The Pathways for Thermal Decomposition of Coals with High Content of Sulphur and Oxygen

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ABSTRACT: This study was undertaken to obtain more definite information about the peculiarity of chemical reactions under the pyrolysis of coals with different content of heteroatoms using the pairs of low- and high-sulphur samples of the same rank (~76–88 % C^{daf}) in parallel experiments. Products were characterized by the standard chemical methods, FT-IR spectroscopy, extraction, liquid and gas chromatography and others. The results suggest that the sensitivity of pyrolysis products yield to changes of coal genetic type as well a coal rank is related to competing rates of volatile release and resolidification processes. The high content of active oxygen- and sulphur-containing groups appears to shift this competition in favour of greater volatile products release and slower resolidification. Phenolic OH (and SH) groups take part in ether bonds or C-C bonds creation by a dehydration reaction in a temperature range of 300-500 °C. This agrees with the high contents of H_2O, CO, CO_2 in gas and asphaltenes in liquid and many -O-, -S- type bridges in solid semi-coking products. In contrast, pyrolysis of the good coking coals results in predominant formation of aromatic structures of semi-coke with polymethylene bridges and produces the gaseous products with high portion of H_2 and CH_4.

KEY WORDS: low and medium rank coals, organic sulphur, pyrolysis products.

Introduction

A genetic type by reductivity is one of the most important characteristic of coals which does not consult in the International Coal Classification and it needs the special attention.

In previous papers (Bechtel et al. 2002, Butuzova et al. 2002, 2004, 2005a, b, c, 2007, Minkova et al. 2004, Turchanina et al. 2005, Marinov et al. 2000) there were investigated the composition and properties of the Donets low-rank coals of different genetic types by reductivity (GTR) in detail. It was demonstrated that LRC (low-reduced) and RC (reduced) types distinguished in the elemental composition, especially hydrogen and sulphur content, and their behavior in the pyrolysis processes. A high reactivity for reduced coals in coking and lacing processes was indicated (Butuzova et al. 2005a). It has been shown that the coals of RC type give fritted and less compact semicokes with a higher volume of pores and lesser relative content of walls (Butuzova et al. 2005b).

It was showen that the organic sulphur content was a major indicator of the Donets coals GTR which correlated with dibenzothiophene/phenanthrene ratio, with the content of hopanes and the $\delta^{13}C$ values (Bechtel et al. 2002).

Using the so-called thermokinetic approach it was demonstrated that the thermal decomposition of RC coal samples proceeds more intensely than for the LRC coal samples. The harmonized kinetic and diffusion ran together with the high pyrolysis rate favored a formation of the carbonized coals of the systematic structure despite a high process rate. Active sites, first of all oxygen and sulphur bridges, play one of the most important role for pyrolysis way and properties of products. It has been suggested the equations for the coal genetic type determination (Mianowski et al. 2005).

The aim of the present paper is elucidation of the connection between coal type by reductivity for coking and non-coking samples (low- and medium- coalification grades) and its ability to thermal transformations in various pyrolysis processes; determination of the influence of sulphur-containing compounds on the chemistry of the pyrolysis processes.

Experimental

Four pairs of Middle Carboniferous Donets coals of the same rank level but different genetic types by reductivity were investigated. According the Ukrainian classification they are low- and medium-rank coals (DSTY 3472-96) which can be subdivided on D (R_r = 0.49–0.71) and G (R_r = 0.96–1.18) grades. Their rank parameters are in correlation with bituminous coals of the International Classification (ECE-UN Geneva 1998).

Petrographic composition of samples is uniform enough: 80–90 % vitrinite. The samples of reduced (RC) and low reduced coals (LRC) were collected from the close coal seams (the distance between stratigraphic columns is less than 100 m). The limestone of a layers roof and finely crystalline pyrite and data about the content of microlithotypes (carbopyrite) with a fine pyrite were used for selecting and testing of a type by reductivity. The coals were classed to a low-reduced or reduced type if the content of carbopyrite was less than 20 % or more than 40 % according to Butuzova at al. (2005a).

