

The role of sulfur in coals plastic layer formation

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Abstract

Coals blends with all possible combinations of high- and low-sulfur coals of the same rank and petrographic composition were pyrolysed in centrifugal field, allowing to separate solid, fluid and gaseous products. It has been shown that replacement of the low-sulfur by the high-sulfur coking coal of the same rank ($\approx 83\text{--}88\%$ C^{daf}) in blends leads to substantial increasing of fluid products yield 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 content of sulfur in coal, content of paramagnetic centers in plastic layer and coal coking ability has been discovered.

Keywords: coal, blend, sulfur, plastic layer

1. Introduction

The differences in coal thermoplastic properties have been attributed to higher hydrogen transfer reactions and to differences in the amount of tar produced during the plastic range [1]. The existing schemes of formation of coal plastic matter ignore a vital role of heteroatoms in coal organic matter (COM) and thus allow no definite prediction of the yield, composition and properties of pyrolysis products. 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 with different sulphur and oxygen contents and their behavior during heating should play a crucial role in understanding of cokemaking as a process.

A particular characteristic of seams from Donets coal basin is the occurrence of high- and low-sulfur coals, of the same rank differing by some physicochemical properties [1]. These differences are due to specified genetic types formed in alluvial or marine depositional environments during diagenesis processes [2].

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

2. Experimental

Two pairs of the isometamorphic Donets coals homogeneous by their petrographic composition, but formed under reductive (RC) or less reductive conditions (LRC) and different by their sulphur

content ($S_t^d=1,09-1,22$ for LRC; $S_t^d=2,49-2,81$ for RC) were used as objects of research. It was coals of J-Grade ($C^{daf} = 85,4 - 86,1$; $V^{daf} = 30,5 - 32,7$; $S_t^d = 1,1 - 4,1$) and G-Grade ($C^{daf} = 83,8 - 85,1$; $V^{daf}=36,0 - 38,7$; $S_t^d = 1,22 - 2,49$ 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. These coals and their blends were thermally treated up to 600°C at the rate of 1500 rev/min using the method of centrifugal thermal filtration (Ukrainian National Standard 17621-89). This method enables one to separate primary products that form the plastic mass, immediately, thus preventing their secondary transformations. The yields of the following products were found: the solid 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. The theoretical plastic mass yield was calculated for the above blends using the rule of additivity.

The EPR-spectra of the coals were recorded on a Bruker ER 200D SRC radiospectrometer at ambient temperature. Active coal with the content of paramagnetic centres (PMC) $N=6.25 \times 10^{16}$ was used as a standard. 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

Figure1 demonstrates a great difference in FNP yields and, therefore, in the caking capacity of coals of the same brand, but different coal-facies. 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.

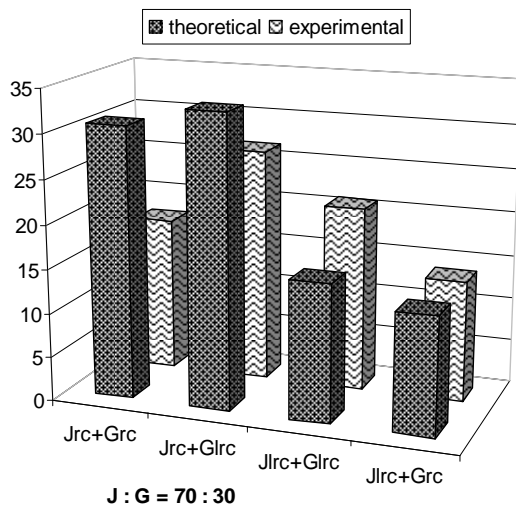


Figure1. A comparative characteristics of the calculated and experimental values for plastic mass yields from samples under investigation

The most advantageous composition (maximum FNP yields) is a blend containing the reduced J-Grade (J_{RC}) and the low-reduced of G-Grade (G_{RC}) coals. The greatest deviation of the experimental values from the calculated by the rule of additivity is observed for the $J_{RC} + G_{RC}$ blend, which permits an assumption about the strongest interaction between the components [3]. To understand the nature of this interaction 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 Table1, PMC concentration (N) in the samples under discussion essentially depends on the components genetic type by reductivity. 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.

