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Extracts of the plastic layer of coals of different reductivity type and their blends

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Extracts of the plastic layer of fat (J-grade) and gas (G-grade) coals of different genetic types by reductivity (GTR) and their blends were comprehensively studied. It was shown that the coking capacity of coals implies a certain balance between the mobile liquids and the macromolecular phases in the plastic state. A new indicator of the coking capacity, was proposed, namely, the proportion of carbenes+carboides/maltenes in the extracts of liquid mobile products of thermal filtration of coals and blends which linearly correlates with the yields of the above products responsible for the coking processes. An optimal blend composition (G - low-reduced ÷ J - reduced coals) which gives a maximum yield of fluid non-volatile products (FNP) saturated with aliphatic components was found.

Key words: Plastic layer, Extracts, Coal, Blends, Coking

INTRODUCTION

A study of coal properties in the plastic state is of great practical and theoretical importance for scientifically based development of optimal coal blends. Penetration and dilatometric conventional methods for characterization of the coal plastic mass are based on determining the width of the plastic state zone, the plastic mass viscosity, resistance, the rate of movement of the metal plate in the coal charge and other physical properties [1]. These methods give no way of assessing the nature of the substances responsible for plastic layer formation and coking.

Very important information can be derived from direct observations of the mesophase. Such data were described by Zubkova [2-4], using a special laboratory unit consisting of a furnace and coking chamber with contrasting elements embedded into the coal charge. The coal charge was irradiated with X-rays during carbonization and all the changes in the charge were registered on a film. The macrostructure of the coal plastic layer and the processes of formation of a solid carbonization residue were described for coals of different rank and caking capacity in different conditions [3, 4].

Extraction is another advanced method of studying the structure of solid fossil fuels, which permits to determine the differences in the composition of products obtained upon their processing [5-8].

Differences in the yield and composition of coal extracts are due to coalification degree and specified coal genetic types by reductivity (GTR). A particular characteristic of seams from Donetsk coal basin in Ukraine is the occurrence of high- and low-sulfur coals of the same rank differing by some physicochemical properties [9-14]. These differences are due to specified genetic types by reductivity formed in alluvial or marine depositional environments during diagenesis processes [11]. Earlier, high reactivity for sulfur coals in coking and lacing processes was established [15].

Previous work has demonstrated that heating of blends with high-sulfur coking coal in the plastic temperature range in a centrifugal field leads to a substantial increase in the yield of fluid non-volatile products in comparison with the blends containing low-sulfur coking coal. An apparent relation between the content of sulfur in coal, the concentration of paramagnetic sites in the fluid non-volatile products and coal coking ability was discovered [16].

The first experimental task in the present study was to isolate the fluid non-volatile products by the method of centrifugal thermal filtration. Then the obtained mobile products should be appropriately separated into characteristic fractions.

The aim of this research was to study the influence of components in fluid non-volatile products of the plastic layer from coals of different type by reluctivity and their blends on the yields of liquid mobile products responsible for the coking processes.

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EXPERIMENTAL

Two pairs of isometamorphic Donetsk coals of different genetic types by reductivity, formed under reductive and less reductive conditions (low reduced – LRC and reduced coals – RC) and their blends, were used as objects of research. Characteristics of the initial coals are given in Table 1. As it is seen, the two coal types G and J-grade coals (≈83-88 % C^{daf}) according to Ukrainian classification differ mainly by their carbon, volatile and ash contents and their pairs with low and higher sulphur contents.

The ratio of different grades of coal in the composed blends was chosen as conventional blend (J:G=70:30) and as J:G=50:50 to assess the feasibility of increasing the share of low coking coals. A distinctive feature of the blends under analysis is the use of all possible combinations of coals of different genetic types by reluctivity, i.e., low-reduced (J_{LRC}, G_{LRC}) and reduced types (J_{RC}, G_{RC}). These coals and their blends are thermally treated up to 600 °C at a rate of 1500 rev/min using the method of centrifugal thermal filtration with separation of the fluid non-volatile products (FNP). This method enables the immediate separation of the primary products that form the plastic mass, thus preventing their secondary transformations [17]. The amount and composition of FNP largely determine the processes of caking and coking.

