

The possibility of sulphur redistribution in the semi-coking products of low-reduced and reduced coals

Oksana Turchanina¹ – Ludmila Butuzova¹ – Vladimir A. Safin² – Lubov Isaeva²

¹ Donetsk National Technical University, 58 Artema str., Donetsk 83000, Ukraine. E-mail: lfb@skif.net

² National Academy of Sciences of Ukraine, L. M. Litvinenko Institute of Physical Organic and Coal Chemistry, 70 R. Luxemburg str., Donetsk 83114, Ukraine

Abstract. The use of coals with high sulphur contents is an important issue for Donetz Basin, where nearly 70% of the coal stock contains more than 3% sulphur. Sulphur content is a main criterion of fuel quality and is connected to a coal's genetic type by reductivity. Three pairs of Donetz low-rank bituminous coals of different genetic types (reduced coal – RC and low-reduced coal – LRC) were studied in this work. A comparative study of the thermal destruction process of RC and LRC coals, and of the distribution of sulphur in the semi-coking products has been carried out.

Key words: Donetz Basin, sulphur in coal, semi-coking products

Introduction

The chemical pre-treatment of coals as a first stage in their processing is widely used in order to effectively obtain the thermal destruction products of coals [such as the semi-coke, coke (Gluschenko 1968), adsorbent (Verheyen et al. 1995) and soluble coal products (Kuznetsov et al. 1994), as well as tar and gas (Boudou et al. 1994)] and to simultaneously utilize coal wastes. By treating coals with various chemicals and altering the conditions under which the reactions occur, it is possible to influence the thermo-chemical transformations of coals and consequently their technical processing. However, the theoretical aspects of coal modification and the chemistry of the thermal destruction process have not been sufficiently investigated to allow the prediction of the results of coal pre-treatment. Developments in pre-treatment methods for high-sulphur, low rank coals are especially desirable for reducing the sulphur content in the solid products.

The goal of this study is to investigate the influence of coal genetic type and coal pre-treatment on the yield and composition of semi-coking products, and the sulphur distribution between different components.

Procedures

Experiments were carried out on the low rank bituminous coals (~76–79% C^{daf}) of reduced (RC) and low-reduced (LRC) types from the Donetz Basin. The petrographic composition of these coals is similar (Vt = 80–89%).

The total organic carbon content (C_{org}^d, wt% of rock) was measured on a Leco carbon analyser.

The petrographic, proximate and ultimate analyses of the samples, including the total (S_T), organic (S_O), pyrite (S_p) and sulphates (S_s) contents of sulphur, were carried out using standard procedures.

The coal samples were chemically treated directly before thermal destruction by the introduction of 1-% solutions of radical polymerization initiator (acrylic acid dinitrile C₈H₁₂N₄ – AAD) and products of coal-tar distillation (absorber oil).

The thermal behaviour of the coals was studied by means of the Fisher method (heating to 520 °C, at a rate of 7 °C/min).

The composition of the semi-coking gas was investigated by means of a VTI gas analyser.

Results and discussion

The characteristics of the coal samples are summarized in Tables 1 and 2.

As can be seen from Table 1, the investigated coals are petrographically homogeneous, with vitrinite contents between 80–89%. Samples of reduced coals (RC) are distinguished by lower vitrinite reflectance values (R_{o,t}), higher inertinite contents, and lithotypes with finely crystalline pyrite.

Proximate and ultimate analyses reflected the distinction in the structure of the coals by different genetic type (Table 2): samples of reduced coals (RC) are distinguished from low-reduced coals corresponding to the same degree of coalification by higher H/C ratios and volatile matter yields, as well as by higher S_O^d, S_p^d, and total sulphur contents. Organic sulphur S_O^d is the main form of sulphur in the investigated samples (Butuzova et al. 2002).

