RESEARCH OF MECHANOCHEMICAL PROCESSING INFLUENCE ON PROCESS OF COAL HYDROGENATION

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The coal mechanochemical processing influence on an liquid products exit in the process of coal catalytical hydrogenation is investigated. Optimum time of coal dispergating is educed. Hydrocarbonic composition of coal hydrogenation products investigated by the chromatography method and positive influence of mechanochemical activation on the process of coal hydrogenation was shown. It is shown by the EPR method that as a result of mechanical processing the coal free-radical conditions (FRC) concentration is increasing as the function of coal activation time is observed. The decrease in FRC concentration is observed in the coal activated during 60 minutes. It testifies that there is a recombination of formed free radicals at more lasting processing of coal. The increase in concentration of trivalent iron is observed at mechanical activation of coal. Apparently, the part of iron which is in a bivalent condition passes in a trivalent condition as a result of mechanical activation. Signal intensity from ions of trivalent iron grows so far as increase in time of comminuting.

Keywords: coal, catalytical hydrogenation, mechanochemical activation

Mechanochemical activation of substances takes place in processes of intense dispersion of a processed material. At the same time both its dispersion and accumulation of activation energy is observed. Physical-chemical characteristics of a coal substance as a whole takes place along with an increase in the specific surface under mechanochemical activation of the substance. The process of mechanochemical reaction of coal activation can be considered as a breaking that leads to an increase in the specific surface due to decrease in geometric size of fractions and opening of pores that were unavailable before. It is also important to consider that during the mechanic impact over coal its activation takes place and is followed by a significant structural alterations in an organic structure of coal [1–2].

The first results of the impact of mechanochemical processing over the output of fluids during the process of coal hydrogenation were received in the work [3–4]. Hydrogenation of coal took place under optimal conditions that were established in the work [5]. Coal of the minefield «Kiyakty» with the following charcteristics (%, mass): W^a – 9,5, A^a – 11,1, V^{daf} – 41,2, C^{daf} – 74,3, H^{daf} – 4,7, O^{daf} – 19,3, N^{daf} – 0,8, S^{daf} – 0,9 was taken as a research object.

Table 1 provides the results of a definite output of fluids during the process of hydrogenation of initial coal and one that has been processed in the aerial environment for 15,30,60 minutes.

Table 1

Impact of the mechanic processing of coal over an output of fluids (T = 420 °C, τ = 15 minutes, m_k (boxite-094) = 0,67 g)

Processing time, min	P_{max}, MPa	Output of fluids, % of mass				Gas output, % of mass	Pulp output, % of mass	Losses, % of mass
		до 180 °C	180–250 °C	250–320 °C	∑			
Correlation coal/paste-formator 1:1								
0	2,8	11,2	8,8	18,8	38,8	15,7	41,2	4,3
15	2,6	10,9	7,9	22,8	41,6	13,6	41,7	3,4
30	2,8	13,9	9,2	21,1	44,2	18,0	34,0	3,8
60	2,8	15,2	8,9	21,6	45,7	17,7	33,1	3,5
Correlation coal/paste-formator 1:2								
0	2,8	12,8	10,3	25,8	48,9	12,0	36,5	2,6
15	3,0	13,2	13,0	25,7	51,9	13,8	30,5	3,8
30	3,1	14,2	12,4	27,9	54,5	13,9	27,7	3,9
60	3,2	13,9	10,7	28,1	52,7	13,2	30,4	3,7

As table 1 shows, the biggest output of fluids is observed under 30 minutes of coal processing. The further increase in time of dispersion does not influence the output of fluids significantly. Obviously, under a continuous mechanoactivation under such conditions a dynamic balance is established: the speed of formation of free radicals becomes comparable to speeds of their recombination due to mechanodestruction. It is testified by the study of par-

amagnet characteristics of the initial coal and one that has been dispersed with the method of electronic paramagnetic resonance (EPR).

The method of EPR was used to study free-radical conditions (FRC) in coal. Concentration of free radicals depends on the conditions of coal processing, a character of reaction system, in which breaking takes place, and also on the nature of the initial coal [6-7]. Table 2 provides the results of these surveys.

Table 2

Parameters of ERP sectors of coal before and after mechanoprocesing

Activation time, minutes	Line width, oersted	FRC concentration, N101 spin/g	g-factor
0	4,0	1,9	2,0021
15	4,1	2,3	2,0022
30	4,5	2,7	2,0018
60	4,4	2,4	2,0026

The analysis shows that, as a result of mechanic processing, increase in FRC concentration is observed depending on time of its activation. In coal that has been activated for 60 minutes a decrease in FRC concentration is observed. It testifies for the fact that recombination of the formed free radicals takes place under a more continuous processing of coal. An increase in concentration of trivalent iron is observed during the mechanoactivation of coal. Obviously, a part of iron that is in bivalent condition transfers into trivalent condition after mechanoactivation. The intensity of signals that come from ions of trivalent iron grows along with an increase in breaking time.

