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INCREASE OF EFFICIENCY OF DESULFURIZATION OF COALS OF THE DIFFERENT GENETIC TYPE BY REDUCTIVITY

Rational usage of coals with high content of sulfur is very important problem for Donetsk basin, because near 70 % of coal stock contains more than 3 % of sulfur. Content of sulfur is important criteria of fuel quality that is connected with genetic type of coals by reductivity.

Three pairs of Donetsk low-rank bituminous coals of different genetic type (reduced coal-RC and low-reduced coal-LRC) were studied in this work. A comparative study of thermal destruction process of RC and LRC coals and distribution of sulfur in the semi-coking products has been carried out.

Introduction

As well known, a high content of sulfur in coals is an effect of the geological history of coal layer formation and one of the most important criterions of their use as a fuel. The content of sulfur in coals is causing a serious environmental and technological problem during their utilization. This problem is very actual for Donetsk Basin because 734 mined seams out of the total of 1009 (73 %) is comprised of coals with sulfur content ~2 % (Fig. 1).

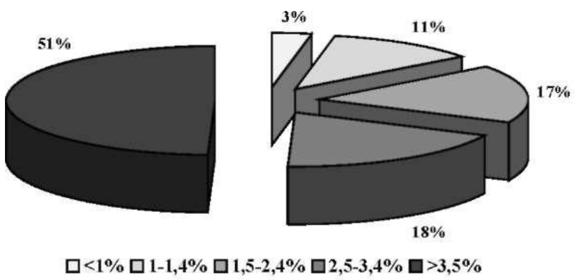

Fig. 1. Distribution of coals of Donetsk basin by content of sulfur

The problem of searching of the ways of coals desulfurization stands before scientists. In order of effectively manage the obtaining of thermal destruction products of coals (i.e. semi-coke, coke [1], adsorbent [2], soluble coal products [3], and also tar and gas [4]) and simultaneously utilize coal wastes, chemical pretreatment of coals as a first stage of their processing is widely used now. Treating coals by various chemicals and changing conditions of the appropriate reactions, it is possible to influence the character of thermochemical transformations of coals and consequently the technological process operation. However, the theoretical aspects of coal modification as well as the chemical side of thermal destruction process are investigated insufficiently to predict concrete ways of coal pretreatment. Developments of pretreatment methods for high-sulfur low rank coals are especially desirable for reduction of the sulfur content in solid products.

The aim of this study was to investigate the influence of coal genetic type and coal pretreatment on the yield and composition of semi-coking products and sulfur distribution between different components.

Experimental

Experiments were carried out on the low rank bituminous coals (~76-79 % C^{daf}) of reduced (RC) and low-reduced (LRC) types of Donetsk basin. The total organic carbon content (C^{d}_{org}, wt % of rock) was measured on a Leco carbon analyzer. The petrographic, proximate and ultimate analysis of the samples, including the total (S^t), organic (S^o), pyrite (S^p) and sulfates (S^s) sulfur were carried out using standard procedures. Chemical treatment of coals carried out directly before the thermal destruction by introduction of 1-% solutions of the radical polymerization initiator (acrylic acid dinitrile $C_8H_{12}N_4$ - AAD) and products of coal-tar distillation (absorber oil). The thermal behavior of coals was studied by means of classical Fisher method (heating up 520 °C with speed 7 °C/min). The composition of the semi-coking gas was investigated by means of gas analyzer VTI.

Results and discussion

Characteristics of the coals are summarized in Table 1, 2. As it can be seen from Table 1, investigated coals are petrographically homogeneous, since the content of the vitrinite reaches 80-89 %. Samples of reduced coals (RC) are distinguished by lower value of vitrinite reflectance ($R^{0,r}$), higher content of inertinite and lithotype with finely crystalline pyrite.

Proximate and ultimate analyses showed distinction in the structure of the coals by different genetic type (Table 2): samples of reduced coals (RC) are distinguished from low-reduced coals corresponded to the same degree of coalification by higher H/C ratio and yields of volatile matter and by higher S_o^d, S_p^d and total sulfur contents. Organic sulfur S^d_o for studied coals is the main form of sulfur [5].