To solve this problem the samples of investigated coals were examined by thermal, physico-chemical analyses. The thermal

Coal mine, seam, Code[*]	Type	A^d	V^{daf}	Y, mm	C^{daf}	H^{daf}	O^{daf}	S_t^d	S_s^d	S_p^d	S_o^d	H/C
Cheluskintsev, l_4 07002034022132	LRC	2.4	35.6	–	79.3	4.9	11.8	2.17	0.04	0.11	2.02	0.74
Trudovskaya, l_4 05001036011032	LRC	1.6	37.3	–	78.4	4.9	13.9	1.05	0.01	0.08	0.96	0.75
Gagarina, m^3 11111728030735	LRC	3.7	28.7	22	87.4	5.1	5.4	0.7	0.06	0.03	0.61	0.70
Zasyad'ko, l_4 10102730021035	LRC	2.6	31.7	23	87.8	5.16	5.09	1.09	0.01	0.24	0.84	0.70
Ukraine, k_8 05012140092831	RC	9.9	41.8	–	77.9	5.3	12.5	2.87	0.11	0.80	1.96	0.82
Trudovskaya, k_8 04012146045831	RC	4.6	46.2	–	76.1	5.4	11.0	5.85	0.05	0.71	5.09	0.86
Gagarina, m^0_4 09111834123734	RC	12.2	35.6	32	83.6	4.9	8.41	3.75	0.05	2.41	1.29	0.71
Zasyad'ko, k_8 09111830022834	RC	2.7	31.7	27	87.3	5.23	5.99	2.81	0.02	1.14	1.65	0.72

[*] Code by International codification system for medium and high rank coals. 1988. ECE-UN Geneva

■ **Tab. 1.** Characteristics of initial coals, wt %.

behavior of coals was studied by classical Fisher method and pyrolysis in the water vapour stream.

The composition of solid pyrolysis products was measured by elemental, technical, petrographic analyses and DRIFT-spectroscopy. The petrography, proximate and ultimate analyses of the samples, including the total (S_t), organic (S_o), pyritic (S_p) and sulphates (S_s) sulphur were determined by standard methods. IR-spectra of solid samples were recorded on a FT-IR "Bio-Rad" FTS-7 spectrometer with DRIFT technique.

Extraction, column chromatography and gas chromatography – mass spectrometry (GC-MS) of the saturated and aromatic hydrocarbon fractions were used to the separation and identification of liquid pyrolysis products (Safin et al. 2005). The determination of semi-coking gas composition was performed on apparatus VTI.

Results and discussion

As can be seen from the Table 1, reduced coals are distinguished by higher S_o^d, S_p^d and total sulphur contents; higher H/C ratio, yields of volatile matter and ash content than low reduced coals corresponded to the same coalification degree. Organic sulphur S_o is the main form of sulphur for studied coals under study, except coking RC coals (mine Gagarina) which are rich in pyrites sulphur, too.

The thickness of a plastic layer is higher for coking RC in comparison with LRC.

The results of semi-coking experiments are given in the Table 2.

These data show that the semi-coking of reduced coals considerably decreases the yield of semi-coke and water, increases the yield of volatile products and conversion degree as compared to isomethamorphic low-reduced coals. Semi-coking of low rank RC samples produce a substantially higher yield of tar than LRC. Semi-cokes from RC are fritted products in contrast with light semi-cokes of the low-reduced coals.

During semi-coking of medium-rank coals yield of tar does not change noticeably but the yield of gas from RC is higher in 2.5–3.0 times comparatively to those of a LRC. So, the destruction processes and removal of the volatile products from the coal organic mass occur more intensive in RC samples what leads to formation of porous structure of semi-cokes with lower strength in comparison with LRC.