The systematic research of the semi-coking processes of low-rank bituminous coals of different genetic types by reductivity was carried out in trials with and without the chemical reagent (Table 3). The chemical pre-treatment method was chosen based on the results of research on the structural-chemical transformations that coal undergoes

Table 1. Vitrinite reflectance and petrographic composition of the studied coals

No.	Coal, seam	Type	$R_{o,r}$ %	Petrographic components %			Mineral components vol. %	Lithotype with finely crystalline pyrite
				Vt	L	I		
1	Cheluskintsev, l ₄	LRC	0.71	87	8	5	2	5
2	Trudovskaya, l ₄	LRC	0.55	86	5	9	11	6
3	Kurakhovskaya, l ₄	LRC	0.66	89	7	4	3	0
1'	Ukraine, k ₈	RC	0.57	83	6	11	11	50
2'	Trudovskaya, k ₈	RC	0.49	80	8	12	4	54
3'	Kurakhovskaya, l ₂ ¹	RC	0.52	80	9	11	7	63

Table 2. Characteristics of initial coals, wt%

No.	Type	W ^a	A ^d	V ^{daf}	C ^{daf}	H ^{daf}	(O + S + N) ^{daf}	S _t ^d	S _s ^d	S _p ^d	S _o ^d	H/C atm
1	LRC	0.8	2.4	35.6	79.3	4.94	15.8	2.17	0.04	0.11	2.02	0.75
2	LRC	1.0	1.6	37.3	78.4	4.95	16.7	1.05	0.01	0.08	0.96	0.76
3	LRC	9.4	5.3	37.2	79.3	5.07	15.6	1.04	0.12	0.07	0.85	0.77
1'	RC	1.5	9.9	41.8	77.9	5.30	16.8	2.87	0.11	0.80	1.96	0.82
2'	RC	0.9	4.6	46.2	76.1	5.43	18.5	5.85	0.05	0.71	5.09	0.86
3'	RC	5.5	8.6	43.0	76.1	5.22	18.7	5.60	0.02	2.44	3.14	0.82

Table 3. Yield of the semi-coking products for the initial and chemically treated RC and LRC type coals, % daf

No.	Type	Initial coal				AAD treated				Oil treated			
		Semi-coke	Water	Tar	Gas	Semi-coke	Water	Tar	Gas	Semi-coke	Water	Tar	Gas
1	LRC	63.5	13.6	6.7	16.2	70.9	9.5	7.2	12.4	70.0	10.5	11.9	7.6
2	LRC	64.8	17.5	9.0	8.7	64.8	16.4	12.3	6.5	66.3	14.4	10.3	9.0
3	LRC	71.9	7.2	5.9	15.0	80.7	2.5	11.8	5.0	–	–	–	–
1'	RC	62.5	11.3	12.9	13.3	66.3	9.0	10.4	14.3	64.3	7.3	11.3	17.1
2'	RC	62.1	10.7	14.3	12.9	63.4	9.6	11.8	15.2	64.7	9.6	13.8	11.9
3'	RC	65.7	8.2	5.8	20.3	73.2	6.4	9.0	11.4	–	–	–	–

Table 4. The characteristics of the initial coals and semi-cokes, wt. %

No.	Coal, semi-coke	Type	A ^d	V ^{daf}	S _t ^d	C ^{daf}	H ^{daf}	Characteristic of semi-coke
1	coal semi-coke	LRC	2.42 3.40	35.6 13.8	2.17 1.40	79.30 87.81	4.94 3.61	powder-like
2	coal semi-coke	LRC	1.60 2.86	37.3 13.0	1.05 1.03	78.40 88.83	4.95 3.19	powder-like
3	coal semi-coke	LRC	5.30 13.4	37.2 18.9	1.04 1.00	79.30 85.01	5.07 3.18	powder-like
1'	coal semi-coke	RC	9.95 12.6	41.8 12.9	2.87 2.40	77.90 86.78	5.30 3.67	fritted
2'	coal semi-coke	RC	4.64 7.30	46.2 12.6	5.85 2.90	76.10 85.28	5.43 3.36	fritted
3'	coal semi-coke	RC	8.60 9.10	43.0 15.0	5.60 1.40	76.10 87.71	5.22 3.21	fritted

during thermal destruction (Butuzova 1990). This process consists of the competing reactions of destruction and synthesis, which are based on the freely radical mechanism. Acrylic acid dinitrile (AAD) was used as the radical polymerization initiator to affect the series of radical reactions. The choice of a second reagent was based on the fact that the

coking ability of coals is connected to their ability to form liquid thermal decomposition products, which do not sufficiently evolve during the thermal destruction of low-rank and unconglomerated coals. In this connection, absorber oil (products distillation of coal tar) was used in the pre-treatment.

