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The microstructure of semi-cokes and cokes of Donetz low-rank coals of different genetic types

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Abstract. The chemistry of low-rank coals of the same rank but different genetic types (reduced – RC, and low-reduced – LRC) have been studied. It has been shown that the coals of RC type give fritted and less compact semi-cokes with a higher volume of pores and lesser relative content of walls. Data from optical microscopy agrees with that of the yield of vapour-gas products of semi-coking from differential thermal analysis and DRIFT-spectroscopy.

Key words: sulphur coals, semi-cokes, cokes, microstructure, additives

Introduction

High sulphur content is an effect of the specific geological history of a coal bed, and is one of the most important criteria of fuel quality. The introduction of sulphur into the coal's organic mass (COM) occurs at the peat stage, resulting in the formation of coals of different genetic types by reductivity. Coal reductivity depends of the facies type. The depositional environment determines which coal facies develops (telmatic, limnic, brackish-marine, calcium-rich). Marine peats are generally high in ash, sulphur, and nitrogen, and contain a higher percentage of pyrite than similar peats laid down in a purely freshwater sequence. The presence of finely crystalline pyrite is a well known index of the degree to which the depositional environment has been reduced. Pyrite and organic sulphur owe their emplacement in the peat to the activity of sulphur-reducing bacteria at high Eh-pH-values and the presence of sulphate ions (Taylor et al. 1998).

Coal-bearing deposits of the Donetz Basin are polyfacies sediments (alluvial and marine). Therefore, coals of reduced and low-reduced types are widely represented there (Geological-geochemical map 1954).

Reduced vitrinite is characterized by light vermeil red or deep red colours in passing light and by darker colours in reflected light. Different types of vitrinite differ not only by colour, but also by structure, particles size, and optical indices.

The quality of coal types is characterized by degree of reductivity. It has been shown that coals of reduced type have better coking quality, higher combustion heat, and higher solubility for organic solvents (Angelova 1959). The influence of the coal's genetic type and method of chemical pre-treatment on its behaviour during pyrolysis has been also noted. Combined methods of chemical and thermal treatment permit the direct modification of the coal's structure, yield, and the composition of the products. These methods include those known for the preparation of activated carbons (Jagtoyen 1993, Saranchuk et al. 1994, Daulan et al. 1998), for obtaining coal soluble products (Bimer et al. 1993, Sugano et al. 2002), or agglutinated materials from low rank sulphur coals (Butuzova et al. 2002a).

Previous studies have shown that brown coal pre-treatment by absorber oil and the acrylic acid dinitrile increases the degree of order and improves cross-linking processes in the coal carbonization products (Butuzova et al. 2002b).

The objective of the present paper is to study the composition, structure, and microstructure of semi-cokes and cokes obtained from the Donets bituminous coals of low-reduced (LRC) and reduced (RC) types (Geological-geochem. map 1954), and also to study the influence of chemical pre-treatment on their optical characteristics.

Procedures

Donetz bituminous coals of similar rank (R_m = 0.49–0.71) but different genetic types were investigated. Their geological age is Middle Carboniferous (Moscovian), and their petrographic composition is uniform: 80–87% vitrinite, 5–8% liptinite, and 5–12% inertinite. Pairs of RC and LRC coals were collected from closely-spaced coal seams separated by distances of less than 100 m. 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 coal.

The samples were analysed according standard procedures.

The thermal behaviour of the coals was studied by differential thermal analyses and classic Fisher and Sapozhnikov methods. Semi-coking and coking were carried out in separate trials with and without a radical polymerization initiator (acrylic acid dinitrile –AAD) or the products of coal-tar distillation (absorber oil). The radical polymerization initiator was introduced to affect the course of radical

Table 1. Changes in the elemental composition and yield of volatiles from coals of RC and LRC types in the process of semi-coking

