

Pyrolysis in the centrifugal field of blends from high- and low-sulphur coals

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Abstract

Coals formed under reductive (RC) and less reductive conditions (LRC) and blends on the basis of these coals were pyrolysed in centrifugal field, allowing to separate solid, fluid and gaseous products.

It has been shown that during plastic stage the blends components chemically interact. The character of this interaction depends on the coal facies. Replacement of the RC by the LRC in blends leads to 2,5-fold increasing of fluid products yield from coking J-Grade coal which can be of great practical value.

Using the EPR and DRIFT-spectroscopy methods the structural peculiarities of the obtained products have been studied. An apparent correspondence between the high content of free radicals in fluid non-volatile products and coal coking ability has been discovered.

Keywords: Coal-facies; Coking ability; Plastic layer; Coal blends

1. Introduction

Limited resources and high cost of coking coals require elaboration of methods for making optimal blends based on available raw materials. The problem of expansion of the raw material base at the expense of optimal inclusion of low-quality (sulphur, oxidized) coals into coke blends without deterioration in coke quality should be given special priority.

The solution of the above problem involves studying the influence of heteroatoms, primarily those of coal sulphur and oxygen, on chemical processes occurring at the stage of plastic state.

There are many different hypotheses explaining the essence of caking and coking processes of solid fuels. However, so far no single universally accepted theory of caking has been proposed. A mechanism of thermochemical conversions of coal organic matter (COM) has been a subject of discussions and is differently treated by various authors. The schemes of formation of coal plastic matter proposed in literature ignore a vital role of heteroatoms in COM and thus allow no definite prediction of the yield, composition and properties of coal products.

It is well known, for instance, that open air storage of coal even for a short period of time results in a substantial decrease in its plasticity. Conversely, the presence of sulphur improves the caking capacity of solid fuels. Thermal transformations of COM heterorganic compounds, as well as the processes of donor hydrogen transfer and redistribution, are determined by the molecular structure of coal. Accordingly, studies of the chemical structure of coals of different coal-facies and different coalification degree (i.e. with different sulphur and oxygen contents) and their behavior during heating should play a crucial role in understanding of caking as a process.

Practical importance of these studies is particularly relevant for coking plants of Ukraine, where most currently mined solid fuels have high sulphur content.

The aim of this research is to study the effect of sulphur content (coal-facies) in individual components of coal blends on the yield and characteristics of the plastic layer responsible for caking.

To solve the problems under discussion the hypotheses developed by the authors of this paper for several years have been used which can be briefly formulated as follows:

- coal organic matter is viewed as a high-molecular compound of heteropolycondensate type with reactivity and properties largely depending on the content of heteroatoms and the form in which they are present in coal;
- thermal destruction of coal is regarded as a process which involves competing reactions of destruction and synthesis based on free radical mechanism;
- the mechanism of synthesis reactions which yield coal “polymer” (i.e. semicoke or coke) upon heating can include reactions of chain polymerization and polycondensation by the functional groups.

2. Experimental

Two pairs of the isometamorphic Denets coals homogeneous by their petrographic composition, but formed under reductive (RC) and less reductive conditions (LRC) and different by their sulphur content accordingly were used as objects of research. It was coals of J-Grade ($\approx 83\text{--}88\%$ C^{daf}) and G-Grade ($\approx 75\text{--}79\%$ C^{daf}) according to Ukrainian classification. On the basis of these coals, blends (J:G = 70:30) with all possible combinations of LRC and RC type coals were prepared.

The samples were thermally treated using the method of centrifugal thermal filtration (CTF) in the Kharkiv Polytechnic centrifuge (National Standard 17621-89). This method enables one to separate primary products that form the plastic mass, immediately, thus preventing their secondary transformations (Birukov 1980). The sample under treatment was heated up to 600°C in the centrifugal field at the rate of 1500 rev/min; subsequently the yields of the following products were found: the over-sieve residue (OR), fluid non-volatile products (FNP) and vapour-gas compounds (VG). The amount and composition of FNP largely determine the processes of caking and coking. Besides, the theoretical plastic mass yield was calculated for the above blends using the rule of additivity:

$$s = a \times w(a) + b \times w(b) \quad (1)$$

where S is the plastic mass yield, %; a , b are the yields of plastic mass from the separate blend components, %; $w(a)$, $w(b)$ are the content of these components in a blend, portions.

