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Pyrolysis of low-reduced and reduced coals of different ranks

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Abstract. Reduced and low-reduced pairs of isometamorphic coals spanning the whole coalification series have been studied. A comparative determination of the yields and properties of the products of various pyrolysis processes has been carried out. A high reactivity for reduced coals in coking and leaching processes was indicated. The solid products of steam pyrolysis were characterized by well developed surfaces, the values of which depend of the coal type by reductivity and coal rank. Desulphurisation effects from thermal treatment were recorded for all samples.

Keywords: reductivity, coalification, pyrolysis, desulphurisation, adsorption activity

Introduction

Sulphur is a major obstruction to the effective and extensive processing of coal. High proportions of sulphur adversely affect coal behaviour during thermal destruction and the quality of the pyrolysis products, and result in air pollution. The careful utilisation and desulphurisation of sulphur coals are problems that have yet to be solved.

Previous investigations indicate that the Donetz coals of reduced type (RC) are distinguished from low-reduced (LRC) coals by a higher content of general and pyritic sulphur, regardless of their rank (Bechlet et al. 2002, Matsenko 1983). Thus, all coal properties depend on rank and genetic type by reductivity (GTR), i.e. on the conditions of peat-formation and coalification. The structure and reactivity of different genetic types of coals of different ranks has not been sufficiently studied. The polyfacies coal deposits of the Donetz Basin are convenient for such an investigation.

The purpose of the present paper is to assess the connection between coal type (GTR and rank) and the ability to undergo thermal transformations in various pyrolysis processes.

Procedures

Pairs of reduced and low-reduced isometamorphic coals spanning the entire coalification series were collected from neighbouring coal seams (separated by less than 100 m) of the

Table 1. Characteristics of initial coal

Sample No.	Coal mine (deposit), coal seam	Type	W^a [%]	A^d [%]	V^{daf} [%]	C^{daf} [%]	H^{daf} [%]	Fix Carbon [%]	S_t^d [%]	S_p^d [%]	H/C
1	Kansk-Achinsk (Ukraine)	LRC	10.9	8.6	46.8	72.7	4.90		0.52	traces	0.81
2	Kurakhovskaya, l_4	LRC	9.4	5.3	37.2	79.3	5.07	61.52	1.29	0.15	0.77
3	Novo-Grodovskaya, l_7	LRC	2.0	1.9	38.6	82.7	5.53		1.79	traces	0.75
4	Kirovskaya Zapadnaya, k_5	LRC	0.5	3.4	15.6	89.6	4.45	81.66	0.62	0.08	0.60
5	Themopolskaya, k_5	LRC	1,1	2.3	7.9	93.3	2.92		0.95	traces	0.37
6	Udarnic, h_3	LRC	5.0	5.2	2.0	95.7	1.65		1.13	0.15	0.21
1^1	Maritza-Iztok (Bulgaria)	RC	8.3	19.8	60.0	64.1	6.80	–	4.70	–	1.27
1^2	Dneprovsk	RC	7.2	11.7	55.8	69.0	6.00		3.93	1.89	1.04
2^1	Kurakhovskaya, l_2	RC	5.5	8.6	43.0	76.1	5.22	50.40	5.00	2.14	0.82
3^1	Novo-Grodovskaya, m_4^2	RC	1.6	3.2	40.5	81.7	5.37		3.05	0.60	0.79
4^1	Kirovskaya Zapadnaya, k_4^{2H}	RC	0.8	10.4	16.6	86.9	4.41	73.59	4.42	2.34	0.61
5^1	Themopolskaya, k_7	RC	0.84	6.4	7.6	90.3	3.07		3.01	2.27	0.41
6^1	Udarnic, h_2	RC	12.9	13.3	3.6	93.9	2.30		4.12	2.18	0.29

W^a – moisture, A^d – ash on dry matter, V^{daf} – volatile matter on dry ash free, S_t^d – total sulphur on dry basis, S_p^d – pyritic sulphur on dry basis

Table 2. Vitrinite reflectance and petrographic composition of the studied coals

Sample No.	Coal mine (deposit), seam	Type	R_o [%]	Petrographic components [% vol.]			Lithotype with finely crystalline pyrite [% vol.]
				V	L	I	
1	(Kansk-Achinsk) Ukraine	LRC	0.46	96	1	3	0
2	Kurakhovskaya, l_4	LRC	0.66	89	7	4	0
3	Novo-Grodovskaya, l_7	LRC	0.76	–	–	2	0
4	Kirovskaya Zapadnaya, k_5	LRC	1.72	–	–	3	0
5	Themopolskaya, k_5	LRC	3.07	90	4	6	4
6	Udarnic, h_3	LRC	5.21	95	2	3	0
1^2	Dneprovsk	RC	0.38	94	5	1	58
2^1	Kurakhovskaya, l_2^1	RC	0.52	80	9	11	63
3^1	Novo-Grodovskaya,m_4^2	RC	0.66	–	–	20	60
4^1	Kirovskaya Zapadnaya, k_4^{2H}	RC	1.66	–	–	17	63
5^1	Themopolskaya, k_7	RC	2.95	84	3	13	49
6^1	Udarnic, h_2	RC	5.06	82	2	16	53