Sample No.	Coal mine, seam	Type	Characteristics of initial coals (1) and semi-cokes (2) [wt%]												Characteristics of semi-cokes, g/100 g of coal			
			V^{daf}		C^{daf}		H^{daf}		$(O + N)^{daf}$		S_t^{d}		S^{daf}		V^{daf}	C^{daf}	S_t^{d}	S_t^{daf}
			1	2	1	2	1	2	1	2	1	2	1	2				
1	Cheluskintsev, l_4	LRC	35.6	13.8	79.3	87.2	4.94	3.61	13.69	7.17	2.17	1.40	2.07	1.42	8.8	55.8	0.89	0.90
2	Trudovskaya, l_4	LRC	37.3	13.0	78.4	88.8	4.95	3.19	15.80	6.68	1.05	1.30	0.85	1.30	8.4	57.6	0.84	0.84
1’	Ukraine, k_8	RC	41.8	12.9	77.9	86.8	5.30	3.67	14.63	6.85	2.87	2.40	2.17	2.71	8.1	54.2	1.50	1.69
2’	Trudovskaya, k_8	RC	46.2	12.6	76.1	85.3	5.43	3.36	13.14	8.23	5.85	2.90	5.33	3.12	7.8	53.0	1.80	1.94

Table 2. Influence of chemical pre-treatment on the microstructure of semi-cokes

Semi-cokes, method of treatment	Groups [%]											
	Diameter of pores [mm]			Wall thickness [mm]				Wall thickness > 0.2 mm	Diameter of pores < 0.2 mm	Z [%]	P [%]	C [%]
	< 0.1	0.1–0.2	0.2–0.5	< 0.05	0.05–0.1	0.1–0.2	0.2–0.5					
1 initial	86.3	9.8	3.9	72.3	23.0	4.7	–	4.7	96.1	57.9	42.1	1.38
1% AAD	91.8	4.9	3.3	74.7	19.6	5.7	–	5.7	96.7	58.9	41.1	1.43
1% oil	84.2	11.5	4.3	72.8	21.7	5.5	–	5.5	95.7	53.8	46.2	1.16
1’ initial	76.1	15.5	8.4	81.2	17.0	1.8	–	1.8	91.6	34.7	65.3	0.53
1% AAD	70.9	21.1	8.0	66.6	28.1	4.5	0.8	5.3	97.8	41.6	58.4	0.71
1% oil	65.0	24.6	10.4	68.9	28.6	2.5	–	2.5	89.6	36.0	64.0	0.56
2’ initial	82.6	13.0	4.4	56.7	36.0	7.3	–	7.3	95.6	46.0	54.0	0.86
1% AAD	80.9	17.0	2.1	60.2	31.6	8.2	–	8.2	97.9	47.5	52.5	0.9-
1% oil	73.9	16.4	9.7	57.3	35.0	7.7	–	7.7	90.3	44.7	55.3	0.81

reactions. Oil was used for initiating synthesis reactions during coking. Coals were pre-treated with solutions of AAD and absorber oil (2 : 1 and 1 : 1), and dried at room temperature to identical weights.

Differential thermal analysis of the samples was carried in a Paulic-Paulic-Erdei Q-1500D thermobalance, at a heating rate of 10 °C . min^{-1} in a closed ceramic crucible.

The microstructure of the semi-cokes and cokes were determined on polished sections by a point-counting method (500 points) on a LOMO MIM-8M optical microscope, with reflected polarized light in either air (magnification ×300) or immersion oil (magnification ×900).

Pore diameters and pore wall thicknesses were quantitatively determined by use of a “scaled” ocular. These data permit the identification of five groups, and the calculation of the proportions of pores and walls inside these groups, a compactness parameter corresponding to the wall surface/pore surface ratio, and the average rate of occurrence for pores and cell walls.

IR-spectra of the solid samples were recorded on a FT-IR «Bio-Rad» FTS-7 spectrometer with a DRIFT technique. The samples were prepared as 5% mixtures of coal with potassium bromide. Multipoint baseline correction was performed using a standard software package.

Results and discussion

Table 1 shows the elemental composition and the volatile yield for RC and LRC type coals and their semi-cokes. The calculation of separate elements, which were saved in the char, demonstrates that carbonisation processes are more effective in reduced samples. There is a greater difference in V^{daf} values for these coals and semi-cokes. The desulphurisation processes are also more intensive during the semi-coking of reduced coals.

The coupled samples under investigation (Nos. 1-1’, 2-2’) created semi-cokes with approximately equal contents of H^{daf} and $(O + N)^{daf}$, i.e. they are isometamorphic.