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

№	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_1	*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	*RC*	0,52	80	9	11	7	63

Table 2. **Characteristics of initial coals, wt. %**

№	Type	W^a	A^d	V^{daf}	C^{daf}	H^{daf}	$(O+S+N)^{daf}$	S^d_t	S^d_s	S^d_p	S^d_o	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 coals, % ^{daf}**

№	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	–	–	–	–
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	–	–	–	–

The systematic research of processes semi-coking of low-rank bituminous coals of different genetic types by reductivity was carried out without or in the presence of chemical reagent (Table 3). The way of chemical pretreatment was chosen proceeding from results of research of structural-chemical transformations of coal under thermodestruction [6]. This process consists of competing reactions: destruction and synthesis, which are based on the freely radical mechanism. As the radical polymerization initiator was used acrylic acid dinitrile (AAD) to affect the run of radical reactions. The choice of second reagent was based on representation that coking ability of coals is connected to their ability to form liquid products of thermal decomposition, which are not evolve enough during thermodestruction of low-rank and not conglomerated coals. In this connection absorber oil (products distillation of coal tar) was used for pretreatment of coals.

Semi-coking of reduced coals leads to a considerable increase in the yield of liquid products, volatile yield comparing with low-reduced coals. Coal pretreatment results in increase of the semi-coke yield and changes of liquid/gaseous products ratio. This process is especially pronounced for semi-coking of pretreated low-reduced coals: increase of the yield of tar and semi-coke, decrease of the yield of semi-coking gas are observed [7]. Semi-coking of low-rank coals in the presence of chemical reagent allows assuming that it is possible to manage an yield of valuable products.

The characteristics of initial coals and semi-cokes obtained are summarized in the Table 4. As can be seen from this table, the decrease in yields of volatile matter (V^{daf}) and total sulfur content for semi-cokes from reduced coals are higher than for semi-cokes from low-reduced coals. LRC results in powder-like semi-cokes when RC results in strong enough fritted semi-cokes [8].

Diagram of distribution of the forms of sulfur in solid products by pyrolysis (Fig. 2) showed effect of desulfurization of semi-cokes. Content of total (S^d_t), organic (S^d_o) and pyrite (S^d_p) sulfur decreases in the greater extent for reduced coals. This effect becomes more evident after chemical pretreatment of coals, peculiarly in presence of the absorber oil. This is a positive moment of thermal destruction of coals with high content of sulfur.

Table 4. **The characteristic of initial coals and semi-cokes, wt. %**

№	Coal, semi-coke	Type	A^d	V^{daf}	S^d_t	C^{daf}	H^{daf}	Characteristic of semi-coke
1	coal	*LRC*	2,42	35,6	2,17	79,30	4,94	
	semi-coke		3,40	13,8	1,40	87,81	3,61	powder-like
2	coal	*LRC*	1,60	37,3	1,05	78,40	4,95	
	semi-coke		2,86	13,0	1,03	88,83	3,19	powder-like
3	coal	*LRC*	5,30	37,2	1,04	79,30	5,07	
	semi-coke		13,4	18,9	1,00	85,01	3,18	powder-like
1'	coal	*RC*	9,95	41,8	2,87	77,90	5,30	
	semi-coke		12,6	12,9	2,40	86,78	3,67	fritted
2'	coal	RC	4,64	46,2	5,85	76,10	5,43	
	semi-coke		7,30	12,6	2,90	85,28	3,36	fritted
3'	coal	*RC*	8,60	43,0	5,60	76,10	5,22	
	semi-coke		9,10	15,0	1,40	87,71	3,21	fritted

Table 5. **Composition and heat of combustion of semi-coking gas, ml/g** ^{daf}

№	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

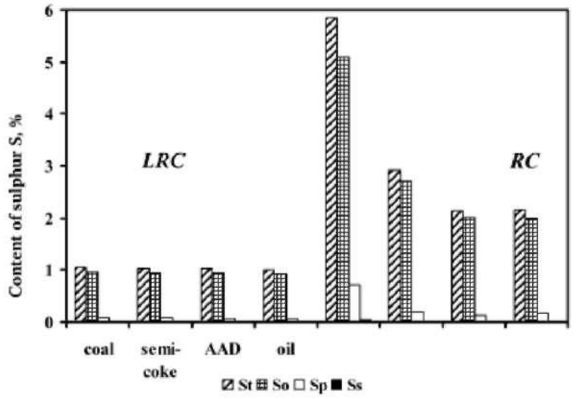

Fig. 2. Distribution of sulfur in LRC and RC coals and in the products of thermochemical destruction