The EPR-spectra of the coals were recorded on a Bruker ER 200D SRC radiospectrometer at ambient temperature. The spectra were recorded as a first derivative absorption line at the time of field scan 200 s. Active coal with the content of paramagnetic centres (PMC) $N=6.25 \times 10^{16}$ was used as a standard. The error of determination for N was 10%; for g -factor -0.0001, and for the line width (ΔH) $\approx 0.2\%$. The concentration of lone electrons was found using a standard sample with the definite concentration of free radicals.

The IR-spectra were recorded on a Bruker FTS-7 spectrometer using the DRIFT technique. Semiquantitative processing of the IR-spectra was performed with the help of the software package Origin 6.1 using the basic-line technique.

3. Results and discussion

Fig.1 show the experimental and calculated data of the yields of FNP, over-sieve residue and vapour-gas compounds from RC and LRC coals and blends on their basis.

Fig.1 demonstrates a great difference in FNP yields and, therefore, in the caking capacity of coals of the same brand, but different coal-facies. Thus, the FNP yield depends both on the rank and redox-conditions during deposition of coals making a coke blend. This indicator is essentially higher (2.5 times) for LRC coals of G-Grade and RC coals of J-Grade as compared with their pairs of the same rank. Replacement of the reduced coal of brand G by

the low-reduced one dramatically increases the yield of fluid mobile products responsible for caking. It should be pointed out that for the blends under discussion the experimental data for the yield of CTF products are in discordance with those theoretically calculated by the rule of additivity. The product yield and deviations in the yield of the plastic mass from the calculated values also depend critically on the coal-facies and differ at the identical grade composition of the blends. Apparently, chemical interaction of the blend components occurs, which depends on the structure of the original coals and determines the quality of the plastic layer (Gryaznov 1983; Zubkova 2002).

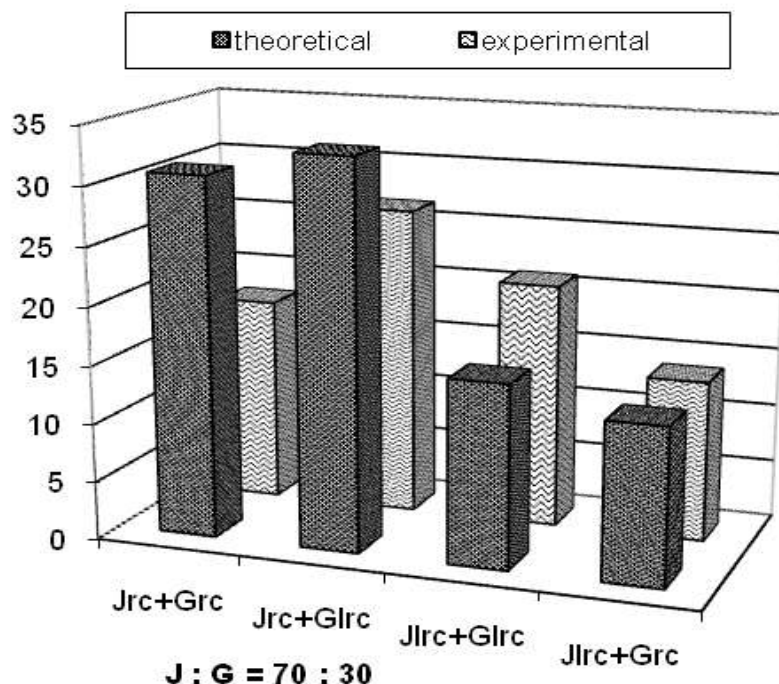


Fig.1

The most advantageous composition giving the maximum yield of the fluid mobile phase at the ratio of the components specified above is a blend containing the reduced J-Grade (J_{RC}) and the low-reduced coal of G-Grade (G_{RC}). The greatest deviation of the experimental values from the calculated ones is observed for the $J_{RC} + G_{RC}$ blend, which permits an assumption about the strongest interaction between the components (Bechtel et al., 2002; Butuzova et al., 2005).