Table 2 shows the results of the semi-cokes’ microstructural determination. As can be seen from the table, the distribution of pores and walls into groups by size depends on the genetic type of the coal and the method by which it is chemically pre-treated. In general, coals of RC type give less compact (C = Z/P) semi-cokes with a higher pore volume (P %) and lower relative content of walls (Z %). This is a weakly-coked material with a lower content of small pores than the semi-cokes of LRC type coals.

The chemical pre-treatment of coals with a radical polymerization initiator results in increasing the semi-cokes compactness due to a decrease of the general pore volume. The amount of thick walls (> 0.2 mm) increases considerably in this case. Pores with diameters within the range of 0.1–0.5 mm develop under the effect of absorption oil.

The effects of chemical pre-treatment on semi-coke compactness and vapour product yield are reported in Fig. 1.

Data from optical microscopy agree with the vapour-gas product yield for semi-coking, and with the results from differential thermal analysis and DRIFT-spectroscopy.

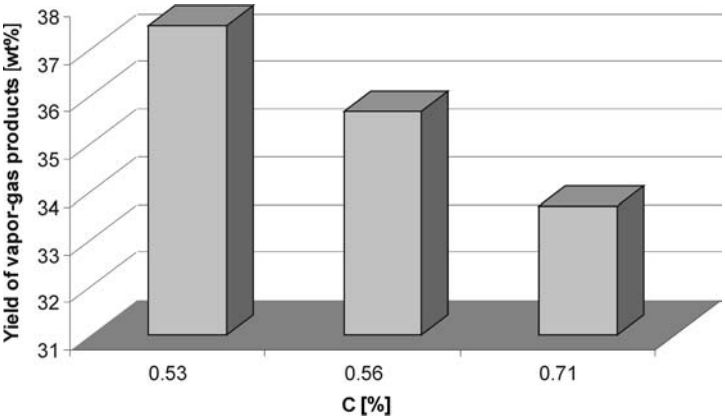

Figure1. Influence of chemical pre-treatment on semi-coke compactness and vapour product yield.

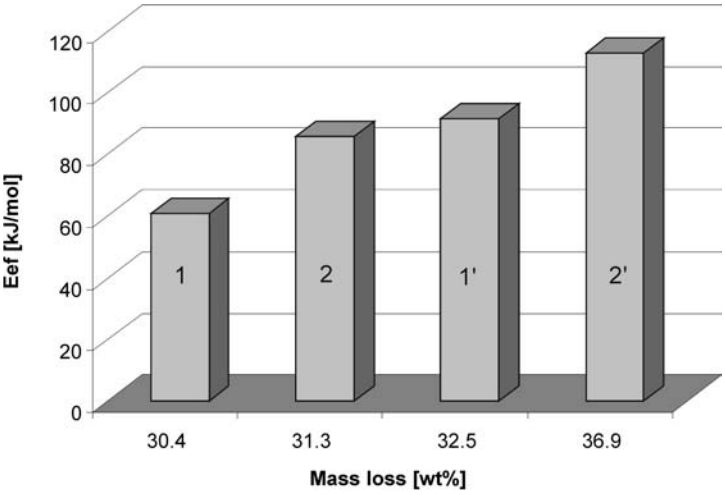

Figure 2. Dependence of mass loss variations on the effective energy of activation of the thermodestruction process of coals.

Samples were heated up to 1000 °C by a non-isothermal pyrolysis technique. The values for the mass loss at 850 °C and the effective energy of activation (E) in the formation of vapour-gaseous products were calculated by the equation:

$$E = 4.57\ T_2\,T_1(\lg K_2 - \lg K_1)/(T_2 - T_1)\ 1000$$

where T_1 and T_2 are the temperature values for two points on a portion of the straight line:

$$\lg[-\lg (m_e - m_t)/m_e] - 1/T;$$

K_1 and K_2 are their corresponding values of $-\lg (m_e - m_t)/m_e$; m is the mass loss at a different temperature.