The following methods of research were used: thermal filtration (National State Standard 17621-89), technical (National State Standard 11014-89, National State Standard 11022-95, National State Standard 2059-95, National State Standard 6382-91) and elemental (National State Standard 24081-95) analyses, and Fourier transform infrared spectroscopy.

Infrared spectra were recorded on a Bruker FTS-7 spectrometer using the DRIFT technique. Semi quantification of the infrared spectra was made using the Origin 6.1 software package by basic-line technique.

Fluid non-volatile products were separated into components (Fig. 1) using the following procedure: first water was removed, then asphaltenes were separated. Hexane-soluble compounds were resolved into alkalis, carboxylic acids, phenols, neutral oils by their consecutive treatment with 10% H_2SO_4, 3% $NaHCO_3$, and 5% NaOH. Neutral oils were chromatographed on silica gel using hexane, benzene or acetone as eluents, with subsequent separation of paraffin-naphthene, aromatic and polar hydrocarbons.

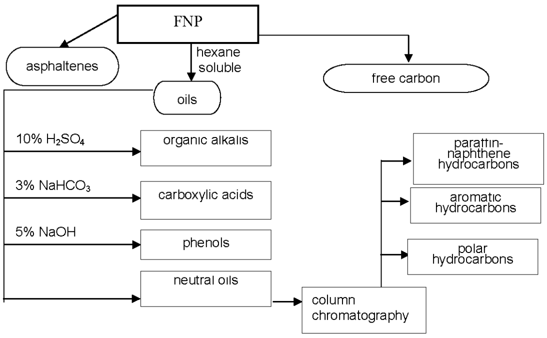

Fig. 1. Scheme of FNP separation into components.

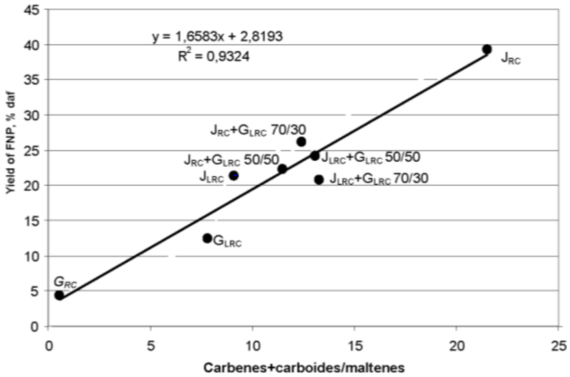

Fig.2. Dependence of the plastic mass yield on the carbenes+carboides/maltenes ratio.

RESULTS AND DISCUSSION

As seen from Table 2, the elemental composition of the thermal filtration products is different for coals and blends. In particular, the hydrogen content in FNP is 2-3 times as much as that in over-sieve residues (OR), which permits to form a plastic layer enriched with a liquid component. The analysis of the sulfur content in the blends showed that in the blend $J_{RC} \div G_{LRC}$ the ratio between J and G components (J : G = 50% / 50% and 70% / 30%) permits to lower the sulfur content in FNP and OR. Accordingly, sulfur-containing components will migrate to the vapour-gas phase.

The method of DRIFT-spectroscopy corroborates the processes of hydrogen redistribution. As can be seen from Table 3, the ratio of the aromatic to the aliphatic hydrogen (I_{1600}/I_{1440}) is dozen times as much for OR compared to FNP. These data convincingly demonstrate that the processes ensuring the formation of the plastic layer proceed most intensively in the blend containing G_{RC} coal. The plastic layer of J-grade coals is saturated with the optimal number of aliphatic and polycyclic aromatic fragments, which are able to form the liquid crystalline state, i.e., the mesophase. Stabilisation of the formed radicals is likely to occur at the expense of the hydrogen of over-grid residues (See Tables 2, 3).

