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The change of disperse composition, porous structure and formation of new coal surfaces of Kiyakty deposit

The obtained experimental data show that in the process of mechanical treatment the initial structure of coals transform, macropores are completely destructed and micropore are partially destructed. The increase in activity can be caused by the growth of the external and internal surface due to formation of new pores and opening of earlier inaccessible pares and on account of the change in the physico-chemical structure of newly formed surfaces. In this connection, the porous structure of coals of different stages before and after their dispersion is considered. Analysis of differential curves of particles distribution by sizes and change of specific surface of coal samples showe that after mechanic activation the change of the disperse composition of the coal occurs one to: grinding and aggregation of the dispersed particles.
Keywords: coal, disperse particles, mechanical activation, specific surface of coal, coal porosity, aggregation of particles

Introduction

One of possible ways of increase of chemical activity of coals is their thin dispersion. In this regard coals passed mechanical activation by dispersion, with the purpose of increase of reactionary ability of raw materials, simplification of technology of preparation of coal, drawing of the catalyst and an intensification of production of liquid fuel.

At a hydrogenation of coals for obtaining of synthetic liquid products it is important to consider physical and chemical characteristics and degree of a metamorphism of coal. In this regard physical and chemical characteristics of coal of a field of "Kiyaky" for the purpose of identification of an assessment of suitability of this coal to processing in liquid products were studied by a hydrogenation method.

Differential curves of coal particles distribution after mechanical activation according to sizes and the change of specific surface of disperse samples showed the change in the disperse composition of coals with the procedure of two processes accompanying fine dispersion of coals: grinding and aggregation of particles.

It is known that substances in a fine disperse state are characterized by not quite usual properties: they become more chemically active, react with other substances violently, sometimes with explosion, they sinter better, form stronger cakes, etc. Pure physical processes of friction or grinding due to application of mechanical forces cause chemical reactions or changes of the reactivity of solid substances [1-3].

Brown coal of Kiyaktin and Shubarkol fields mined on industrial scale which is a typical representative of coals from the fields of Kazakhstani Central regions was used for the study.

Materials and methods

In this work we used a centrifugal-planetary mill working according to the principle of gravitational grinding on account of interaction of two centrifugal fields. The velocity of platform rotation makes up 700 rotations per minute and the velocity of milling vessels makes up 1200 revolutions per minute.

The parameters influencing the efficiency of grinding are the volume occupied by balls, the size of balls, the volume of the substance being milled,

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the ratio of the mass of powder to the mass balls and others. When carrying out experiments on mechanochemical treatment of raw materials, taking into account the above mentioned parameters the time of action was varied from 10 to 30 minutes. The ratio of the mass of power and milling balls (mp/b) made up 1/4; 1/7; 1/10;1/15;

The fractional composition of milled coals was determined by the method of sedimentation analysis.

Results and discussion

Any mechanical effect on coal is accompanied by its dispersion. The disperse composition of the obtained coal powders is significantly effected by the time of mechanical action. When grinding coals of Kiyakty and Shubarkul deposits (Table 1), some general regularities were revealed which were well observed by the differential curves of distribution of particles according to their sizes after mechanical treatment of coals in the mill.

Table 1 – The content (%) of particles depending on the time of milling.

Coal	depending on the time of milling	Radius of particles, mkm					
		<0,5	0,5-1	1-2	> 2	rmax	rmin
Kiyakty	5	54,1	29,2	H,1	2,6	25	1,3
	10	58,5	24	14	3,5	32	1,2
	20	66,5	22,2	8	3,3	28	1,3
Shubarkul	5	43	45,4	9	2,6	45	2,9
	10	41,5	40,5	12,5	5,5	40	2,5
	20	23	55	14,3	7,7	35	2,6
	30	23	59	11,6	6,4	34	2,5

Differential curves of distribution of particles according to their sizes (Figure1) have one maximum indicating the presence of one f the most probable fraction in the polydisperse system. At a longer period of coal treatment the maximum on the curve shifts to the side of smaller radii of particles. This indicates the fact that smaller particles predominate in the fraction most probable by mass.

At further treatment larger particles are produced and maximum on the differential curves shifts to the side of larger radii of particles. Such change in the disperse composition of coal can be explained by the procedure of two processes accompanying fine dispersion of coals: grinding and aggregation of the dispersed particles.