Table 3. Quantitative indices of the macrostructure of cokes obtained from coals of different genetic type

Sample No.	Diameter of pores [%]						Wall thickness [%]					Z [%]	P [%]	C [%]
	< 0.01 mm	0.01–0.02 mm	0.02–0.04 mm	0.04–0.05 mm	0.05–0.1 mm	0.1–0.2 mm	< 0.01 mm	0.01–0.02 mm	0.02–0.04 mm	0.04–0.05 mm	0.05–0.1 mm			
1	23.0	20.9	18.3	11.9	25.9	–	24.6	28.8	26.7	13.1	6.8	53.4	46.6	1.15
2	23.6	21.6	29.2	9.3	16.3	–	19.7	24.3	33.2	6.6	16.2	55.9	44.1	1.27
1’	6.1	15.7	34.4	17.0	20.4	6.4	24.5	19.3	34.9	13.6	7.7	38.0	62.0	0.61
2’	5.7	15.5	25.2	10.1	37.0	6.5	31.6	24.1	34.6	8.3	1.4	30.4	69.6	0.44

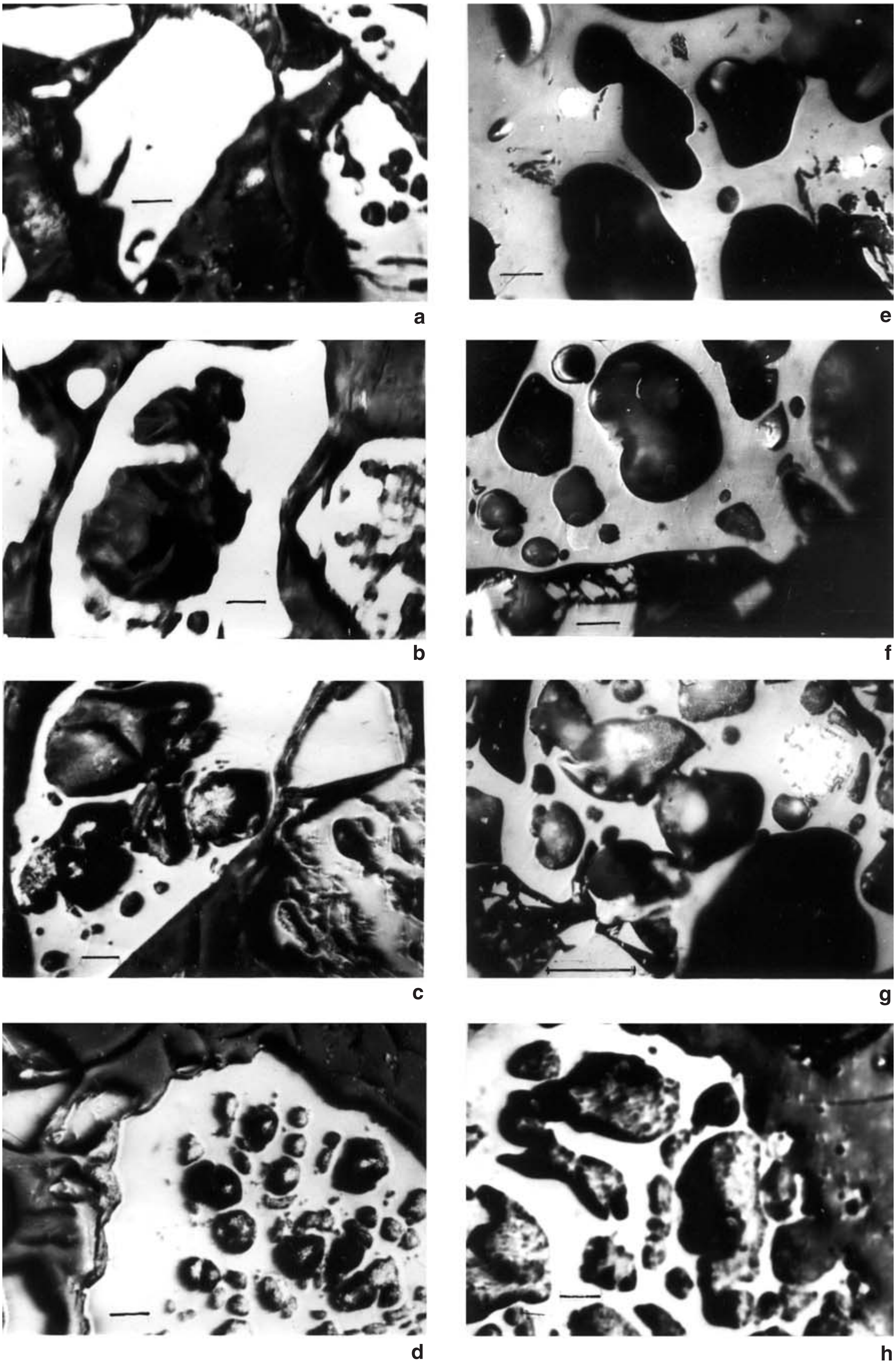

Figure 3. Microstructure of cokes obtained from coals of LRC (figs a–d) and RC (figs e–h) type.

