Bituminous Coals Thermodestruction by the Thermofiltration Method

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ABSTRACT: Coking coals of the same rank but different genetic types (reduced and low-reduced) have been studied by means of coal chemistry. It has been shown that reduced coals and low-reduced coals are distinguished by composition, structure and thermal behavior. These facts have been explained with various associations of high-condensed aromatic blocks in coal macromolecules.

KEY WORDS: coking coals, genetic types by reductivity, thermofiltration, coal structure.

Introduction

Coal properties depend not only on the coal rank. Some coals of the same rank and the close petrographic composition but with aberrant properties occur in the same coal field. Abnormal coals have been found in the Durham and the Ruhr coal fields, the Donetsk and the Kuznetsk basins (Murchison and Pearson 2000, Amosov 1963). Such coals are called reduced (RC) and low-reduced (LRC) type or perhydrous and subhydrous coals in compliance with monograph (van Krevelen 1981). But both of categorizations are not the same. The genetic type by reductivity refers to geological characteristics of coal seams and indicates conditions of peat-forming plants decomposition. The presence of limestone layers above the coal seams, and finely crystalline pyrite within them proved to be reliable signs of a reduced type of Donetsk coals (Bechtet et al. 2002).

According to the literature and previous investigations, RC and LRC of the same rank differ by following:

- composition of coal organic mass (COM), H/C (atm.) (Butuzova et al. 2005a, Butuzova et al. 2002)
- some special feature of COM structure (Butuzova et al. 2005b, Iglesias et al. 2002)
- coking ability (Butuzova et al. 2005b)
- yields of pyrolytic products, their composition etc. (Murchison and Pearson 2000, Iglesias et al. 2002, Butuzova et al. 2005a, Butuzova et al. 2002).

But these facts have been interpreted from the position of RC and LRC structures. The structure and reactivity of the different genetic coal types have not been well studied till now.

№	Coal mine, seam	Type	$R_{o,r}$ [%]	Petrographic components [% vol.]			Lithotype with finely crystalline pyrite [% vol.]
				Vt	L	I	
1	Gagarino m_3	LRC	1.18	85	3	12	1
2	Zasiadko l_4	LRC	1.01	89	6	5	0
1′	Gagarino m_4^0	RC	0.96	87	3	10	82
2′	Zasiadko k_8	RC	0.96	83	3	14	56

$R_{o,r}$ – vitrinite reflectance, Vt – vitrinite, L – liptinite, I – inertinite.

■ **Tab. 1.** Vitrinite reflectance and petrographic composition of the sampled coals.

The thermofiltration method was used for present investigations. This thermal method has large potential for study of coking coal structures, transformations of their organic mass under heating. The thermofiltration make possible to save nonvolatile components of a coal plastic layer and to study last one by different methods such as an extraction, chromatography and FT-IR spectroscopy.

The main aim of the present study was investigation to obtain more information concerning of GTR influence on a yield of pyrolytic products, a conversion of heated coking coals organic mass and a composition of coal plastic layer.

Procedures

Representative coal samples from Donetsk Basin were used in this study. Two pairs of reduced and low-reduced coking coals were selected from closely spaced coal seams separated by distances of less than 100 m. (Geological-geochemical map 1954). The geological factors were used for identification of genetic types by reductivity of selected coals. All coals were characterized as a petrographic homogeneous. Middle content of vitrinite was about 85 % (Table 1). The samples were analyzed according standard procedures; the thickness of plastic layer by Sapozhnikov's method (Y) was applied as characteristic of coal coking ability. The ultimate and proximate analyses of investigated coals are shown in the Table 2.

