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INFLUENCE OF MECHANICAL ACTIVATION ON ALKYLATION AND EXTRACTABILITY OF COAL

M.P. Kulikova[1ξ], Yu.D. Kaminskii[2]
[1]Tuvinian Institute for Exploration of Natural Resources, Siberian Branch of the Russian Academy of Sciences, Kyzyl, Russia
[2]Institute of the Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia

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Abstract

Results of studies of influence of mechanical activation on alkylation and extractability of coal of the Kaa-Khem deposit have been presented. Samples of coal, on being heated in a neutral-reducing environment condition on a 300-400 °C interval, undergo moderate agglomeration. On heating of coal in a neutral-reducing environment condition over 450-600 °C interval, ebullition and removal of a highly boiling coal fraction occur. Mechanical activation decreases parameters of thermal destruction of coals. In response to mechanical activation reacting power of coal increases at the cost of formation of new pores and opening of inaccessible pores. The process of coal alkylation goes intensely in the case of preliminary mechanical processing of coal. This can best be done by vibration mill. Alkylation of activated charcoal increases solubility of coal. The regularities of changes of structure and properties of coals under mechanical activation and alkylation can be used in processes of processing of solid fuels.

Introduction

Coals of Kaa-Khem and Chadan deposits (Tuva) are not only an effective energy carrier for fuel energy industry, but are considered as perspective raw material for coke-chemical and chemical industry as well. According to four classification parameters (R_0, Σ OK, V^{daf}, and y), the coals of the Ulug seam, occurred within Kyzyl-Erbek trough, can be assigned to gas, gas-rich, rich, and coke ranks, alternating in the southwestward direction. The gas coals comprise 21 % of forecast resources of the Ulug seam in this trough, gas-rich coals – 34 %, rich coals – 45 %, and coke coals – less than 1 % [1]. The coals are low-ash and low-sulphur and are characterized by a high content of volatile. At the present time the coal application is mainly energetic. Preliminary technological processing of coals is not used. Revealing of structural features, conditioned their uniqueness, is the urgent problem for solving of questions of Tuvinian coals rational use.

One of possible ways of coal modification and coal processing efficiency upgrading is mechanical activation with following alkylation. The exploration target was coals of the Kaa-Khem deposit. The alkylation increases reactivity of coals in processes of solution, hydrogenation, and etc. Alkyl residue insertion into activated charcoal promotes solubility of coal because of partial destruction of coal samples – cleavage of methylene and ethereal bonds and etc.

Experimental

The characteristics of coal are given in Table 1.

Table 1. The characteristics of coal of Kaa-Khem deposit

Technical analysis, %			Elemental analysis on organic mass, %					Coal grade
W^{α}	A^d	V^{daf}	C	H	N	O	S	
1.2	5.9	48.9	84.00	5.52	1.08	9.19	0.21	Gas

Mechanical activation of coal samples was conducted by dry method in vibration and planetary mills. After mechanical action, the coals underwent alkylation by isobutyl alcohol. The way of initiation of grinding bodies and respectively the character of breakage in vibration mills are other than in planetary mills. The body frame of the vibration mill is positioned on springs or rubber mounts and is filled by small grinding bodies. The motion of grinding bodies makes an unbalanced spindle driven by electric motor. In operation the grinding bodies and processed material come into rotation away from the spindle rotation, causing material attrition. Abrasive action is intense, so a high specific surface of material is attained. In the planetary mill, gravity field action upon grinding balls is replaced by centrifugal force. The centrifugal force caused by rotor spinning is tens times greater than the force of gravity that permits grinding bodies to be smaller without decrease of their kinetic energy. Pebbling of solid matter simultaneously with decrease of a particle size results in injection of mechanical energy into a structure of matter and formation of various defect, being of considerable importance in further transformations. This gives rise to a qualitatively new surface and increase of reactivity.

Under study there was an influence of mechanic activation on thermal destruction, alkylation and solubility of coals from Kaa-Khem deposit. Dynamics of thermal destruction of coal samples has been studies using derivatograph of the MOM-1000 type (Hungary) in a temperature interval up to 900 °C at a heating rate 10 deg/min.