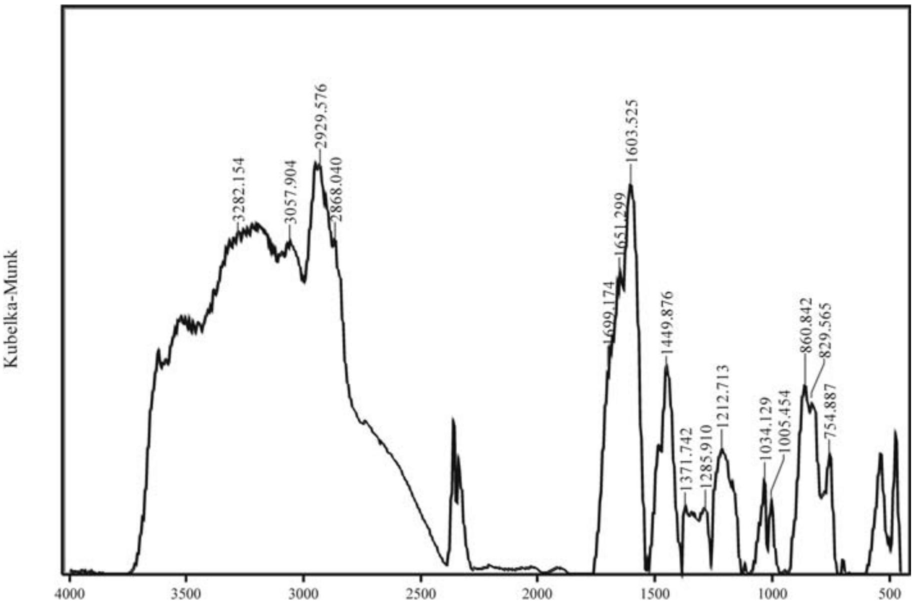

Figure 4. DRIFT-spectrum LRC low-rank coal (Sample No. 1).

As is seen in Fig. 2, the E value changes considerably with the change of coal genetic type. The maximal E values are observed for reduced coals, which agrees with the higher value of mass loss at 850 °C. Decreasing the thermodestruction process E for LRC results in the stepwise decrease of the mass loss value. An inversely proportional linear relation between the parameters E and the mass loss value at 850 °C has been observed.

The investigation of cokes from coals of different genetic type has shown that they are characterized by negligible pore volume and wall thickness, mostly less than 0.1 mm (Table 3). Within this size range, cokes of LRC coals contain higher quantities of small pores than do cokes of the RC type. However, it must be noted that cokes of the RC type contain considerable quantities of large pores, which are absent in the cokes of low-reduced coals.

The thickness of the walls is approximately the same for cokes of different coal types. It can be seen from the Table 3 that higher total porosity and lower total wall thickness are typical for cokes of reduced coals rather than low-reduced coals.

The quantitative indices of coke microstructure are graphically demonstrated by microphotographs (Fig. 3). The figure shows that cokes of low-reduced coal are black powders, which consist predominantly of separate particles outlined by a fused coal layer with the pores in the centre. Some grains are without pores. This explains the formation of a powder-like solid residue from this fuel after thermal destruction.

For cokes obtained from reduced coals, a more developed porous structure is typical. Grains of an analysed sample are fused between each other, thus demonstrating the formation of weakly-coked solid residue. In this case, pore walls have a considerably smaller size compared to those of LRC type cokes. There are small fragments of coke walls. The walls of cokes are isotropic in polarized light.

Infrared spectroscopy with DRIFT techniques were applied to the semi-quantitative evaluation of the origin of structural peculiarities in coals of different genetic types. The LRC and RC spectra contain a set of absorption bands (Fig. 4) due to the following functional groups: H-bonded hydroxyl (≈ 3300 cm^{-1}); aliphatic CH_3, CH_2 and CH groups (2970, 2920, 1440, 1380 cm^{-1}); C_{ar}-H bonds (≈3050 and 900–700 cm^{-1}); aromatic C=C bonds (≈≈1600 cm^{-1}); carbonyl functional groups (1725, 1700, 1650 cm^{-1}), including quinines (1653–1663 cm^{-1}); -C-O- groups (≈ 1280 cm^{-1}). The band at 1100 cm^{-1} is assigned to -S- groups because it correlates with the elemental composition of coals and semi-cokes.