Table 3 presents the comparative data on the composition of semi-coking gaseous products obtained from the non-coking and coking coals of different genetic types by reductivity. As can be seen from this table, the main component of gas is methane, the content of which reaches 106.42 ml/g for coking RC and 59.52 for LRC. The gas from low-rank reduced coals differs from that of low-reduced coals by having higher contents of H_2, H_2S and smaller content of CH_4. The gas evolved

N	Coal mine, seam	Type	Semi-coke	H_2O	Tars	Gas
1	Cheluskintsev, l_4	LRC	63.5	13.6	6.7	16.2
2	Trudovskaya, l_4	LRC	64.8	17.5	9.0	8.7
3	Gagarina, m^3	LRC	84.4	2.3	5.3	8
5	Zasyad'ko, l_4	LRC	82.7	3.2	5.9	8.2
6	Ukraine, k_8	RC	62.5	11.3	12.9	13.3
7	Trudovskaya, k_8	RC	62.1	10.7	14.3	12.9
8	Gagarina, m^0_4	RC	71.8	1	4.7	22.5
9	Zasyad'ko, k_8	RC	71.7	1.5	6.1	20.7

■ **Tab. 2.** Yield of semi-coking products, wt %.

№	Coal mine, seam	Type	H_2S	CO_2	C_mH_n	CO	H_2	CH_4
1	Cheluskintsev, l_4	LRC	9.07	30.61	5.18	22.19	12.63	82.28
2	Trudovskaya, l_4	LRC	2.73	11.48	2.87	14.77	20.50	57.85
4	Zasyad'ko, l_4	LRC	1.99	15.46	3.17	6.54	46.02	59.52
1′	Ukraine, k_8	RC	9.93	26.17	4.12	18.05	43.85	66.19
2′	Trudovskaya, k_8	RC	29.08	11.78	4.78	14.06	47.18	54.85
4′	Zasyad'ko, k_8	RC	19.76	3.89	5.61	6.54	55.39	106.42

■ **Tab. 3.** The composition of the semi-coking gas, ml/g^{daf}.

№	Type	T, ºC	Relative intensity, cm^{-1}												Relative region
			OH 3300	CH_{ar} 3050	CH_{al} 2970	CH_{al} 2920	I_x/I_{1600} C=O 1725	C=O 1700	C=O 1650	CH_{al} 1440	C-O 1280	I_x/I_{2920} 1700 2920	2970 2920	3050 2920	S_x/S_{1600} CH_{ar} $S_{700-900}$
1	LRC	20	0.93	0.93	1.03	1.03	0.65	0.78	0.88	0.76	0.56	0.76	1.00	0.90	0.48
		520	0.63	0.87	0.75	0.70	0.60	0.66	0.72	0.88	0.82	0.94	1.07	1.24	5.39
2		20	0.95	0.91	0.99	0.99	0.74	0.77	0.86	0.72	0.61	0.78	1.00	0.92	0.49
		520	0.70	0.79	0.75	0.74	0.73	0.72	0.77	0.87	0.72	0.97	1.01	1.07	4.87
1′	RC	20	0.81	0.78	0.97	0.97	0.54	0.61	0.83	0.77	0.66	0.63	1.00	0.80	0.70
		520	0.71	0.87	0.83	0.79	0.86	0.88	0.85	0.94	0.91	1.11	1.05	1.10	7.41
2′		20	0.88	0.87	0.94	0.94	0.74	0.75	0.85	0.73	0.61	0.80	1.00	0.93	0.58
		520	0.85	0.90	0.87	0.83	0.87	0.86	0.87	0.93	0.85	1.04	1.05	1.08	6.19

■ **Tab. 4.** The results of IR-spectroscopy of low-rank RC and LRC coals and semi-cokes.

from coking RC contains higher contents of methane, hydrocarbons, hydrogen, hydrogen sulphide, but smaller content of carbon dioxide.

An increase in the content of CH_4 and other hydrocarbons in gas indicate a more complete splitting of alkyl radicals from COM and their subsequent decomposition with the abstraction of the methyl group and methane.

The data obtained by DRIFT spectroscopy allowed to conclude that the main difference between the structure of non-coking RC and LRC samples consists in the less number of the reactive COOH, -OH and C=O oxygen-containing groups (1,650–1,725, 3300 cm^{-1}), but in the greater number of the ether C-O groups (1,280 cm^{-1}) and C_{ar}-H groups ($S_{900-700}$) in reduced coals (Table 4, Fig. 1).