Table 1. Characterization of analysed coals

Mine	Coal grade	Type	Technical analysis, %				Elemental analysis, % daf		
			W^a	A^d	S^d_t	V^{daf}	C	H	O+N
Tsentralnaya	G, k_7	LRC	2.2	5.2	1.22	36.0	85.1	5.11	8.71
Dimitrova	G, l_1	RC	2.1	4.4	2.49	38.,7	83.8	5.34	9.50
Zasiadko	J, l_4	LRC	1.4	2.6	1.09	31.6	87.8	5.16	7.00
Zasiadko	J, k_8	RC	0.8	2.7	2.81	31.7	87.3	5.23	7.20

Table 2. Elemental composition of the centrifugal thermal filtration products of coals and blends

Thermal filtration products of coals and blends		The ratio of J / G components, %	C	H	S
Fluid non-volatile products	G_{LRC}		84.04	6.55	1.11
	G_{RC}		82.50	7.08	2.28
	J_{LRC}		86.57	4.40	1.05
	J_{RC}		84.68	6.34	1.76
	$J_{LRC} \div G_{LRC}$	70 / 30	70.69	4.45	0.75
	$J_{LRC} \div G_{RC}$	70 / 30	86.47	4.43	1.95
	$J_{RC} \div G_{RC}$	50 / 50	84.72	6.26	2.15
		70 / 30	83.79	5.44	2.,55
	$J_{RC} \div G_{LRC}$	50 / 50	85.16	5.27	1.86
		70 / 30	83.81	5.85	1.84
Over- sieve residues	G_{LRC}		86.98	2.70	0.88
	G_{RC}		87.25	2.78	0.85
	J_{LRC}		89.91	2.39	1.04
	J_{RC}		91.47	1.02	2.81
	$J_{LRC} \div G_{LRC}$	70 / 30	81.44	2.25	1.25
	$J_{LRC} \div G_{RC}$	70 / 30	91.19	1.38	0.90
	$J_{RC} \div G_{RC}$	50 / 50	87.86	2.36	1.79
		70 / 30	83.79	2.44	1.68
	$J_{RC} \div G_{LRC}$	50 / 50	68.68	2.82	2.24
		70 / 30	82.89	2.82	1.30

A comparison of two over-grid residues (OR) obtained from blends with different reductivity type of of J-grade coal ($J_{LRC} \div G_{LRC}$ and $J_{RC} \div G_{LRC}$) shows that in the latter case the solid residue is characterised by virtually ten times as high relative content of the aromatic hydrogen. Thus, when J-grade reduced coal is added to the blend, FNP is intensively saturated with hydrogen (C-H_{aliph}). The solid residue is enriched with aromatic fragments, i.e., gives up hydrogen. Judging by the experimental and theoretic yield of the plastic layer [16], there is a sufficient number of aromatic and aliphatic components in FNP of the blend ($J_{LRC} \div G_{LRC}$) to achieve stabilisation of the products of bridge bonds destruction with hydrogen. The ratio C-H_{ar} / C-H_{aliph} (I_{1600}/I_{1440}) is much the same for FNP and OR. In FNP of other blends, a part of aromatic hydrogen carriers formed from J-grade coal, is spent on stabilisation of gas (G-grade) coal decomposition products, which is confirmed by a decrease in the experimental, as compared to the theoretic yield of FNP products [18]. The maximum difference between the I_{1600}/I_{1440} values in OR and FNP was recorded for the $J_{RC} \div G_{LRC}$ blend, which corroborates maximum hydrogen transfer in this system.

Table 3. The ratios of characteristic absorption bands in DRIFT spectra

Coals, fluid non-volatile products, over-sieve residues of coals and blends (F:G=70:30)		Relative intensity
		I_{1600}/I_{1440}
Coals	G_{LRC}	1.894
	G_{RC}	1.804
	J_{LRC}	1.638
	J_{RC}	1.321
Fluid non-volatile products	G_{LRC}	1.458
	G_{RC}	0.928
	J_{LRC}	2.071
	J_{RC}	1.671
	$J_{RC}÷G_{RC}$	1.586
	$J_{RC}÷G_{LRC}$	0.179
	$J_{LRC}÷G_{LRC}$	2.417
	$J_{LRC}÷ G_{RC}$	2.253
Over- sieve residues	G_{LRC}	13.540
	G_{RC}	5.002
	J_{LRC}	-
	J_{RC}	-
	$J_{RC} ÷ G_{RC}$	7.638
	$J_{RC}÷ G_{LRC}$	20.352
	$J_{LRC}÷G_{LRC}$	2.165
	$J_{LRC}÷ G_{RC}$	17.155

The differences in the sulfur and ash content and the elemental composition of the reduced and low-reduced coals account for their different behaviour during thermal processing. Notably, the impact of the genetic type by reductivity is dissimilar in coals of different ranks.