The thermal decomposition of coals was carried out by the termofiltration procedure (GOST 17621-72). The last one is based on centrifugation of a coal sample with simultaneous quick heating up to 600 °C. This technique allows separating nonvolatile components of a plastic mass without secondary thermal transformation from a remaining COM which does not be able to transform to a plastic layer. The termofiltration process was realized in the centrifuge which was constructed in Kharkov Polytechnic Institute (Birukov 1980). The nonvolatile components (LNP) accumulated in a cold collector; the non-transformed residue of COM (NTR) stayed on the metal filter; the volatile matters exuded through a gap between the collector and the metal filter. The experimental conditions: speed of the

№	Coal mine, seam	Type	Characteristics of initial coals [wt. %]								
			W^a	A^d	V^{daf}	Y [mm]	S_t^d	C^{daf}	H^{daf}	$(O+N)^{daf}$	S^{daf}
1	Gagarino m_3	LRC	1.2	3.7	28.7	22	0.70	87.4	5.1	6.9	0.6
2	Zasiadko l_4	LRC	1.4	2.6	31.7	16	1.09	87.8	5.16	7.0	0.8
1′	Gagarino m_4^0	RC	0.8	12.2	35.6	32	3.75	83.6	4.9	10.0	1.3
2′	Zasiadko k_8	RC	0.8	2.7	31.7	27	2.81	87.3	5.23	7.2	1.7

■ **Tab. 2.** Ultimate and proximate analysis of the coals.

centrifuge – 1500 revolutions per minute, reheat temperature up to 600 °C, heat rate ‒65 °C per minute.

The obtained LNP were parted by extraction. The exhaustive extraction was carried out in a Greffe apparatus consecutively with hexane, benzene and acetone. After distilling off the solvent, the extracts were dried in vacuum and separated. The asphaltenes were determined as insoluble in hexane and benzene soluble. The hexane-soluble fractions were washed by 10 wt. % H_2SO_4, 13 wt. % $NaHCO_3$ and 10 wt. % NaOH. Then base-, acid- and phenol-free fractions (neutral oils) were separated into saturated, aromatic hydrocarbons and polar heterocompounds by silica gel chromatography using hexane, benzene and acetone as eluents.

Gas chromatography-mass spectrometry (GC/MS) analyses of the saturated and aromatic hydrocarbons were performed on a gas chromatograph directly coupled to a mass spectrometer (HP 6890 with MD 5973). A capillary column HP1MS 30 m × 0.32 mm with fused-silica film of thickness 0.25 µm was used. Helium was the carrier gas; rate of gas flow was 1.2 ml. per minute. The GC oven temperature was programmed from 85 to 320 °C at a rate of 5 $°C.min^{-1}$, the temperature of injector was 300 °C.

The insoluble solid remains after Greffe's extractions were analyzed by FT-IR spectroscopy. IR-spectra were recorded on the "Bruker" spectrometer. The samples were prepared as 5 % tablets of coal with KBr. The IR spectra were obtained in the range 700–4,000 cm^{-1}. Multipoint baseline correction was performed using the Origin software package.

Results and discussion

The yields of the main termofiltration coal products are listed in the Table 3.

The experimental data shows that reduced coals give the higher quantity of the liquid nonvolatile products than low-reduced coals. It is compensated by large yield of the solid residue after spinning of LRC. These facts agree with the thickness of plastic layer by Sapozhnikov's method (Table 2) and point out a better coking ability of RC. But it is not true for process in conditions of standard Fisher's method. Previous data for investigated semi-coking coals indicated that LRC formed a durable, finely porous semi-coke, and RC made a bellied, breakable solid residue (Safin et al. 2005).

Coal mine, seam	Type	LNP (daf%)	Volatile matters (daf%)	NTR (daf%)
Gagarino m_3	LRC	22.4	19.9	57.7
Zasiadko l_4	LRC	17.1	23.4	59.5
Gagarino m_4^0	RC	38.7	21.3	40.0
Zasiadko k_8	RC	42.0	17.3	40.7

■ **Tab. 3.** The yields of the termofiltration products.

