical structure has a certain similarity with the structure of the initial coals. Thus, the analysis of CP-MAS spectra and also the results of editing of the spectra showed that the obtained hypercoals is just a little different from the initial coals. At that they are characterized by a slight increase of an aliphatic component and presence of amide groups due to interaction with the solvent.

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