The semi-coking of reduced coals considerably increases the yield of liquid and volatile products as compared to low-reduced coals. Coal pre-treatment increases the semi-coke yield and changes the liquid/gaseous product ratio. This process is especially pronounced for the semi-coking of pre-treated low-reduced coals, increasing the tar and semi-coke

yield and decreasing the semi-coking gas yield (Butuzova et al. 2001). The semi-coking of low-rank coals in the presence of a chemical reagent suggests the possibility of managing the yield of valuable products.

The characteristics of initial coals and semi-cokes obtained are summarized in Table 4.

As can be seen from this table, the decrease in the volatile matter yield (V^{daf}) and the total sulphur content of semi-cokes from reduced coals is higher than in those from low-reduced coals. LRC results in powder-like semi-cokes while RC results in strong, fritted semi-cokes (Turchanina et al. 2003a).

A diagram of the distribution of the forms of sulphur in solid products from pyrolysis (Fig. 1) shows the effects of semi-coke desulphurization. The contents of total (S_t^d), organic (S_o^d), and pyrite (S_p^d) sulphur decreases to a greater extent in reduced coals. This effect becomes more evident after chemical pre-treatment, particularly in the presence of the absorber oil. This is a positive moment of thermal destruction of coals with high sulphur contents.

Table 5 presents comparative data on the composition of gaseous products obtained from the semi-coking of coals of various genetic types by reductivity before and after chemical pre-treatment.

The main component of the semi-coking gas is methane (CH_4), the content of which reaches 56% for low-reduced coals and 38% for reduced coals. The gas from reduced coals differs from that of low-reduced coals by having higher contents of hydrogen (H_2), hydrogen sulphide (H_2S), and carbon dioxide (CO_2).

The heat of combustion of the semi-coking gas (kJ/m^3) was calculated by the following formula (Pankratov 1995):

$$Q = 108 \cdot \text{H}_2 + 126 \cdot \text{CO} + 234 \cdot \text{H}_2\text{S} + 358 \cdot \text{CH}_4 + 712 \cdot \text{C}_m\text{H}_n,$$

where the coefficients are the heats of combustion of the gaseous components:

H_2 , CO , H_2S , CH_4 , C_mH_n , in vol. %.

The heat of combustion of the semi-coking gas is higher for low-reduced coals. This is connected to the large methane content. Chemical pre-treatment of coals by the radical polymerization initiator and absorber oil significantly decreases the hydrogen, methane, and carbon oxide contents of the semi-coking gas. This effect is observed most notably after adding AAD. These changes indicate the occurrence of processes of synthesis in the coal's organic mass, and consequently increase the semi-coke yield. The hydrogen sulphide that evolves dur-