In contrast, the coking coals IR spectra contain the absorption bands of C=O groups only at 1,750 cm^{-1} which due to carbonyl functional groups in saturated compounds. As seen from the Table 5, the samples of RC are distinguished for lesser ratio number of the C-O- bonds and small content of the reactive oxygen-containing groups. The reduced coals are characterized by high content of total oxygen O^{daf} (Table 1). This fact together with DRIFT data prove that the unreactive oxygen is present predominantly in the form of ether groups in low-rank samples and it is involved in heterocycles in the medium rank coals.

Semi-coking process causes considerable changes in the nature of IR-spectrum manifested by an increase in the relative intensity of the absorption band of C_{ar}-H groups to C_{al}-H groups ($I_{3,050}/I_{2,920}$) and in increasing the ratio $I_{1,700}/I_{2,920}$. This ratio characterizes thermal unstable structures and the strength of intermolecular interactions. Index $I_{1,700}/I_{2,920}$ is 3 to 6 times higher for coking coals in comparison with non-coking (1.2–1.8 times), especially for RC (6 and 1.8 times). Increasing this parameter in
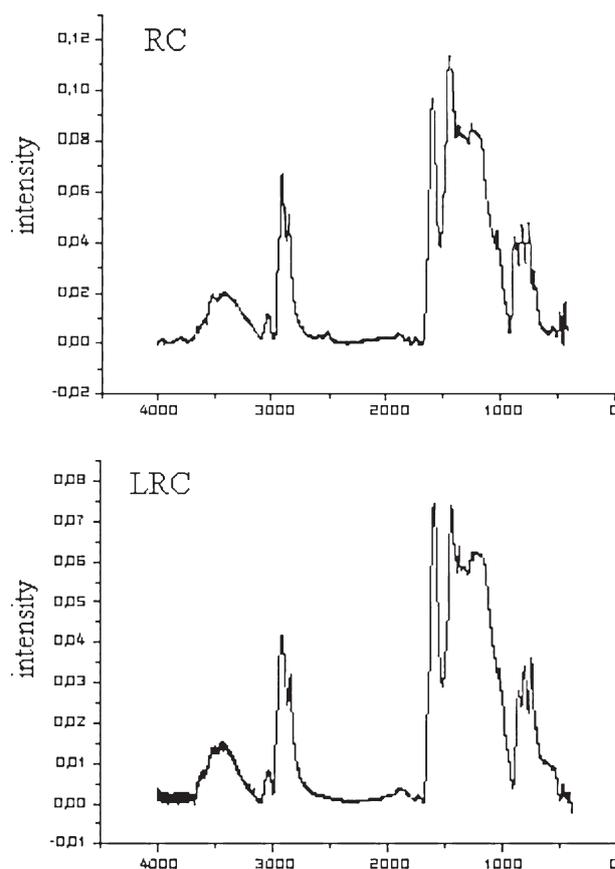
■ **Fig. 1.** DRIFT-spectrum RC and LRC coking coals (mine Gagarina).
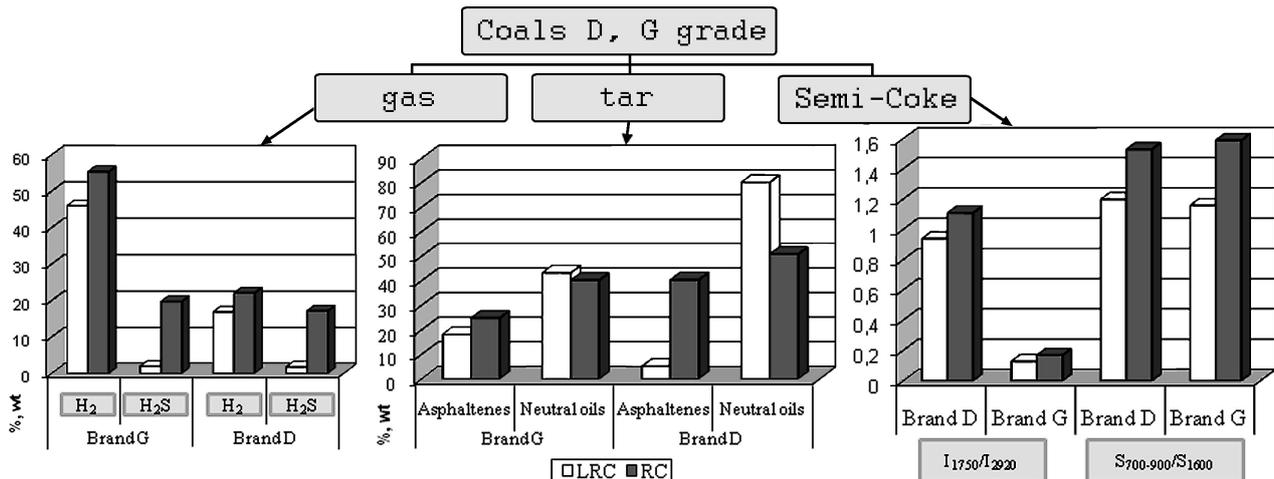
■ **Fig 2.** Indexes for genetic type by reductivity determination.
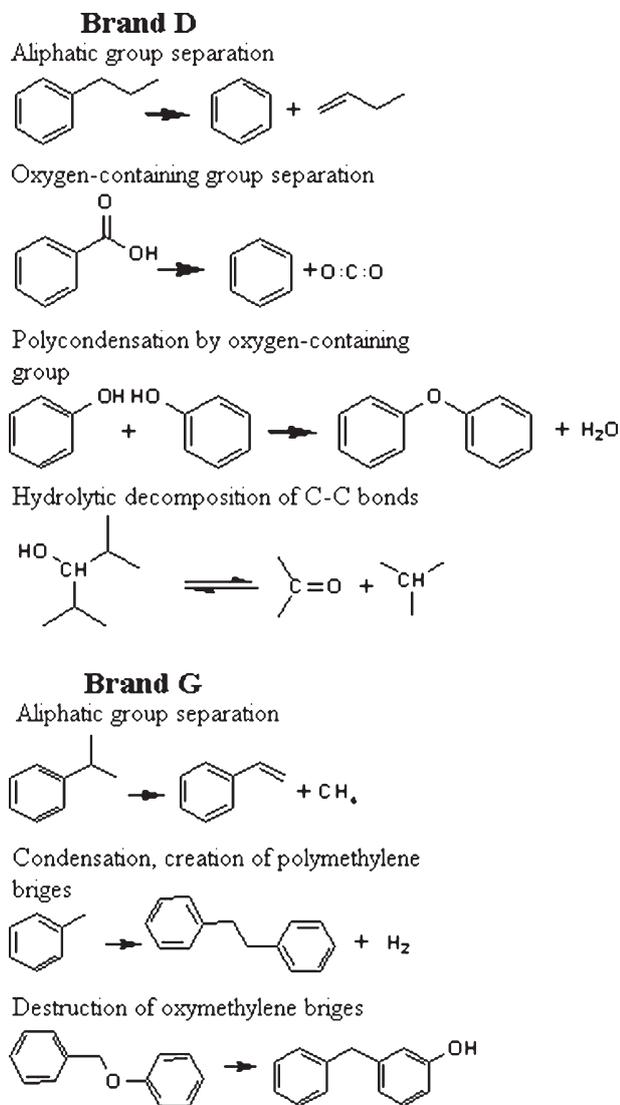
■ **Fig. 3.** The mechanism of the prevalent thermal transformations for coking and non-coking coals.

the RC semi-cokes characterizes them as structures with more developed polyconjugation system.

At the same time semi-coking of the reduced samples produce sharp increase in C-H_{ar}-groups content (2–10 times for low-rank coals and 1.3–1.4 times for medium rank coals). It could be due to high rates of aromatization and lacing processes, especially for non coking low-rank coals.