This observation is verified by the data on the change of the specific surface of coals when being

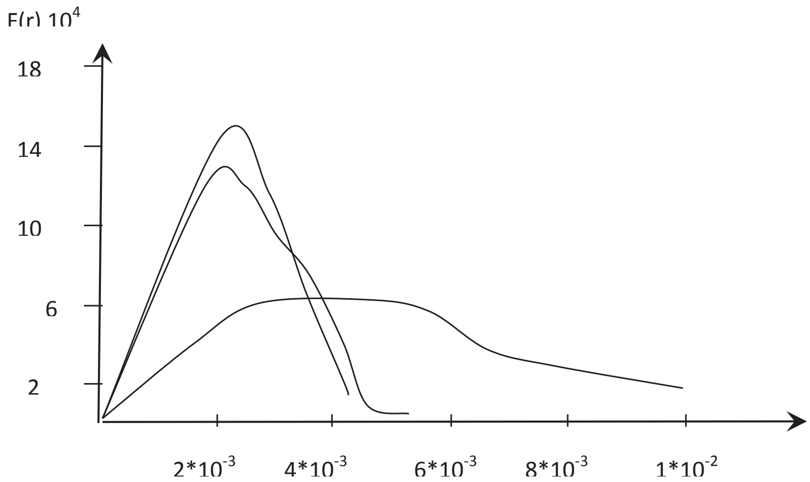

Figure1 – Differential curves of distribution of coal particles according to their sizes.

ground in the mill during mechanochemical treatment (Table 2). The specific surface of dispersed samples increase with the time of mechanical treatment of coals reaching the maximum value (the process of dispersion prevails) and then decreases (the process of aggregation prevails). Destruction of coal particles and their aggregation depending on the rank of coal develop at different periods of grinding.

Table 2 – The change of specific surface (m2/g) depending on the time of grinding for different coals.

Coal	Duration of grinding, min				
	2	3	5	10	20
Kiyakti	0,45	0,5	0,69	0,89	0,45
Shubarkul	0,75	0,8	0,85	0,77	0,68

Figure 2 presents curve 1 of the change of the external specific surface at the period of mechanical action corresponding to the change in coal porosity is shown in the same figure (curve 2).

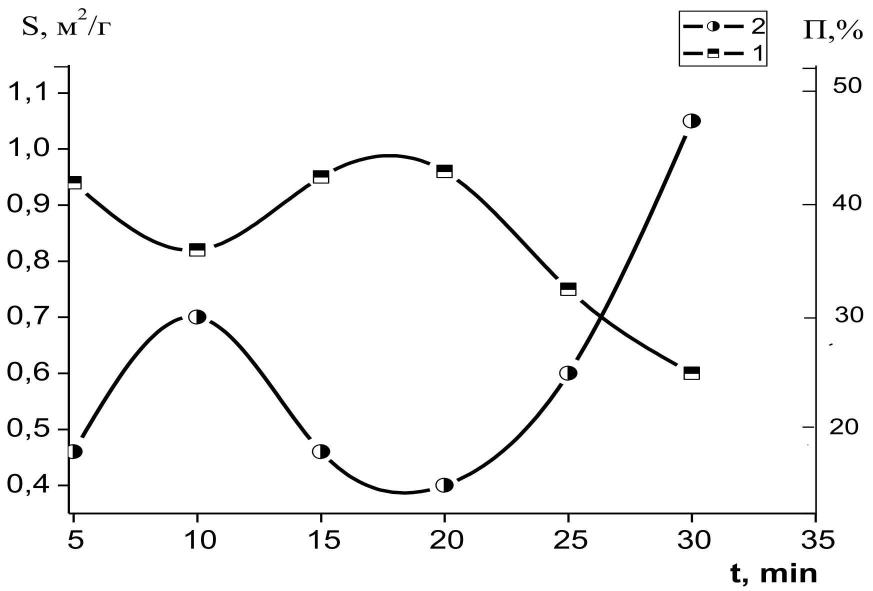

Figure 2 – The change of specific surface S of milled coals (1) and porosity of coal (2) depending on the time of treatment.

Comparison of curves 1 and 2 shows that the change of specific surface is in inverse relationship with the change in porosity of coals of different dispersion stages depending on the strength of the material.

In the process of dispersion, the activity of coals in regard to different reagents increases. The increase in activity can be caused by the growth of the external and internal surface due to formation of new pores and opening of earlier inaccessible pares and on account of the change in the physico-chemical structure of newly formed surfaces. In this connection, the porous structure of coals of different stages before and after their dispersion is considered.

Characteristics of the porous structure of coals is conditioned by the volume of micro- and transition pores, the change of bulk density, specific surface of coals before and after their dispersion.

Table 3 presents the indices of the porous structure of initial coals and after grinding them during 20 minutes. The investigation results show that volumes of micropores decrease. As a consequence, the specific surface increases also, in comparison with that of initial coal.

Table 3 – The indices of the porous structure of initial coals after grinding them during 20 minutes.

Initial coal and after dispersion during 20 min	Specific surface m2/g	porosity, %	Bulk density g/mm
Kiyakti brown			
Initial	0,5	0,45	0,8
Dispersed	0,9	0,32	1,4
Shubarkul			
Initial	0,7	0,5	0,9
Dispersed	0,8	0,4	1,1

These data are also confirmed by the data of electron microscopic pictures (Figures 3 and 4).