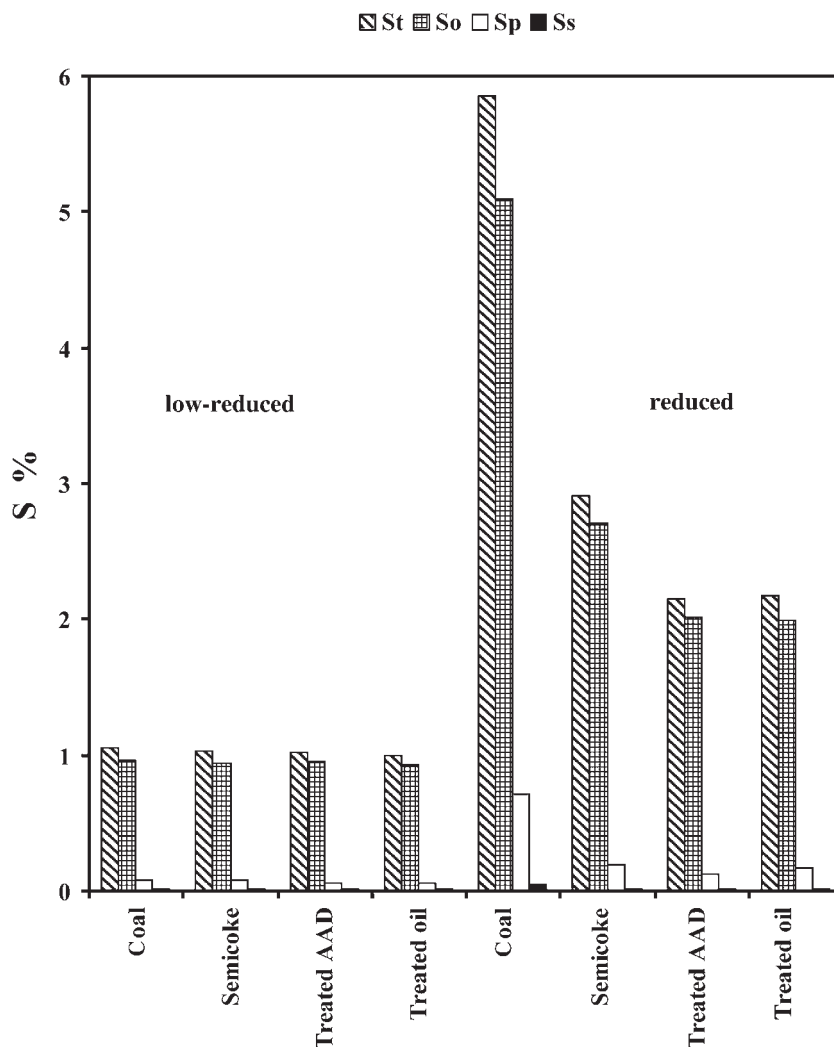


Figure 1. Distribution of sulphur in the initial low-reduced and reduced coals, and in the products of their thermo-chemical destruction.

Table 5. Composition and heat of combustion of the semi-coking gas, $\text{ml/gr}^{\text{daf}}$

No.	Type	Treatment	H_2S	CO_2	C_mH_n	CO	H_2	CH_4	Q kJ/m^3
1	LRC	–	9.07	30.61	5.18	22.19	12.63	82.28	23,164
		AAD	10.71	13.64	4.12	19.42	10.11	75.03	25,206
		oil	11.21	7.50	2.56	9.39	6.76	40.22	23,555
2	LRC	–	2.73	11.48	2.87	14.77	20.50	57.85	24,346
		AAD	2.80	10.73	2.40	8.00	9.60	39.21	24,460
		oil	2.87	14.26	3.09	13.94	15.22	57.03	24,456
3	LRC	–	2.65	32.81	3.24	20.90	24.87	62.68	20,441
1'	RC	–	9.93	26.17	4.12	18.05	43.85	66.19	19,077
		AAD	12.05	25.44	6.83	14.66	42.99	63.31	20,526
		oil	13.11	30.80	6.15	20.15	40.02	61.86	20,284
2'	RC	–	29.08	11.78	4.78	14.06	47.18	54.85	18,750
		AAD	32.46	12.49	4.16	17.15	40.12	50.10	19,150
		oil	32.75	7.24	4.22	13.06	32.13	46.67	19,984
3'	RC	–	35.09	36.00	1.60	22.44	43.89	59.57	15,808

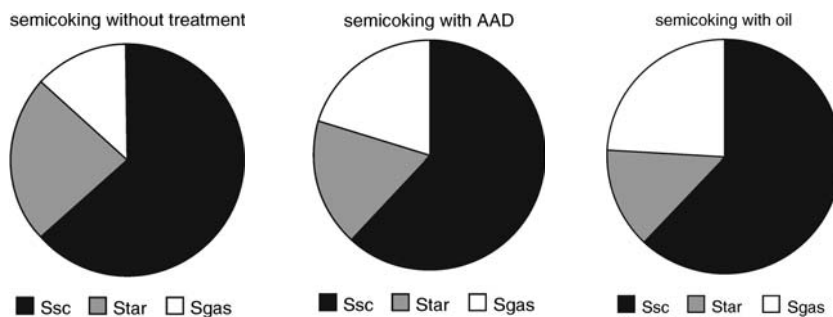


Figure 2. Distribution of sulphur in the semicoking products of low-reduced coals: semi-coke (Ssc), tar (Star) and gas (Sgas).

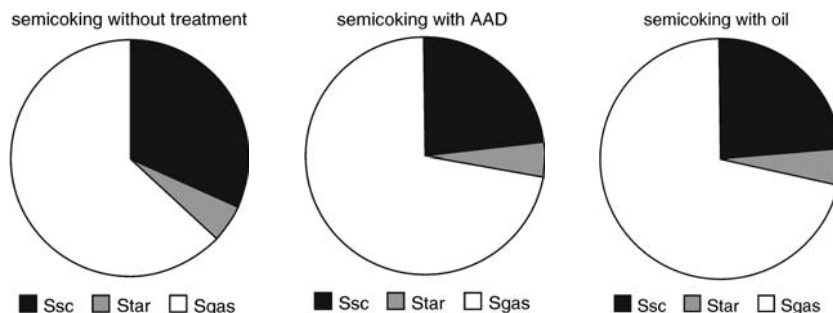


Figure 3. Distribution of sulphur in the semicoking products of reduced coals: semi-coke (Ssc), tar (Star) and gas (Sgas).