To understand the nature of interaction between the components in a coke blend it is useful to compare the parameters of the EPR-signals for the original coals, blends and their thermal filtration products.

As is seen from Table 1, PMC concentration (N) in the samples under discussion essentially depends on the components genetic type by reductivity. The value of this indicator is drastically different for type LRC and RC coals of brand G (G_{LRC} and G_{RC}). The value for N is about 30 times higher for the reduced coal and practically equals the number of PMCs in type LRC coal of brand J. When the G_{RC} coal is transformed into a plastic state, the basic amount of PMCs remains in the solid product, i.e. the over-sieve residue, whereas in FNP the concentration of PMCs is ≈ 35 times lower.

Conversely, the G_{LRC} coal containing a minimum amount of PMCs generates free radicals into FNP during thermal filtration. The J_{LRC} and J_{RC} coals behave in a similar way, the latter forming FNP with the PMC concentration ≈ 4 times higher than that in the original coal. An increase in the value of N seems to be due to the processes of monomolecular radical

decomposition and the system of polyconjugation capable to stabilize radicals in the liquid phase. At the same time, an increase in the yield of liquid thermodestruction products is observed, which is 2.5 times higher for the reduced coals as compared to the low-reduced ones. These results indicate that reactions resulting in the formation of the plastic layer occur with the participation of free radicals. The effective values of the g-factor for the coals under examination, for the blends and the products of their thermal filtration are similar. They go down from 2.0040 to 2.0039 only for the low-reduced G_{LRC} and J_{LRC} coals.

Coals, fluid mobile products, over-sieve residues of coals and blends		N, spin $g^{-1} \times 10^{-17}$	Line width $\Delta H, E$	g-factor
coal	G_{LRC}	2,24	6,43	2,0039
	G_{RC}	64,25	6,79	2,0040
	J_{LRC}	64,28	7,02	2,0039
	J_{RC}	43,16	5,21	2,0040
fluid mobile products	G_{LRC}	38,50	6,06	2,0040
	G_{RC}	1,78	6,01	2,0040
	J_{LRC}	114,9	6,25	2,0040
	J_{RC}	159,9	6,26	2,0040
	$G_{RC} + J_{RC}$	110,50	7,07	2,0040
	$G_{LRC} + J_{RC}$	111,40	6,92	2,0040
	$G_{LRC} + J_{LRC}$	43,14	5,79	2,0040
	$G_{RC} + J_{LRC}$	45,38	5,68	2,0040
over-sieve residues	G_{LRC}	-	-	2,0040
	G_{RC}	61,14	6,64	2,0040
	J_{LRC}	6,5	6,92	2,0040
	J_{RC}	4,0	6,60	2,0040
	$G_{RC} + J_{RC}$	-	-	2,0039
	$G_{LRC} + J_{RC}$	0,11	4,00	2,0040
	$G_{LRC} + J_{LRC}$	0,028	4,04	2,0040
	$G_{RC} + J_{LRC}$	0,19	5,23	2,0040

Table 1. Paramagnetic characteristics of the samples of coals and blends under analysis

It is well known (Vasilieva et al., 1973) that there are three types of PMCs in the coals and semicokes, which give two broad signals ($\sim 7 E$) with the g-factors of 2.0042 and 2.0030 and one narrow (1,0-1,5 E) signal with the g-factor of 2.0025. The signal with the g-factor of 2.0030 corresponds to radicals of aryl type, whereas that with the g-factor of 2.0042 is assigned to oxygen- and sulphur-containing radicals. A narrow signal whose share in the general intensity of the spectra does not exceed 1 % cannot be registered in air atmosphere. Proceeding from all the above, an increase in the value of the g-factor for the reduced coals can be accounted for by growing intensity of a signal with a greater g-factor and results from the formation of condensed aromatic sulphur-containing radicals, which agrees with the data of the ultimate analysis.

The line width is determined by the magnetic dipole interaction, exchange forces, local fields created by the matrix, and thermal motion. Therefore, the J_{RC} coals characterized by narrower EPR signals ($\Delta H \sim 5.21 E$) as compared to the J_{LRC} coals ($\Delta H \sim 7.02 E$), contain the most stable PMCs, which are concentrated in the depth of rigid supermolecular formations.