Thus, during the mechanoactivation of coal an increase in trivalent iron concentration is observed. Obviously, a part of iron that is in bivalent condition transfers into trivalent condition after mechanoactivation. It appears that an increase in concentration of trivalent iron, as in [8], increases the speed of hydrogenation process. It is possible that changes in structure of coal can have a positive impact upon the hydrogenation process and lead to an increase in fluids output.

To study the impact of mechanoprocessing of coal over the liquefaction degree, the processed coal was further treated with 0,4 % solution of natrium hydroxide (Table 3).

Table 3

The impact of mechanochemical processing over the output of fluids
(T = 420 °C, τ = 15 minutes, m_k (boxite-094) = 0,67 g)

Output of humic acids, % of mass	Processing time, min	Work pressure, MPa	Output of fluids, % of mass				Gas output, % of mass	Pulp output, % of mass	Losses, % of mass
			under 180 °C	180–250 °C	250–320 °C	Σ			
Correlation coal/paste-formator 1:1									
0	0	2,7	11,2	8,8	18,8	38,8	15,7	41,2	4,3
20,3	15	2,7	15,4	11,8	18,2	45,4	14,4	39,2	1.1
22,1	30	2,6	18,2	10,7	19,2	48,1	14,2	33,4	4,3
20,8	60	2,2	21,6	11,5	16,2	49,3	9,9	37,3	3,5
Correlation coal/paste-formator 1:2									
0	0	2,8	12,8	10,3	25,8	48,9	12,0	36,5	2,6
20,3	15	3,0	14,6	11,2	29,0	54,8	13,9	27,3	4,0
22,1	30	3,0	18,5	12,6	28,4	59,5	13,7	23,9	2,9
20,8	60	3,4	19,0	11,1	28,0	58,1	14,2	26,0	3,7

As table 3 shows, under the hydrogenation of coal that has been treated with alkali, output of fluids grows up to 59,5 % of mass. Here output of gas grows insignificantly, compared to the initial coal, and equals 13,9–14,2 % of mass, and the output of benzol fraction grows significantly and equals 18,5–19,0 % of mass. Output of humic acids equals 20,3–22,1 % of mass.

Destruction of coal substance structure takes place under mechanochemical process-

ing. It is shown by the IR-spectres of the initial and processed coal (Table 4). In the IR-spectres of coal that has been processed mechanically for 30 minutes absorption lines that are typical for valent oscillations of amines, carbon acids, aromatic hydrocarbons, aromatic and aril-alkile ethers, nitriles.

In coal that has been processed with alkali, intensity of absoption lines that are typical for valent oscillations of amine groups, acid diamers, aromatic and aril-alkile ethers decreases significantly in comparison to the initial coal. It can testify the destruction of the coal mass and discharge of major hydrocarbon components of humic acids. In coal that has been processed with alkali presence of acid-content and aliphatic thermally-unstable structures is registered. It can condition the increase in coal conversion during the process of its catalytic hydrogenation.

Table 4

Characteristics of IR-specres of coal that has been processed mechanically for 30 minutes (I) and coal that has been treated with a 0,4 % solution of alkali (SA) (s – strong lines, med – medium lines, w – weak lines)

Oscillation nature	Connection type	Frequency, cm'1	
		Initial coal (I)	(SA)
VoH(linked)	Acid diameter	3190–2530 (ср.)	3170–2520 (сл.)
VNH free	Amines	3420 (с.)	3450 (сл.)
VCN	Nitriles	2230 (сл.)	2260 (ср.)
VC = 0	Carbonyl acid links	1700 (с.)	1690 (сл.)
Vc-c	Arenes	1590 (ср.)	1585 (с.)
Vcoc	Complex ethers	1275 (ср.)	1220 (сл.)
8он	Spirits, phenols, acids	1370 (ср.)	1330 (с.)

Chromatographic analysis of benzol fraction of the mechanically-processed coal (Table 5) shows a decrease in content of paraffine hydrocarbons, increase in contents of aromatic hydrocarbons, in difference to the hydrocarbon structure of the initial coal. Besides, a decrease in contents of olefin hydrocarbons is observed. This data proves that a deeper destruction of coal macromolecule that influences characteristics of the coal distillate output, takes place under mechanochemical processing of coal.

Table 5

Hydrocarbon structure of benzols of hydrogenation of the initial coal and coal that has been treated mechanolchemically

Hydrocarbon structure	Content, 5 of mass	
	Initial coal	Mechanochemically treated coal
Paraffines	32,68	27,46
Iso-paraffines	24,16	23,95
Arenes	12,23	29,74
Naphthenes	11,72	11,74
Olefines	5,99	3,88
Diene	0,92	0,21
Cyclic olefines	1,02	-
Unidentified substances	11,28	3,02

Thus, preliminary mechanochemical processing provides for an increase in degree of coal conversion during the hydrogenation process. A deeper conversion is proved by an increase in output of benzol fraction.

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