Table 6. X-Ray analyses for the initial coals and semi-cokes

No.	Type	Treatment	T [°C]	L_c	L_a	L_a/L_c	d_{002}	h/l	I_{cr}
1	LRC	–	20	1.27	1.54	1.05	0.356	1.42	0.79
		–	520	1.45	2.03	1.40	0.356	2.32	1.59
		AAD	520	1.70	2.37	1.39	0.356	2.83	1.48
		oil	520	1.63	2.58	1.58	0.356	2.44	1.13
2	LRC	–	20	1.16	1.99	1.72	0.356	1.46	0.82
		–	520	1.57	2.50	1.59	0.356	3.46	1.77
1'	RC	–	20	1.31	1.48	1.25	0.356	0.59	0.69
		–	520	1.36	2.65	1.95	0.356	1.43	1.79
		AAD	520	1.36	2.73	2.01	0.356	1.67	1.25
		oil	520	1.57	2.36	1.50	0.356	1.89	1.23
2'	RC	–	20	1.20	1.71	1.43	0.356	0.68	0.42
		–	520	1.31	2.92	2.23	0.356	1.97	1.85

ing pyrolysis is higher for reduced coals, and increases in the presence of the chemical reagents.

Figs 2 and 3 show the distribution of sulphur in the products of thermal destruction in coals of various genetic types by reductivity, and the influence of chemical pre-treatment on this process.

As shown in Fig. 2, during the semi-coking of low-reduced coals without treatment most of the sulphur remains in the semi-coke (62%), while up to 23% of it passes to the tar, and the rest goes into the gas. Chemical pre-treatment results in the desulphurisation of the solid products, including the tar, and an increase of the sulphur content (as H_2S) in the semi-coking gas.

The distribution of sulphur between the products of thermal destruction is different in the semi-coking of reduced

coals (Fig. 3). As much as 32% of the sulphur remains in the solid products, while up to 63% transforms into semi-coke gas and a negligible part transforms into tar. The introduction of the radical polymerization initiator and absorber oil results in the desulphurization of the semi-coke. Thus, the sulphur contents in the semi-coke and tar decrease by 8% and 1% respectively, while its content in the semi-coking gas increases up to 72% (Turchanina et al. 2003b).

Chemical pre-treatment has a considerable influence on coal reactivity, yield, and composition of semi-coking products. It changes the sulphur distribution and structural parameters of the solid products. X-Ray analyses have shown that under the action of additives the stack sizes and degree of order (h/l) increase: for low-reduced coals by 1.6–2.4 times, and for reduced coals by 2.4–2.9 times (Table 6). The semi-coking of reduced coals in the presence of AAD results in a 1.8–2.0 fold expansion of the lattices (L_a) and in a 2.3–4.4 fold increase in the proportion of the “crystalline” phase (which indicates the degree of network lacing, and facilitates desulphurization and the cross-linking processes in the coal carbonization products (Fig. 4).

Following the chemical pre-treatment of the coals, changes in the supermolecular organization parameters are observed in the semi-coke. As a consequence we observe an increase of “crystallite” (L_c) and of the h/l parameter by 3.2 times for reduced coals and by 1.7 times for low-reduced coals. This confirms the influence of chemical reagents in the solid products and the formation of strong fritted semi-cokes from high-sulphur coals (RC).

Conclusions

Low-rank bituminous reduced and low-reduced coal vary in composition and structure. These variations cause them to behave differently during thermal destruction. These differences are as follows:

1. During the process of semi-coking reduced coals create strong fritted semi-cokes, while the low-reduced coals create powder-like semi-cokes.
2. Thermal destruction of reduced coals results in a higher yield of semi-coking gas and tar. The same treatment of low-reduced coals results in a higher yield of semi-coke.