Coal mine, seam	Type	Neutral oils (daf%)	Carbonic acids (daf%)	Phenols (daf%)	Organic bases (daf%)	Asphaltenes (daf%)	Acetone-soluble (daf%)	∑. solubles (daf%)
Gagarino m_3	LRC	8.52	0.02	3.87	0.76	11.08	1.11	25.36
Zasiadko l_4	LRC	7.13	0.19	1.40	0.27	9.30	1.87	20.16
Gagarino m_4^0	RC	4.02	0.07	1.26	0.28	6.17	2.27	14.07
Zasiadko k_8	RC	3.10	0.23	0.57	0.34	4.51	1.50	10.25

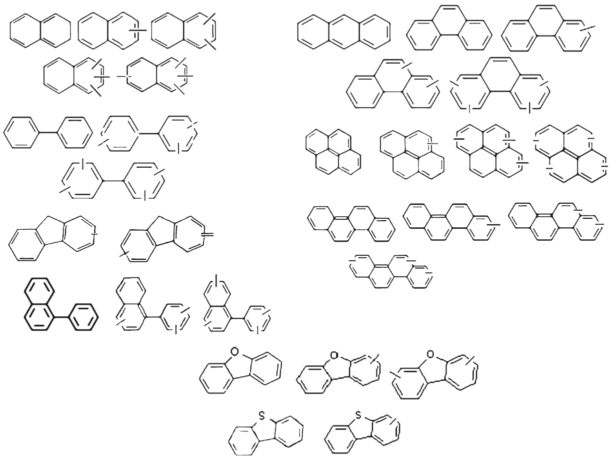
■ **Tab. 4.** Composition of extracts obtained from liquid nonvolatile products.

The amounts of different fractions obtained by the LNP exhaustive extraction are collected in Table 4. Data, despite the same conditions of the process, show considerable variations in their composition which depend on the genetic type by reductivity. For LNP obtained from low reduced coals, a more solubility in organic solvents is typical. It can be explained by the fact that LRC plastic layer enriched by more low molecular products.

The neutral oils characterized by GC/MS amounts to only 6 wt. % of the organic matter of LNP, nevertheless, this bitumen provides valuable and specific information on the thermal behavior of different coking coals. The neutral fractions of RC and LRC have various compositions and contain n-alkanes, polycyclic aromatic compounds and heterocyclic hydrocarbons. The aromatic structures identified by GC/MS in the hexane and benzene eluates from the silica gel column chromatography of neutral oils are summarized in the Fig. 1.

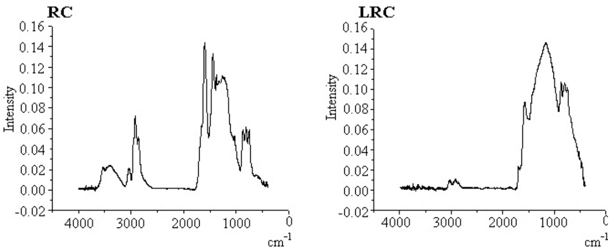
The data show the presence of *n*-alkanes with long chains, LNP from reduced coals have C_{14} – C_{31} hydrocarbons and low reduced coals – C_{15} – C_{31} hydrocarbons. Aromatic hydrocarbons are mainly represented as polycyclic aromatic structures which contain 2–4 condensed benzene rings with aliphatic side-chains. The content of polyaromatic systems without saturated substituents is negligible. The neutral oils include many various biphenyl-conformable structures, which represented in the form of aliphatic substituents homologs, too. About 75 organic compounds included dibenzofurane and dibenzothyophene derivatives were found in the liquid products after of centrifugation (Fig. 1).

A comparative determination of the yield and composition of the obtained neutral oils was carried out. The results are gathered in the Fig. 2. It can be seen from these figure that amount and distribution of determined compounds are closely coupled with the genetic type by reductivity of coking coals.