Table 4 compares the relative intensities (areas) of the absorption bands of individual components. As can be seen from the table, the RC samples are distinguished by their greater proportion of -S-, -O-, and C_{ar}-H bonds, and by the smaller content of the reactive oxygen-containing groups.

Semi-coking of the samples results in the loss of some aliphatic groups, the increase of the relative content of C_{ar}-H and CH_3 groups to that of the total content of aliphatic groups, the increase in the strength of intermolecular interactions (1700/2920), and the creation of an increasingly developed polyconjugation system. The areas of absorption bands corresponding to the –S- ($S_{110-100}$) and C_{ar}-H ($S_{900-700}$) groups are much higher (in 2 and 10 times) for RC semi-cokes. This could be due to high rates of aromatisation and lacing processes.

Chemical pre-treatment decreases the relative content of –S- and C_{ar}-H structures, which is consistent with the data.

Thus, hydrogen- and sulphur-rich reduced coals were formed under marine transgressions during early diagenesis. They contain a greater proportion of -S- and -O- bonds, which facilitate their destruction. These bonds also promote reactions with high values of effective activation energy, and encourage the removal of active functional sulphur- and oxygen-containing and aliphatic groups. Several periods of consumption and accumulation of bridge bonds differing in thermal stability are observed during heating (Butuzova and Krzton 2003). They act as cross-bonding agents that prevent the tight arrangement of structural units and provide microporosity, compactness, and microstructure in semi-cokes and cokes.

Conclusions

Differences in the origin of the structure and microstructure in coals, semi-cokes, and cokes of low-reduced and reduced samples have been shown. These effects can be altered by different methods of chemical pre-treatment.

RCs and their semi-cokes are distinguished by their greater proportion of -S-, -O-, and C_{ar}-H groups. Their semi-cokes and cokes are a weakly-coked material with less compactness and higher pore volume than semi-cokes of LRC type coals.

The results of this paper indicate that the carbonisation of oil- and AAD-treated coals improves the cross-linking processes in coal carbonisation products. The dependence of coal structure and reactivity on genetic type is fairly strong.

Table 4. The results of IR-spectroscopy of coals and the products of their thermal and thermochemical destruction

Sample No.	Type	T [°C]	Chemical treatment	Relative intensity												Relative region S_x/S_{1600}	
				I_x/I_{1600}									I_x/I_{2920}				
				4000	3300	3050	2970	2920	1725	1700	1650	1440	1280	$\frac{1700}{2920}$	$\frac{2970}{2920}$	$\frac{3050}{2920}$	$S_{1100–1000}$	$S_{900–700}$
1	LRC	20	–	0.48	0.93	0.93	1.03	1.03	0.65	0.78	0.88	0.76	0.56	0.76	1.00	0.90	0.12	0.48
		520	–	0.73	0.63	0.87	0.75	0.70	0.60	0.66	0.72	0.88	0.82	0.94	1.07	1.24	0.26	5.39
		520	AAD	0.62	0.59	0.79	0.66	0.64	0.58	0.63	0.73	0.80	0.70	0.98	1.03	1.23	0.24	3.91
		520	oil	0.61	0.53	0.78	0.64	0.61	0.56	0.61	0.71	0.80	0.71	1.00	1.05	1.28	0.23	3.28
1’	RC	20	–	0.40	0.81	0.78	0.97	0.97	0.54	0.61	0.83	0.77	0.66	0.63	1.00	0.80	0.52	0.70
		520	–	0.86	0.71	0.87	0.83	0.79	0.86	0.88	0.85	0.94	0.91	1.11	1.05	1.10	1.29	7.41
		520	AAD	0.70	0.62	0.83	0.71	0.67	0.71	0.73	0.78	0.87	0.78	1.09	1.06	1.24	1.24	4.87
		520	oil	0.78	0.65	0.85	0.76	0.72	0.78	0.79	0.80	0.89	0.82	1.10	1.06	1.18	1.21	3.57

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