3. Chemical pre-treatment by the radical polymerization initiator and absorber oil increases the semi-coke yield by 7–9 %, and decreases the sulphur contents 1.1–2.5 times for low-reduced coals and 1.7–3.9 times for reduced coals.
4. During semi-coking most of the sulphur of reduced coals is transformed into semi-coking gas, while in low-reduced coals it is transformed into semi-coke and tar.

The proposed method of chemical pre-treatment allows the redistribution of sulphur between liquid, solid, and gaseous products. This pre-treatment provides significant desulphurization of the semi-coke received from reduced coals, and the desulphurization of tar in the semi-coking of the low-reduced coals.

Reduced coals may be applied as an additive to a coking blend, as they do have coking ability. During thermal destruction, most of the coal's sulphur transforms into the hydrogen sulphide of the semi-coking gas. This process can be rectified by chemical pre-treatment. However, it is necessary to control the composition of the gases so as not to worsen environmental conditions.

References

- Boudou J. P., Bimer J., Salbut P. D., Cagniant D. and Gruber R. (1994): Effect of selective chemical modification of coal on tar and gas formation during pyrolysis. *Fuel* 73, 6, 907–917.
- Butuzova L. F., Isajeva L. N., Saranchuk V. I. (1990): Transformations of the various forms of oxygen at pyrolysis of brown coal. *Khimiya tvjordogo topliva* 1, 9–15.
- Butuzova L., Marinov S., Matsenko G., Skirtochenko S., Turchanina O., Isaeva L., Krzton A. (2002): Relation between the petrographic and chemical properties of low-reduced and reduced coals of Donetz Basin. *Polish Geological Institute Special Papers* 7, 45–49.
- Butuzova L., Turchanina O., Isajeva L., Matcenko G. (2001): Effect of the coal genetic type on the pyrolysis products composition and structure. *Proc. 9th Coal Geology Conf.*, 4.

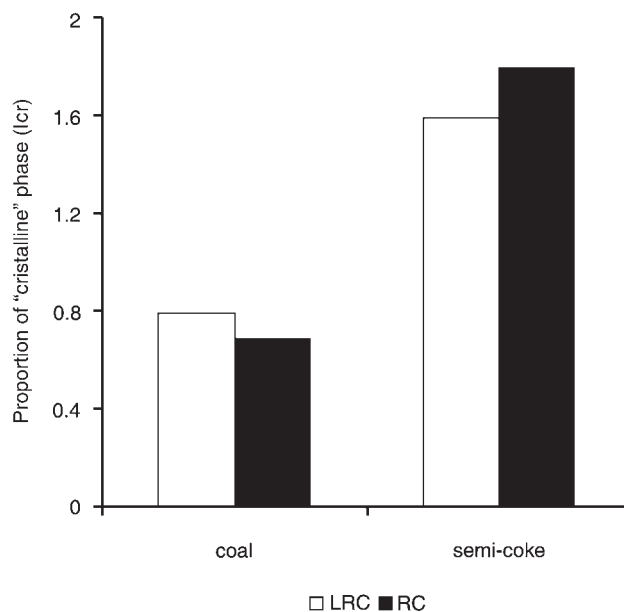


Figure 4. The proportion of the "crystalline" phase for coals of different genetic type by reductivity, and the products of their thermal destruction.

- Gluschenko I. M. (1968): *The thermal analysis solid fuels*. Moscow.
- Kuznetsov P. N., Bimer J., Salbut P. D., Sukhova G. I., Korniyets X. D., Djega-Mariadassou G., Brodzki D., Sayag C., Gruber R. (1994): Chemical alteration of coals and their reactivity with tetralin and methanol under liquefaction. *Fuel* 73, 7, 901–906.
- Pankratov G. P. (1995): *The collection of tasks on heattechnics*. Vyshaya shkola, Moscow.
- Turchanina O. N., Butusova L. F., Isajeva L. N., Bechtel A. (2003b): Peculiarity of structure of the sulphur coals. *Vopr. khimii khimichnoy technologii* 3, 147–150.
- Turchanina O. N., Butusova L. F., Safin V. A., Butuzov G. N. (2003a): Ecological problems of processing of the sulphur coals. *Vopr. khimii khimichnoy technologii*, 2, 139–142.
- Verheyen V., Rathbone R., Jagtoyen M., Derbyshire F. (1995): Activated extrudates by oxidation and KOH activation of bituminous coal. *Carbon* 33, 6, 763–772.