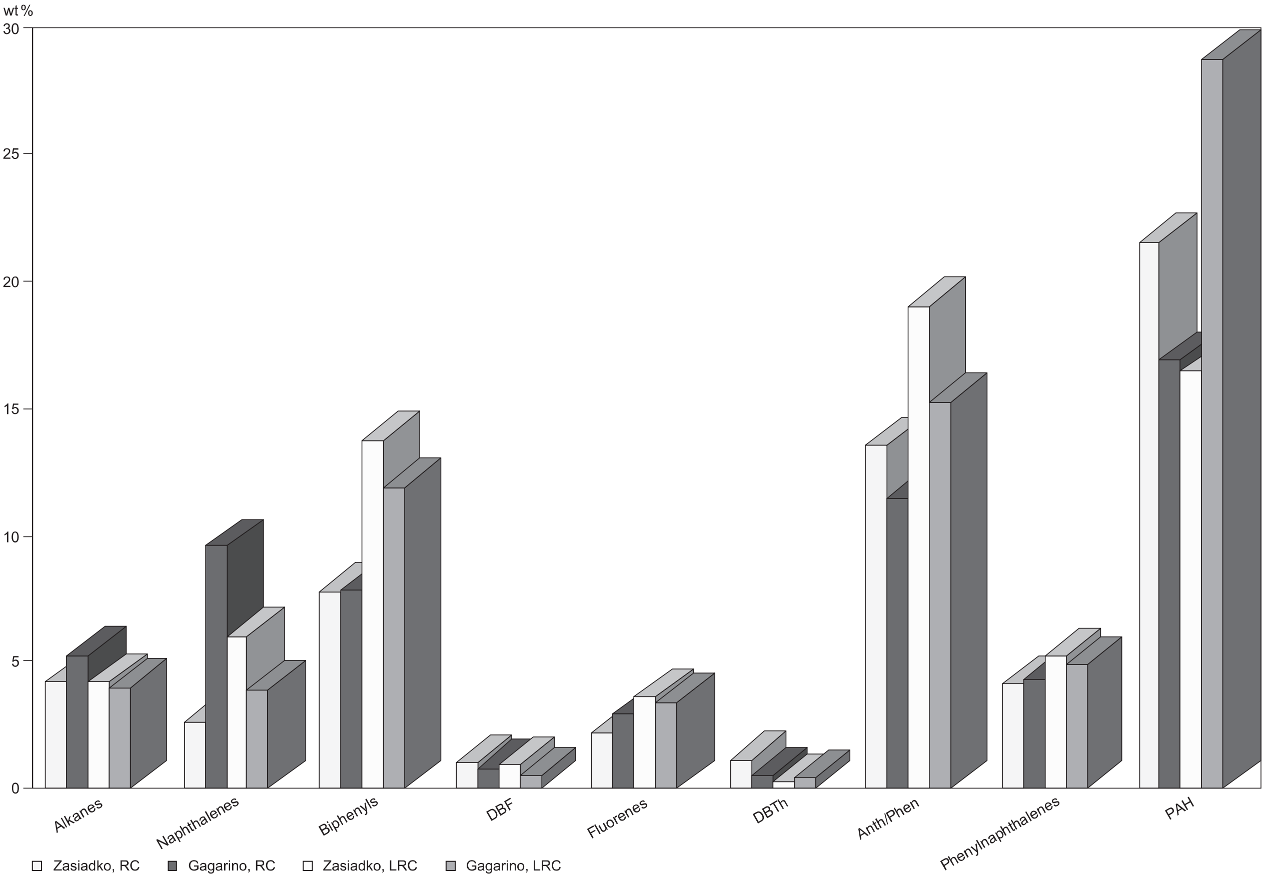
■ **Fig. 1.** Aromatic structures identified in neutral oil from LNP.