The maximum rigidity of the polyconjugated areas is observed for solid residues of thermal filtration of the blends ($\Delta H \sim 4.00 - 4.04 \text{ E}$). As is well known (Butuzova et al., 1997; Fowler, Bartle, 1989; Butuzova et al., 2009; Pilawa et al., 1993), the width and form of broad resonance lines in the EPR-spectra of coals are basically determined by hyperfine interaction (HFI) with magnetic nuclei.

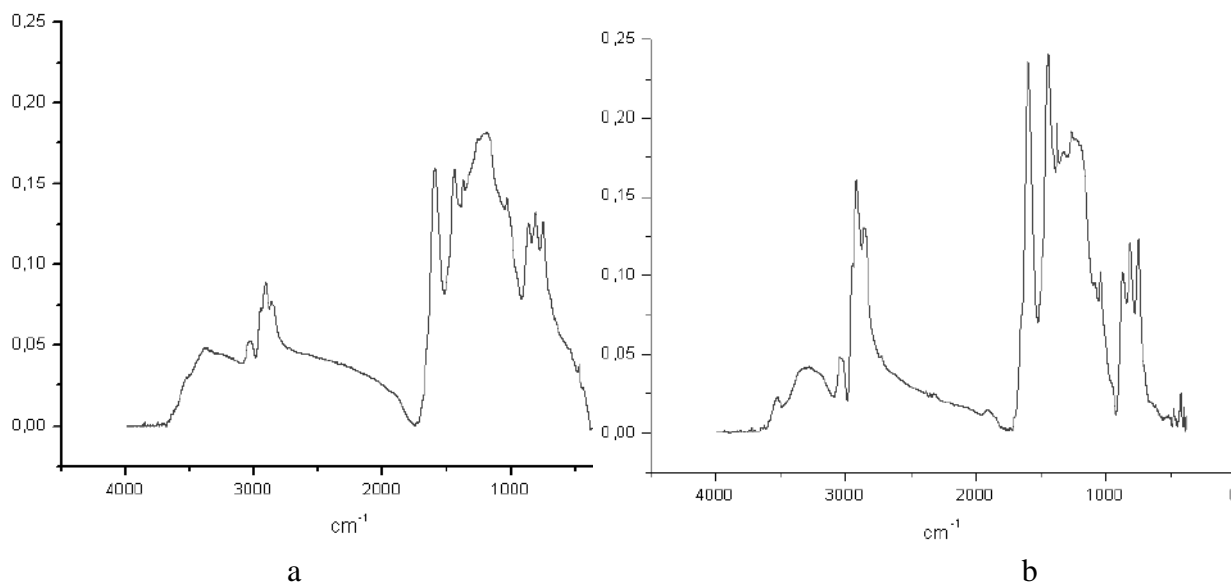


Fig. 2

Thus, the observed differences in the paramagnetic properties of RC and LRC coals indicate greater molecular rigidity of polyconjugated areas in the structure of reduced coals, primarily the J_{RC} coal.

Let us consider changes of paramagnetic characteristics of coals in thermal filtration products of the blends with different compositions. When coal of J_{RC} is added to coals of brand G (G_{LRC} and G_{RC}), the concentration of PMCs in FNP drastically goes up (by 2.5 times). In the FNP based on J_{LRC} coal the concentration of PMCs is 2.6 times lower. The value of N for all non-volatile residues is several orders of magnitude lower as compared to FNP, particularly for the $G_{LRC} + J_{LRC}$ blend, which is distinguished by a greater value of the experimental as against the theoretical FNP yield. It can be assumed that in this case the interaction of the components leads to the destruction of the rigid three-dimensionally cross-linked matrix. In the other blends an inverse phenomenon is observed, i.e. a decreased experimental as opposed to the calculated FNP yield. Apparently, this is the result of cross interaction of the products obtained from different blend components. If we assume that in the $G_{RC} + J_{LRC}$ blend the interaction of the components is minimal (i.e. the experimental and the calculated FNP values are roughly equal), it can be concluded that addition of the coal of brand J of type LRC brings about an increase in the FNP yield up to 13.8 % in contrast with the 4.8 % yield value for the G_{RC} coal. In the $G_{RC} + J_{RC}$ blend the interaction of the components is maximal (i.e. the experimental FNP value is much lower than the calculated one), which gives rise to an increase in the value for OR, broadening of the EPR-signal and a decrease in the amount of PMCs in OR. Nevertheless, PMC concentration in FNP remains high.