Table 5 presents comparative data on composition of gaseous products obtained at semi-coking of the coals of various genetic types by reductivity before and after chemical pretreatment. The basic component of semi-coking gas is methane (CH_4), its content reaches 56 % for LRC coals and 38 % for RC coals. The gas of reduced coals differs by higher contents of hydrogen (H_2), hydrogen sulfide (H_2S) and carbon dioxide (CO_2) in comparison with the composition of gas of the low-reduced coals.

Heat of combustion of semi-coking gas (kJ/m^3) is calculated under the following formulae [9]:

$$Q = 108 \cdot H_2 + 126 \cdot CO + 234 \cdot H_2S + 358 \cdot CH_4 + 712 \cdot C_mH_n,$$

where: 108, 126, 234, 358, 712 - coefficients are appropriate heats of combustion of components of gas; H_2, CO, H_2S, CH_4, C_mH_n - vol. % of components in gas mixture.

Heat of combustion of semi-coking gas is higher for low-reduced coals that are connected to the large methane content. Chemical pretreatment of coals by the radical polymerization initiator and absorber oil significantly decreases the hydrogen, methane, and carbon oxide contents of semi-coking gas. This effect is expressed most brightly after adding AAD. These changes testify the realization of processes of synthesis in organic mass of coal and, as a consequence, bring to increase of semi-coke yield. The hydrogen sulfide evolving during pyrolysis is higher for reduced coals and grows at the presence of the chemical reagents.

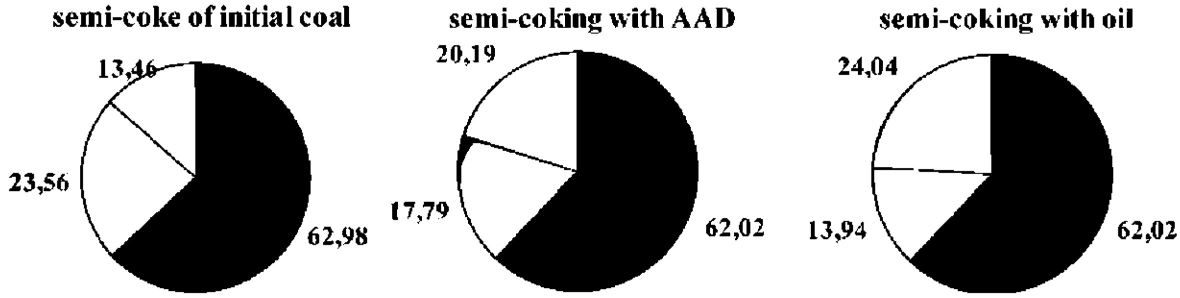

Fig. 3. Distribution of sulfur in the semi-coking products of low-reduced coals: semi-coke (black color), tar (gray color) and gas (white color)

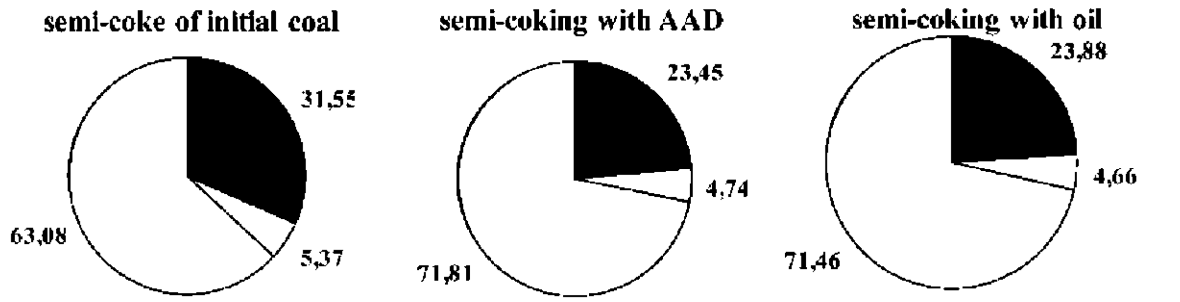

Fig. 4. Distribution of sulfur in the semi-coking products of reduced coals: semi-coke (black color), tar (gray color) and gas (white color)

Table 6. **X-Ray result for initial coals and semi-coke**

№	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

Fig. 3, 4 show distribution of sulfur in the products of thermal destruction of the coals of various genetic types by reductivity and influence of chemical pretreatment on this process. As showed at Fig. 3, during the semi-coking of low-reduced coals without treatment the basic part of sulfur remains in semi-coke (63 %), up to 23,5 % of sulfur passes in tar, and other part - in gas. The chemical pretreatment results in desulfurization of the solid products, tar and increase of the sulfur contents (as H^2S) in semi-coking gas.