Extracts of fluid mobile products were taken and their structural-group composition (SGC) was thoroughly examined to extend knowledge of the mechanism of the coking process. The structural-group composition (SGC) of the extracts of liquid mobile products (Table 4) is presented by a group of hexane-soluble (maltenes or oil), hexane–insoluble, but toluene–soluble (asphaltenes) compounds, and a sediment formed upon washing of asphaltenes with hot toluene (carbenes and carboides). FNP composition essentially depends on the coal genetic type by reductivity, as is evident from the results of the structural-group analysis. The proportion of asphaltenes in the extracts of reduced gas coals is three times as much as that of low-reduced G-Grade coals. An inverse dependence is observed for FNP extracts of fat coals. The content of asphaltenes decreases twice from 9.30% in FNP of J_{LRC} coal down to 4.51% in FNP of J_{RC} coal. A similar picture is seen in the content of maltenes for the pairs G_{LRC} ÷ G_{RC} and J_{LRC} ÷J_{RC}. Maltenes of G_{RC} coals yield 4 times more, and those of J_{RC} coals half as much hexane-soluble products compared to low-reduced coals.

Thus, genetic type by reductivity (GTR) of coals has a great impact on the yields of particular soluble compounds. A detailed analysis of maltenes composition in the G_{LRC} ÷ G_{RC} pair (Table 4) has shown that in the hexane-soluble part of the extract of fluid mobile products of the G_{RC} coal there are more phenols (7.1 times) and organic alkalis (6 times), more carboxylic acids and neutral oil in comparison with the G_{LRC} extract. For the J_{LRC} ÷ J_{RC} pair the difference in maltenes composition basically shows in a decreased content of organic alkalis and decreased content of carboxylic acids (1.2 times) in the FNP extract of J_{LRC} as compared to J_{RC} coals (Table 4).

The differences in the structural-group FNP composition of the blends made up of fat and gas coals (J- and G-grade) primarily consist in a substantially higher (~ two-fold) content of asphaltenes in the extracts of the blends containing low-reduced fat coals.

The fluid non-volatile products extracts of the blends with different component ratios also differ in their SGC, first and foremost, by the content of mobile low-molecular products (maltenes) and by the content of high-molecular components (carbenes/carboides and asphaltenes). It follows from the data obtained that the caking properties of the blends are related to both the amount and the composition of FNP.

Close linear correlation between the carbenes+carboides/maltenes ratio and the yield of liquid mobile products from coals and blends was established. The graphical representation of this function can be found in Fig. 2. The correlation coefficient value is R^2=0.9324. The data prove conclusively that the coking capacity of coals presupposes a balance in the system between the mobile phase, i.e., hydrogen carrier, and its donor, i.e., the macromolecular phase.

Table 4. Results of structural-group analysis of liquid non-volatile thermal filtration products of the coals and blends, wt.% from FNP amount

Coal grade, type, percent composition of components	FNP yield, % daf	Maltenes					Asphaltenes	Carbenes + carboides
		Organic alkalis	Carboxylic acids	Phenols	Neutral oils	∑ Maltenes		
G_{LRC}	12.44	0.30	0.38	1.87	7.62	10.17	10.38	79.45
G_{RC}	4.28	1.79	0.58	13.26	29.5	45.13	30.45	24.42
J_{LRC}	21.33	0.27	0.19	1.40	7.3	8,9	9.0	81.71
J_{RC}	39.28	0.34	0.23	0.57	3.0	4.24	4.1	91.25
J_{RC} ÷ G_{LRC} 50/50	22.22	0.24	0.40	0.92	6,.1	7.87	1.0	90.23
J_{RC} ÷ G_{LRC} 70/30	26.19	0.27	0.60	0.88	5,.6	7.31	1.3	90.96
J_{LRC} ÷ G_{LRC} 50/50	24.11	0.34	1.50	0.17	4,.2	6.63	6.7	86.70
J_{LRC} ÷ G_{LRC} 70/30	20.71	0.65	0.51	1.35	4.0	6.61	5.51	87.88

Table 5. The composition of neutral oils obtained from the plastic layer of coals of different types by reductivity and blends on their basis, wt.%