The present investigation reveals that the hexane-solubles have high content (above 5 wt. %) of n-alkanes. The neutral oils from reduced coals contain more aliphatic compounds than from their isomethamorphic pairs of LRC. Liquid products from low-reduced coals contain higher total sum of aromatic hydrocarbons with four- and three- condensed benzene rings. Also, pyrolysis of RC conduct to an enrichment of neutral oils with dibenzofuranes and dibenzothyophenes compounds. According to these facts, it is obvious that macromolecule networks of RC are made of major quantity of aliphatic fragments, and the organic mass of LRC have more condensed aromatic systems. A great quota of heterocyclic hydrocarbons in "RC neutral oils" comes out from high content of S and O in original reduced COM.



■ **Fig. 3.** IR-spectra of insoluble part LNP.

The data about structures of insoluble solid residue after Greffe's extractions of LNP have been received by IR-spectroscopy. Forms of IR-spectra of NTR are included in the Fig. 3. The figure shows that view of spectra from NTR of reduced coals is typical for nonpyrolysed coking coals. The observed spectra have been compared with IR-spectra of original RC and LRC (Safin et al. 2005). Sharp distinctions are observed only in decrease a set of absorption bands due to aliphatic functional groups (2,970, 2,920, 1,440 and 1,380 cm^{-1}). Spectral characteristics of "low-reduced NTR" differ a lot from original LRC.



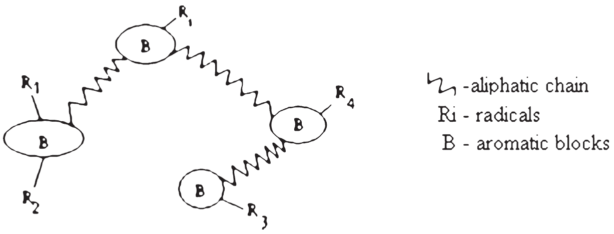
■ **Fig. 2.** Composition of neutral oils DBF-dibenzofurane, DBTh-dibenzothyophene, Anth/Phen-sum of anthracene and phenantrne, PAH-polyaromatic hydrocarbons.

The pyrolysis of coking reduced coals at 600 °C result in creation of high molecular organic compounds like original coal macromolecules. In whole obtained NTR are defined by a lack of aliphatic part of coal organic mass and by increasing of -C-O- groups absorption bands (1,650, 1,250 and 1,150 cm^{-1}).

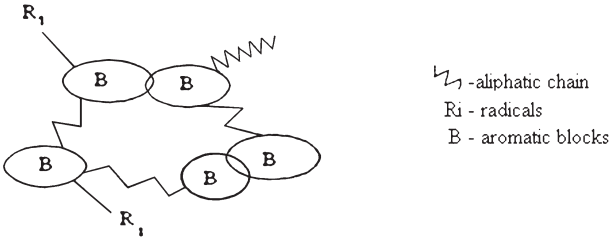
Conclusions

Coking reduced and low-reduced coals are distinguished by their behavior during pyrolysis processes. These variations are caused of different composition and structures of COM.

Probably, the difference in structures of organic mass for RC and LRC due to differing connection of high-condensed aromatic blocks (B) in coal macromolecules. The macromolecules of reduced coals consist of high condensed aromatic systems which bonded by less aromatic or by aliphatic fragments (Fig. 4). Macromolecules of RC are notable by a higher quantity of relatively weakly bonds (-CH_2-, -S-) than isomehtamorphic LRC pairs. For that reason, such coals generate a major quantity of LNP, but these thermal products are attributed by a higher amount of an association. The aromatic system of LRC macromolecule is equidistributed throughout extension (Fig. 5). The COM of LRC generates the nonvolatile components of plastic layer with a low molecule mass which involve a big sum of phenols and asphaltenes. These products have better mobility to macromolecule coal network and better reactivity. Therefore, the coking low-reduced coals form durable, finely porous semi-coke though low coking ability determinating by different methods.



■ **Fig. 4.** The hypothetic “block” structure of reduced Donetsk coking coals.



■ **Fig. 5.** The hypothetic “block” structure of low-reduced Donetsk coking coals.

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