At the semi-coking of reduced coals other picture of distribution of sulfur between products thermal destruction is observed (Fig. 4). Up to 32 % of sulfur remains in the solid products, up to 63 % of sulfur transform into semi-coke gas and only insignificant part of sulfur transforms in tar. The introduction in system of the radical polymerization initiator and absorber oil results in desulfurization of the semi-coke. Thus, the content of sulfur in semi-coke and tar decreases on 8 % and 1 % accordingly, and in semi-coking gas it is increased up to 72 % [10].

Chemical pretreatment has a considerable influence on the coal reactivity, yield and composition of semi-coking products. It results in changing of the sulfur distribution and structural parameters of solid products. X-Ray characteristics have shown that under the action of additives the stack sizes and degree of order (h/l) increases: for low-reduced coals in 1,6-2,4 times, and for reduced coals - in 2,4-2,9 times (Table 6). Semi-coking of reduced coals in the presence of AAD results in a 1,8-2,0 fold acceleration of the lattices extent (L^a) and in a 2,3-4,4 fold - the proportion of «crystalline» phase which indicates the connection lacing, improvement of the cross-linking processes in the coal carbonization products and desulfurization effect.

After the chemical pretreatment of the coals changes in supermolecular organization parameters are observed for the semi-coke. As a consequence we observe an increase of heights of «crystallite» (L^c) and of parameter h/l in 3.2 times for reduced coals and in 1.7 times for low-reduced coals. This confirms influence of chemical reagents on sewing process in the solid products and formation of strong fritted semi-cokes from high-sulfur coals (RC).

Conclusions

Thus, low-rank bituminous reduced and low-reduced coal are various by composition and structure, that determine their different behaviour during thermal destruction. These differences are following:

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

2) The chemical pre-treatment by the radical polymerization initiator and absorber oil lead to increase of yield of the semi-coke on 7-9 % and to decrease of the contents of sulfur in it in 1.1-2.5 times for low-reduced coals and in 1.7-3.9 times for reduced coals.

3) Under the semi-coking the most part of sulfur of reduced coals transform into semi-coking gas, and in the case low-reduced coals - into semi-coke and tar.

The method of the chemical pre-treatment proposed allows to manage the process of redistribution of sulfur between liquid, solid and gaseous products. This pre-treatment provides significant desulfurization of the semi-coke, received from reduced coals, and desulfurization of tar under the semi-coking of the low-reduced coals. Reduced coals may be applied as the additive to coking blend, because they have coking ability. Under the thermal destruction the most part of sulfur of the coal transforms in to hydrogen sulfide of semi-coking gas. The run of this process can be corrected by chemical pre-treatment. However, it is necessary to control the composition of gases in order to not worsen a condition of an environment.

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ПІДВИЩЕННЯ ЕФЕКТИВНОСТІ ЗНЕСІРЧУВАННЯ ВУГІЛЛЯ РІЗНИХ ГЕНЕТИЧНИХ ТИПІВ ЗА ВІДНОВЛЕНІСТЮ

Раціональне використання вугілля з високим умістом сірки є дуже важливою проблемою для Донецького басейну, оскільки понад 70 % вугільних пластів містять понад 3 % сірки. Вміст сірки є важливим критерієм оцінювання якості вугілля, що пов'язаний з генетичним типом вугілля за відновленістю.

У роботі було досліджено три пари низькометаморфізованого кам'яного вугілля Донецького басейну різних генетичних типів (відновлене вугілля RC та низьковідновлене вугілля LRC). Було проведено порівняльне дослідження процесів термічної деструкції та розподіл сірки у продуктах напівкоксування цього вугілля.