R_o – reflectance, V – vitrinite, L – liptinite, I – intertinite

Table 3. Characteristics of the products of water vapour pyrolysis for coals of different genetic types and coalification degrees (500 °C, 2h)

Sample No.	Coal seam	Type	Yield of pyrolysis products [wt%]			Adsorption activity of semi-coke by iodine [mg/g]
			Semi-coke	Tars	Gas + H_2O losses	
1	(Kansk-Achinsk) Ukraine	LRC	27.0	10.0	63.0	520
2	Kurakhovskaya, l_4	LRC	46.7	14.7	38.6	500
3	Novo-Grodovskaya, l_7	LRC	75.0	15.0	10.0	400
4	Themopolskaya, k_5	LRC	85.0	1.5	13.5	130
5	Udarnic, h_3	LRC	80.0	0.1	19.9	150
1^1	(Maritza –Iztok) Bulgaria	RC	47.8	15.4	36.8	303
02^1	Kurakhovskaya, l_2	RC	48.7	15.1	35.2	420
3^1	Novo-Grodovskaya,m_4^2	RC	55.8	12.5	31.7	270
5^1	Themopolskaya, k_7	RC	85.0	0.1	15.0	130
6^1	Udarnic, h_2	RC	87.0	0.1	12.9	110

Donetz Basin. They were selected based on their variable sulphur contents and the composition of the surrounding rocks.

The petrographic, proximate and ultimate analyses of the samples, including the total (S_t), organic (S_o), pyritic (S_p) and sulphate (S_s) sulphur were determined according standard procedures and by a LECO MAC-400 automatic analyser.

The thermal behaviour of the individual coals was studied by the Fisher method, and in water vapour under atmospheric pressure by the method of Minkova et al. (1991). The adsorption activity of the solid products was determined by iodine. In addition to the yield of products, determined in each individual experiment, special consideration was given to the distribution of the various sulphur fractions between the pyrolysis products.

Results and discussion

The main characteristics of the coals are given in Table 1 and Table 2. As can be seen from these tables, RC of all coalification series are distinguished from LRC by higher hydrogen, sulphur, and ash contents, higher yields of volatile matter, lower contents of fixed carbon, lower reflectance values (R_o), and very high contents of the lithotypes with finely crystalline pyrite. Changes in the H/C ratios are observed for RC and LRC samples with increasing coalification degree. These differences are less substantial for middle-rank coals.

The coals under investigation are petrographically homogeneous with high proportions of vitrinite (> 80%). The inertinite group of macerals is negligible in LRC, but attains values of 11–20% in the RC samples.

Results obtained from the water vapour pyrolysis of coals are shown in Table 3. This table demonstrates the changes taking place in the yield of pyrolysis products with increasing coalification degree for parent coals of different genetic types by reductivity. These changes clearly depend on both coal parameters. The LRC product yields vary significantly when the coalification degree is higher. The yield of primary tars is maximised in coals of middle rank.

Conversely, the tar yields vary regularly with increas-

Table 4. The comparative results of pyrolysis experiments for Ukrainian (Kansk-Achinsk) and Bulgarian (Maritza-Istok) lignites

Components, fractions	Characteristics of pyrolysis products [wt%]			
	Kansk-Achinsk (Ukraine)		Maritza-Istok (Bulgaria)	
	Pyrolysis in water vapour stream	Pyrolysis by Fisher	Pyrolysis in water vapour stream	Pyrolysis by Fisher
Semi-coke	27.0	47.0	47.8	55.9
Tars	10.0	2.0	15.4	10.2
Gas + water +losses	63.0	51.0	36.8	34.9
Activity by iodine [mg/g]	520	150	303	40
Composition of resins [wt%]				
Free carbon	–	–	3.2	3.2
Asphaltenes	47.3	16.3	28.0	35.8
Base	2.6	0.8	1.1	0.8
Acid	1.2	0.7	1.1	0.4
Phenolic	14.9	10.8	9.6	15.3
Neutral	23.2	61.4	56.4	43.5
Losses	10.8	10.0	0.3	1.1
Composition of neutral oil fractions				
Aliphatic	38.9	9.6	35.8	25.8
Aromatic	34.5	78.6	39.5	42.1
Polar	23.1	11.8	21.5	27.5
Losses	3.5	0.0	3.2	4.6

Table 5. The comparative results of pyrolysis experiments for RC and LRC low-rank coals

Components, fractions	Characteristics of pyrolysis products [wt%]			
	Kurakhovskaya, l_4 (LRC}		Kurakhovskaya, l_2 (RC)	
	Pyrolysis in water vapour stream	Pyrolysis by Fisher	Pyrolysis in water vapour stream	Pyrolysis by Fisher
Semi-coke	46.7	71.9	48.7	63.7
Tars	14.7	5.9	15.1	13.9
Gas+water +losses	38.6	22.2	36.2	22.4
Activity by iodine, mg/g	500	–	420	–
Composition of tars [wt%]				
Free carbon		24.40		14.67
Asphaltenes		5.16		40.40
Base		1.55		10.62
Acid		4.75		1.75
Phenolic		7.70		9.66
Neutral		56.43		22.85
Losses		0.01		0.30

ing coalification degree for RC: the largest contents of tars and vapour-gas products are removed from lignite and low-rank coal, and the least by anthracite.