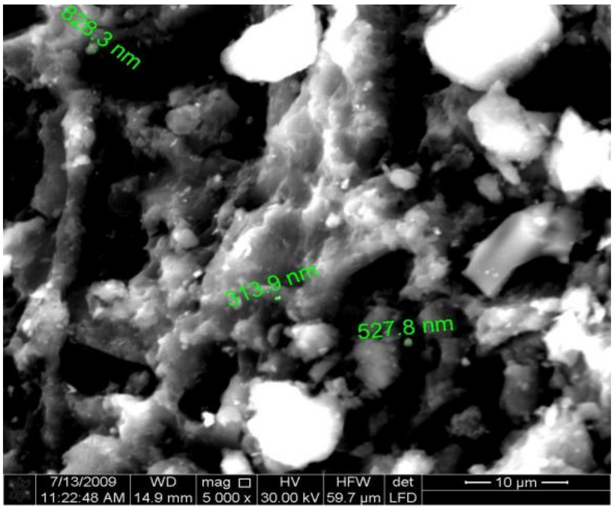

Figure 3 – Electron microscopic picture of Kiyakty deposit coal before mechanical activation.

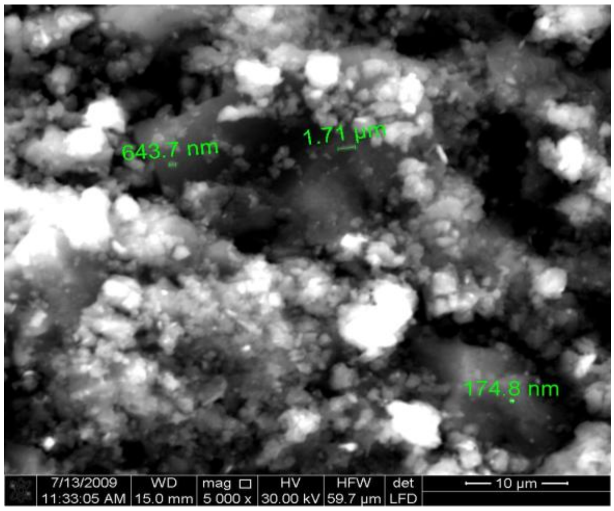

Figure 4 – Electron microscopic picture of Kiyakty deposit coal after mechanical activation.

The sample contains large separate massive particles with the size up to 4-5 µm (Figure3) as well as aggregates of different forms and sizes, minimum sizes making up 300-500 nm.

After mechanical activation (Figure4) there remain massive particles with the size of 1-2µm, however aggregates loosen and particles mainly have sizes 1000-500nm and particles with the size of 200 nm can b distinguished.

The obtained experimental data show that in the process of mechanical treatment the initial structure of coals transform, macropores are completely destructed and micropore are partially destructed. Accessibility to micropores increases, therefore the measurable volume of these pores grow due to the increase of bulk density. Alongside with transformation of the initial porous structure, there form new secondary pores which are newly formed microcracks.

After mechanical action on brown and bituminous coals in the mill sedimentation analysis showed the following character of the change in the specific surface of freshly prepared powders depending on the time of treatment (Table 4).

During the first 5-10 minutes of grinding the specific surface of coals sharply increases. At a longer period of action the growth of the specific surface of coals decreases. Such change in the specific surface can be explained by the processes of grinding and aggregation of dispersed particles.

In the process of storage of dispersed coals the specific surface decreases (Table 4). One of the reasons of this can be closing of newly formed cracks after unloading and the decrease in accessibility of pores. All this indicates the fact that in the process of mechanical action and after new structure not only forms but also "lives" [4-5].

Table 4 – The change of the specific surface of coals after mechanical treatment in the mill.

Coal	Duration of grinding, min	Effective Specific surface S0',sm2/g	
		freshly made	in some days after preparation
Kiyakty brown	0	6,6	6,6
	5	31,2	8,6
	10	42,1	10,6
	20	24,3	13
Black Shubarkul	0	1,57	1,57
	5	38,3	4,8
	10	43,7	4,5
	20	49,8	7,5
	50	47,5	6

Sedimentation analysis registers the aggregates being formed as separate large particles. The data of sedimentation analysis have shown that in the period of the highest velocity of grinding (up to 5-10min) coal is milled mainly up to the size of 0.2-1 mkm. The presence of defects in the structure of particles of micrometer sizes is mainly represented by micro and mesopores. The mechanical strength of such particles increased compared to that of initial larger ones.

Therefore, their destruction requires much power and the rate of formation of new surfaces decreases; the specific surface only grows up to some limit. The highest rate of dispersion, i.e. formation of new surfaces, is observed at the initial stage of mechanical action, the specific surface increasing by two orders. After reaching maximum the specific surface remains constant or decreases owing to aggregation of mechanically treated particles. At this stage dispersion practically discontinues and observed high activity of coals is determined by deformation of the solid substance of coal.

Conclusion

Differential curves of distribution of coal particles according to sizes after mechanical activation have one most probable fraction in the polydisperse system. At a longer period of coal treatment maximum on the curve shifts to the side of smaller radii of particles. This indicates the fact that in the most probable mass fraction smaller particles prevail. At further treatment larger particles are produced and maximum on differential curves shifts to the side of larger radii of particles.

Such change in the disperse composition of coal can be explained by the procedure of two processes accompanying fine dispersion of coals: grinding and aggregation of the dispersed particles.

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