Coal grade, type, percent of components	Paraffin-naphthene fraction	Aromatic fraction	Polar fraction	Losses
G_{LRC}	55.5	27.7	12.4	4.4
G_{RC}	55.4	27.8	15.0	1.8
J_{RC} ÷ G_{LRC} 50/50	54.6	29.1	15.1	1.2
J_{RC} ÷ G_{LRC} 70/30	52.7	31.6	12.2	3.5
J_{LRC} ÷ G_{LRC} 50/50	57.4	27.6	15.0	-
J_{LRC} ÷ G_{LRC} 70/30	52.9	31.4	15.6	0.1

A comparison of the blends (J / G = 70 / 30) including fat (J-grade) coals of different GTR shows that the J_{RC} component promotes a decrease in the neutral oil content in maltenes regardless of its relatively low content in FNP of the initial coal. These data are in excellent agreement with the IR-spectroscopy results of the respective FNP. The concentration of CH_{aliph} groups is 13.5 times higher in FNP of the J_{RC} ÷ G_{LRC} blend in comparison with the J_{LRC} ÷ G_{LRC} blend (Table 3). Accordingly, the method of structural-group analysis substantiates the leading role of GTR of J-grade coals at the stage of plastic layer formation in a blend. The data obtained unambiguously indicate that it is necessary to take into account the GTR of coals when making coking blends.

Fractional composition of neutral oils in Table 5 demonstrates that the composition of neutral oils of gas coals (G-grade) of different GTR is similar and appears to have little effect on the composition of the blend extracts, which is sufficiently homogeneous and differs little from the composition of gas coal extracts. However, it is noteworthy that when the proportion of fat coal (J-grade) in the blend increases, the share of the paraffin-naphthene fraction decreases, whereas that of the aromatic fraction of neutral oils increases.

CONCLUSION

The results of a detailed study of the extracts from the plastic layer of coals of different genetic types by reductivity and their blends are described. The main part of the extracts is composed of carbenes+carboides (24-91%) and maltenes. Quantity of carbenes+carboides increases during coalification processes and is much higher for blends, containing middle-rank coal of reduced type. Obviously, their segregation at the early stages of thermal decomposition is very important for the formation of a plastic layer and subsequent formation of the coke structure. DRIFT-spectroscopy analysis of the extracts revealed significant quantitative differences in the composition of components extracted from different coals and blends.

The extracts obtained from J-grade coals are characterized by a higher content of carbenes+carboides in comparison with G-grade coals, which corresponds to their higher FNP yield and higher caking ability.

It was shown that the caking ability of coals requires some balance between the mobile and the macromolecular phases in a plastic state. A new indicator of caking – the ratio of carbenes+ carboides/maltenes in extracts of liquid products of coals and blends was suggested. This indicator correlates with the yield of plastic layer which is responsible for the caking process. The optimal composition of the blends which gives the highest yield of plastic layer, saturated with aliphatic components, was cleared. Therefore, for good caking capacity of a blend during pyrolysis a certain correlation between the amount of relatively higher-molecular FNP components insoluble in neutral low-boiling solvents and the amount of relatively low-molecular maltenes, is needed to ensure the mesophase mobility.

Excessive amount of asphaltenes in FNP is highly undesirable and can be avoided by varying the proportion of strongly coking coals in a blend.

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ЕКСТРАКТИ НА ПЛАСТИЧНИЯ ПЛАСТ ОТ ВЪГЛИЩА С РАЗЛИЧЕН ТИП ПО РЕДУКТИВНОСТ И ТЕХНИ СМЕСИ

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(Резюме)

Изучени са екстрактите на пластичния пласт от тлъсти (J-ранк) и газови (G-ранк) въглища с различен генетичен тип по редуктивност (ГТР) и техни смеси. Показано е, че коксуващият капацитет на въглищата предполага определен баланс между подвижната течна и макромолекулната фаза в пластично състояние. Предложен е нов индикатор за коксуващия капацитет, а именно отношението карбени + карбоиди / малтени в екстрактите на течните подвижни продукти от термичната филтрация на въглища и техни смеси, което линейно корелира с добивите на по-горе споменатите продукти, отговорни за коксуващите процеси. Намерен е оптимален състав на сместа (G- ниско редуцирани ÷ J- редуцирани въглища), който дава максимален добив на флуид нелетливите продукти (ФНП), наситени с алифатни компоненти.