The data obtained permit to attribute the optimal properties of the $G_{LRC} + J_{RC}$ blend to the highest PMC concentration in FNP.

Fig. 2 shows the spectra of the plastic masses of two blends made of the low-reduced grade G and J coals (Fig. 2a) and the reduced coals of the same grades (Fig. 2 b). It follows from the Figure that the RC coals yield the plastic layer characterized by high content of aliphatic groups ($\nu = 2920\text{cm}^{-1}$ and 1440cm^{-1}).

Table 4 demonstrates the results of measuring the intensity of the absorption bands in the DRIFT spectra of solid residues and fluid mobile thermal filtration products for the coals and blends under discussion. As is seen from Table 3, when J_{LRC} coal by J_{RC} the concentration of oxygen-containing OH-groups and the content of CH_{al} groups in the blends increases. The $G_{LRC} + J_{RC}$ blend is characterized by a minimal proportion of -O-, -S- groups and CH_{ar} groups.

The J_{RC} coal enriched with aliphatic hydrogen is likely to promote an increase in the FNP yield, which agrees with the data of Table 2. This can be seen from a higher intensity of the bands for valence and deformation vibrations of CH_3 -, CH_2 - и CH - groups ($2920cm^{-1}$, $1440cm^{-1}$), and from a lower relative intensity of bands at I_{3040}/I_{2920} and I_{1600}/I_{1440} .

Coals, fluid mobile products, over-sieve residues of coals and blends		Absolute intensity													Relative intensity						
															I_x/I_{2920}	I_x/I_{1440}	I_x/I_{1600}				
		3150+	3380	3040	2920	2850	1650+	1700	1600	1440	1370	1260	1190	1030	860	810	750	1190	1260	3040	1260
coal	G_{LRC}	0,09	0,05	0,18	0,13	-	0,26	0,14	0,03	0,06	0,07	0,09	0,04	0,05	0,04	0,37	0,34	0,30	0,45	1,89	0,24
	G_{RC}	0,07	0,05	0,18	0,14	-	0,26	0,14	0,03	0,06	0,06	0,11	0,04	0,06	0,05	0,33	0,32	0,26	0,41	1,80	0,23
	J_{LRC}	0,05	0,04	0,18	0,14	-	0,25	0,15	0,04	0,05	0,07	0,03	0,07	0,08	0,05	0,37	0,31	0,23	0,36	1,64	0,22
	J_{RC}	0,03	0,04	0,20	0,15	0,05	0,21	0,16	0,04	0,05	0,06	0,02	0,08	0,08	0,06	0,31	0,25	0,19	0,31	1,32	0,24
fluid mobile product	G_{LRC}	0,07	0,08	0,22	0,15	-	0,17	0,12	0,03	0,05	0,06	0,03	0,06	0,08	0,06	0,28	0,24	0,36	0,45	1,46	0,31
	G_{RC}	0,09	0,07	0,22	0,13	0,01	0,10	0,10	0,04	0,04	0,04	0,01	0,03	0,04	0,05	0,20	0,18	0,34	0,38	0,93	0,41
	J_{LRC}	0,07	0,02	0,06	0,04	-	0,09	0,04	0,01	0,02	0,03	0,01	0,03	0,03	0,03	0,45	0,39	0,27	0,52	2,07	0,25
	J_{RC}	0,08	0,02	0,08	0,06	-	0,12	0,07	0,02	0,03	0,03	0,02	0,04	0,04	0,04	0,40	0,32	0,23	0,36	1,67	0,21
	$G_{RC} + J_{RC}$	0,04	0,04	0,15	0,12	-	0,19	0,12	0,04	0,05	0,06	0,04	0,08	0,09	0,09	0,42	0,34	0,25	0,41	1,59	0,26
	$G_{LRC} + J_{RC}$	0,09	0,02	0,88	0,68	-	0,16	0,87	0,03	0,03	0,04	0,02	0,05	0,06	0,05	0,04	0,03	0,03	0,04	0,18	0,19
	$G_{LRC} + J_{LRC}$	0,04	0,03	0,06	0,05	-	0,11	0,04	0,01	0,03	0,04	0,02	0,04	0,04	0,03	0,55	0,48	0,48	0,70	2,42	0,29
over-sieve residues	$G_{RC} + J_{LRC}$	0,02	0,03	0,07	0,06	-	0,14	0,06	0,02	0,04	0,05	0,02	0,07	0,07	0,05	0,65	0,55	0,42	0,65	2,25	0,29
	G_{LRC}	-	-	-	-	0,01	0,06	0,01	-	0,01	0,01	0,01	0,03	0,02	0,01	-	-	-	2,78	13,54	0,21
	G_{RC}	0,04	0,01	0,01	-	-	0,05	0,01	-	0,01	0,01	0,01	0,05	0,04	0,03	2,84	1,05	3,22	0,48	5,00	0,10
	$G_{RC} + J_{RC}$	-	-	-	-	0,01	0,06	0,01	0,01	0,02	0,02	0,01	0,04	0,03	0,02	-	-	-	1,88	7,64	0,25
	$G_{LRC} + J_{RC}$	-	-	-	-	0,01	0,06	0,01	-	0,02	0,02	0,01	0,04	0,04	0,02	-	-	-	6,03	20,35	0,30
	$G_{LRC} + J_{LRC}$	-	-	-	-	0,01	0,02	0,01	0,01	0,04	0,04	0,02	0,03	0,03	0,01	-	-	-	4,18	2,17	1,93
$G_{RC} + J_{LRC}$	-	-	-	-	0,01	0,06	0,01	-	0,02	0,02	0,01	0,03	0,02	0,01	-	-	-	4,42	17,16	0,26	