So, the semi-cokes are distinguished from aliphatic-rich initial coals by the higher ratio number of the C-H_{ar}-groups and ether bridges bonds which act as cross-bonding agents, prevent tight arrangement of structural units and provide compactness and microstructure of semi-cokes.

DRIFT data show that the cleavage of weak aliphatic bonds, aromatization and polycondensation reactions take place at 500 °C in all samples. But there are the differences between pyrolysis processes for caking and non-caking coals (Fig. 3).

Semi-coking of coking coals results in an decrease of the quota of ether groups and short aliphatic chains (CH_3/CH_{al}), but increase of the content of phenolic groups. Evidently, in this case the aryl methyl ethers with -CH_2-O- bridge are cleaved with formation of phenol. Then the toluene-like structures are associated, split off H_2 and producing the polymethylene bridges between aromatic rings are occurred. This is in agreement with the high content of CH_4 and H_2 in gas (Table 3).

The main reactions in oxygen-rich non-coking coals are the decomposition reactions leading to gases such as CO and CO_2 and polycondensation reactions by oxygen-containing groups, forming water. The content of carbon oxides in semi-coking gas is in 2–3 times higher in comparison with gas of coking coals (Table 3).

Therefore the mechanism of semi-coke formation depends on the concentration of the oxygen (sulphur)-containing groups in the coal, the thermal decomposition or polycondensation of which leads to obtaining different products. Herewith the predominantly formation of oxymethylene or polymethylene bridges in the semi-cokes of noncoking and coking coals accordingly was established by DRIFT-data. It explains the difference in the package method of the aromatic rings and coals coking ability.

Important indexes for genetic type by reductivity determination can be suggested: the content of organic sulphur in coal;

№	Type	T, °C	Relative intensity										Relative region
			I_x/I_{1600}							I_x/I_{2920}			S_x/S_{1600}
			OH	CH_{ar}	CH_{al}	CH_{al}	C=O	CH_{al}	C-O	2950	1750	3040	CH_{ar}
			3400	3040	2950	2920	1750	1440	1280	2920	2920	2920	$S_{700-900}$
3	*LRC*	20	0.26	0.14	0.39	0.72	0.03	0.52	0.29	0.54	0.04	0.20	0.89
		520	0.82	0.14	0.21	0.46	0.06	0.40	0.32	0.47	0.13	0.30	1.16
3′	*RC*	20	0.27	0.13	0.53	0.88	0.02	0.74	0.25	0.60	0.03	0.15	1.15
		520	0.63	0.15	0.40	0.79	0.13	1.03	0.18	0.51	0.17	0.20	1.59

■ **Tab. 5.** The results of IR-spectroscopy of middle-rank RC and LRC coals and semi-cokes.

the relative content of H_2, H_2S in gas; the relative content of asphaltenes and neutral oil in liquid products; I_{1700}/I_{2920} and $S_{700-900}/S_{1600}$ values by DRIFT spectroscopy in semi-cokes (Figure 1).

The obtained data demonstrate the very important role of sulphur- and oxygen-containing compounds for coal structure and reactivity.

Conclusions

There have been shown the differences in the origin coals, semi-cokes and cokes structure and microstructure for low-reduced and reduced samples and the possibility to change them by the chemical pretreatment.

RC and their semi-cokes are distinguished for the greater ratio number of the -S- and -O- and C_{ar}-H groups. Their semi-cokes and cokes are a weak-coked material with less compactness, a higher volume of pores in comparison to semi-cokes of LRC type coals.

The results of this paper prove that the dependence of the coal structure and reactivity on genetic type is fairly strong. The reactions of -S- and -O- containing groups affect the course of thermodestruction processes permitting directed variations in the yield and composition of liquid, solid and gaseous products, the degree of COM conversion.

The results presented in this paper prove that during thermodestruction of coking coals the processes related with the cleavage of ether groups and with changes in the package method of the aromatic rings via the polymethylene bridges are of considerable importance.

This results evidence that existing coals classification system can be improved if the coal type by reductivity is taken in consideration.

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