The solid products of steam pyrolysis were characterised by well developed surfaces. Their values depend on the coal rank and GTR. In general, the iodine number of activated carbons from LRC is higher than from isometamorphic RC.

A comparative determination of the yield and properties of products during various pyrolysis processes has been carried out. The results of pyrolysis experiments are summarised in tables 4 and 5. It can be seen from these tables that the primary tar yields are higher for RC than for LRC. On the other hand, tar removal (volatile matter removal) in water vapour pyrolysis is also significantly higher than by the Fisher method.

Tables 4 and 5 show variations in the composition of the liquid pyrolysis products of the RC and LRC samples. The contents of neutral fractions decrease, but the contents of asphaltenes and phenolic largely increase in RC tars obtained by the Fisher method. These components cause the coking and leaching processes during pyrolysis. These results are consistent with the weak coking ability of low-rank RC.

Pyrolysis of low-reduced brown coal with water vapour, as opposed to Fisher pyrolysis, sharply reduces the

Table 6. Sulphur forms of the original coals and semi-cokes of water vapour pyrolysis

Sample No.	Coal seam	Type	Origin coal		Semi-coke		ΔS_t^d [%]	ΔS_p [%]
			S_t^d [wt %]	S_p [wt %]	S_t [wt %]	S_p [wt %]		
1	(Kansk-Achinsk) Ukraine	LRC	0.52	traces	0.50	traces	3.8	-
2	Kurakhovskaya, l_4	LRC	1.29	0.15	1.03	traces	20.1	100
3	Novo-Grodovskaya, l_7	LRC	1.79	traces	1.35	traces	24.6	-
5	Themopolskaya, k_5	LRC	0.95	traces	0.70	traces	26.3	-
6	Udarnic, h_3	LRC	1.13	0.15	1.0	traces	11.5	100
2^1	Kurakhovskaya, l_2	RC	5.00	2.14	1.06	0.19	78.8	91.2
3^1	Novo-Grodovskaya, m_4^2	RC	3.05	0.60	2.15	traces	29.5	100
5^1	Themopolskaya, k_7	RC	3.01	2.27	2.31	0.59	23.2	74.0
6^1	Udarnic, h_2	RC	4.12	2.18	2.97	0.93	27.9	57.3

S_t – total sulphur, S_p – pyritic sulphur, ΔS_t – total sulphur decrease, ΔS_p – pyritic sulphur decrease

yield of neutral oils and the content of aromatic fractions in them.

The differences in the comparison of neutral oils are more substantial for the products of Fisher pyrolysis. Oils of LRC are especially rich in aromatic components.

The effects of coal and pyrolysis type on the distribution of different sulphur forms are given in Table 6. High levels of desulphurisation can be achieved (23–79% of S_t^d), especially from pyritic sulphur (from 57 to 100%) which decomposes at semi-coking temperatures according to the following equations (Ersahan et al. 1997):

$$FeS_2 \rightarrow FeS + S$$
$$FeS_2 + H_2 \rightarrow FeS + H_2S$$
$$FeS + H_2 \rightarrow Fe + H_2S$$

The decomposition of pyrite began at 400 °C and became faster at 450 °C.

Desulphurisation effects of thermal treatment were recorded for all samples, but the sulphur contents decreased more during the pyrolysis of reduced coals with higher sulphur content. High amounts of tar in the pyrolysis products indicates the high reactivity of reduced coals. The influence of coal GTR is especially pronounced in standard Fisher retort pyrolysis.

Conclusions

It was demonstrated that LRC and RC types of every coal rank are distinguished by elemental composition, especially of hydrogen and sulphur, and by their behaviour during pyrolysis processes.

There are differences in the quality of the active sites involved in coal's thermodestructive process. These sites, such as those of oxygen and sulphur bridges, significantly affect a coal's pyrolysis and the properties of the resulting products (Marinov et al. 2000).

Sulphur reduction, volatile matter removal, and the yield and properties of semi-coke products were affected significantly by differences in metamorphic grade, coal GTR, and the nature of pyrolysis.

The present authors hope that these results will contribute to existing ideas concerning changes in the properties of organic matter during thermal destruction, and that they will be used toward improving the system by which coals are classified.

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