Table 2. The results of IR-spectroscopy of coals and the products of their thermal destruction

If FNPs of the J coals are compared, a similar tendency to a decrease in the relative content of CH_{ar} , ether and thio-ether groups in FNP of reduced vs. low-reduced coals can be traced.

A comparison of two solid residues with different types by reductivity of J-coal in the blend ($G_{LRC} + J_{LRC}$ and $G_{LRC} + J_{RC}$) shows that in the second case the solid residue is characterized by the 10-times higher relative content of aromatic hydrogen, whereas the over-sieve residue is enriched with ether and thio-ether groups.

Thus, when the J_{RC} coal is added to the above blend, FNP is rapidly saturated with hydrogen and the solid residue with aromatic and bridge segments, which conduces to the formation of the plastic layer and subsequently to caking coke.

A comparison of the IR-spectra of G_{LRC} and G_{RC} coals and their over-sieve residues demonstrates that low-reduced coal and its OR are also distinguished by a much higher H_{ar}/H_{al} and $-S-$ ($-O-$)/ H_{al} ratio as compared to G_{RC} . Besides, solid residues of G_{LRC} have an appreciably higher aromaticity and lacing degrees at the expense of oxygen-containing bridges than the G_{LRC} coal OR.

4. Conclusions

The data of processing the DRIFT spectra corroborate the idea about chemical interaction of the blends components which depends on the coal-facies of the original coal and determines the quality of the plastic layer.

Generally, a replacement of one of the blend components by coal of the same rank but different genetic type by reductivity changes the structure-group composition of thermal filtration products.

The differences in the sulphur content and elemental composition of reduced and low-reduced coals are responsible for their different behaviour during thermal processing. Notably, the influence of the coal-facies is different for coals of different ranks.

It should be pointed out that in all cases a replacement of the G_{LRC} by the G_{RC} component in a blend results in a drastic decrease in the yield of fluid mobile products. On the contrary, a replacement of the J_{LRC} by the J_{RC} ingredient results in an increase in the FNP yield by 2.5 times. Accordingly, the redox-conditions of coal formation ambiguously affects the behaviour of coals of different ranks.

The data obtained unambiguously indicate that it is necessary to consider the coal-facies when making coking blends.

Enormous available literature on commercial coking coals and blends makes no allowances for the genetic type of the components by reductivity being confined to the analysis of the effect of rank and petrographic content. Therefore, the existing methods for prediction of coking ability cannot be justifiably applied when making decisions on interchangeability of coals in coke blends for a number of coal basins.

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