Table 1. The results of EPR and IR-spectroscopy of coals and the products of thermal destruction

Coals, fluid mobile products, over-sieve residues of coals and blends		Paramagnetic characteristics			The results of IR-spectroscopy					
		N, spin $g^{-1} \times$ 10^{-17}	ΔH , E	g-factor	Relative intensity					
					I_x/I_{2920}			I_x/I_{1440}		I_x/I_{1600}
					1190	1260	3040	1260	1600	1260
origin coals	G_{LRC}	2,24	6,43	2,0039	0,37	0,34	0,30	0,45	1,89	0,24
	G_{RC}	64,25	6,79	2,0040	0,33	0,32	0,26	0,41	1,80	0,23
	J_{LRC}	64,28	7,02	2,0039	0,37	0,31	0,23	0,36	1,64	0,22
	J_{RC}	43,16	5,21	2,0040	0,31	0,25	0,19	0,31	1,32	0,24
fluid mobile products	G_{LRC}	38,50	6,06	2,0040	0,28	0,24	0,36	0,45	1,46	0,31
	G_{RC}	1,78	6,01	2,0040	0,20	0,18	0,34	0,38	0,93	0,41
	J_{LRC}	114,9	6,25	2,0040	0,45	0,39	0,27	0,52	2,07	0,25
	J_{RC}	159,9	6,26	2,0040	0,40	0,32	0,23	0,36	1,67	0,21
	$G_{RC} + J_{RC}$	110,5	7,07	2,0040	0,42	0,34	0,25	0,41	1,59	0,26
	$G_{LRC} + J_{LRC}$	111,4	6,92	2,0040	0,04	0,03	0,03	0,04	0,18	0,19
	$G_{LRC} + J_{LRC}$	43,14	5,79	2,0040	0,55	0,48	0,48	0,70	2,42	0,29
	$G_{RC} + J_{LRC}$	45,38	5,68	2,0040	0,65	0,55	0,42	0,65	2,25	0,29
over- sieve residues	G_{LRC}	-	-	2,0040	-	-	-	2,78	13,5	0,21
	G_{RC}	61,14	6,64	2,0040	2,84	1,05	3,22	0,48	5,00	0,10
	J_{LRC}	6,5	6,92	2,0040	-	-	-	-	-	-
	J_{RC}	4,0	6,60	2,0040	-	-	-	-	-	-
	$G_{RC} + J_{RC}$	-	-	2,0039	-	-	-	1,88	7,64	0,25
	$G_{LRC} + J_{RC}$	0,11	4,00	2,0040	-	-	-	6,03	20,3	0,30
	$G_{LRC} + J_{LRC}$	0,03	4,04	2,0040	-	-	-	4,18	2,17	1,93
	$G_{RC} + J_{LRC}$	0,19	5,23	2,0040	-	-	-	4,42	17,2	0,26

The J_{RC} coal is forming FNP with the PMC concentration ≈ 4 times higher than that in the original coal. 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 (Fig.1). These results indicate that reactions resulting in the formation of the plastic layer occur with the participation of free radicals.

The J_{RC} coals characterized by narrower EPR signals ($\Delta H \sim 5.21$ E), contain the most stable PMCs. The maximum rigidity of the polyconjugated areas is observed for solid residues of thermal filtration of the blends ($\Delta H \sim 4.00 - 4.04$ E). The width and form of broad resonance lines in the EPR-spectra of coals are basically determined by hyperfine interaction with magnetic nuclei [4,5]. 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. 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. These data obtained permit to attribute the optimal properties of the $G_{LRC} + J_{RC}$ blend to the highest PMC concentration in FNP.

The RC samples yield the plastic layer characterized by high content of aliphatic groups (2920cm^{-1} and 1440cm^{-1}). When J_{LRC} coal replacement by J_{RC} in the blends the relative concentration of CH_{al} groups in the FNP increases. The $G_{LRC} + J_{RC}$ blend is characterized by a minimal relational proportion of $-\text{O}-(-\text{S})/\text{CH}_{al}$ groups ($I_{1190,1260}/I_{2920}$) and proportion of $\text{CH}_{ar}/\text{CH}_{al}$ (I_{3040}/I_{2920} and I_{1600}/I_{1440}) groups. So, FNP of the blend with J_{RC} coal 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 $-\text{S}-(-\text{O})/H_{al}$ ratio as compared to G_{RC} .

4. Conclusions

Generally, a replacement of one of the blend components by coal of the same rank but different sulfur content (different genetic type by reductivity) changes the PMC concentration, structure-group composition and yield of thermal filtration products. The heteroatoms content in coals determines the quality and quantity of the plastic layer and the character of interaction between the blends components. The data obtained unambiguously indicate that it is necessary to consider the coal-facies when making coking blends.

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