ξ email: mpkulikova@mail.ru

Results and Discussion

The conducted studies revealed that low-melting and highly volatile fractions, contained in the coal composition, determined a behavior and property of material under its pyrolysis. Derivatograms of studied coals are presented in Fig. 1.

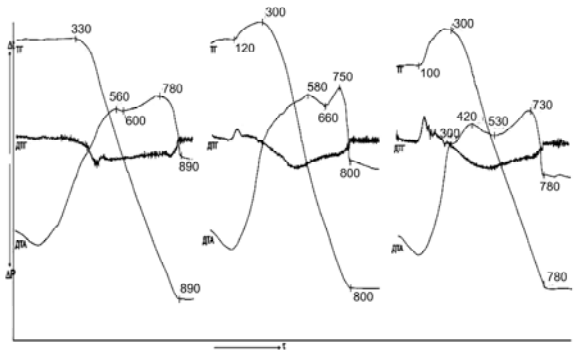

Figure 1. Derivatograms of studied coals (1 – initial coal (left), 2 – mechanically activated in vibrating mill (15 min) (middle), and 3 – mechanically activated in planetary mill (2 min)) (right)

The preliminary mechanic activation of colas of Kaa-Khem deposit causes decrease of a temperature of the beginning of coal melting to the temperature 300-310 °C. As this takes place, temperatures of subliming ("ebullition") beginning are shifted too and the step of subliming overlaps the expanded step of melting [2]. The samples of coal (initial and mechanically activated) were exposed to alkylation. Isobutyl alcohol was used as the alkylating agent and 3-% solution of H_3PO_4 was used as the catalytic agent. Alkylation time was 1, 2, and 3 hours. The studies indicate that the mass of alkylated coals increase in the raw initial coal → coal activated in the planetary mill → coal activated in vibrating mill. Hence the process of alkylation goes intensely in the case of preliminary mechanical processing of coal, and action of vibrating mill is more effective.

The coal samples (initial, mechanically activated, and alkylated) were exposed to extraction by alcohol benzene blend (1:1) in the Soxhlet process vessel during 6 hours. Firstly, the extraction may be thought of as solution of low-molecular components, located within pores of coal matter. Secondly, it can be envisioned as observed partial destruction of semipolar bonds between macromolecules of coal and insertion of solvent molecules in their place, that is, destruction of a supramolecular structure. Under reaction conditions the solvent molecules are in the gaseous phase and can penetrate into most hard-to-reach areas of porous coal matter. The solvent, having the property to transmit hydrogen atoms, promotes rapid depolymerizing of organic matter of coal. The yields of extracts, produced from initial, activated, and modified (mechanic activation + alkylation) coals, are different. The yield of coal extracts from modified coal (activation in vibrating mill + alkylation) is higher than in other cases. The results of studies have been presented in Table 2.

In response to alkylation of hard coal by isobutyl alcohol in the presence of phosphoric acid, the coal solubility increases not only

Table 2. Yield of coal extracts, %

Solubility (alcohol benzene blend)	
Initial coal	5,1
Activated coal (vibrating mill)	6,2
Activated coal (planetary mill)	5,7
Activated coal (vibrating mill + alkylation)	14,2
Activated coal (planetary mill + alkylation)	8

at the cost of their depolymerizing, but introduction of alkyl residue into the aromatic structure of coal. The presence of alkyl residue increases a distance between aromatic structures of adjacent molecules and decreases attractive forces, so coal produces products of less molecular weight, more soluble.

The coal samples (initial, mechanically activated, and alkylated) have been tested for contents of oxygen-containing groups, carboxyl groups, phenolic hydroxyls, and carbonyl groups. It is necessary to take into account the content and forms of bonds of oxygen at determining of reacting power of coal structure fragments in technological processes (pyrolysis, hydrogenation, gasification, and etc.). The qualitative analysis of functional groups in coal is rather difficult because the one part of oxygen is absolutely unreactive and the other part becomes active only after hydrolysis of coals. Data on distribution of oxygen atoms throughout functional groups in coal samples are presented in Table 3.

Table 3 Distribution of oxygen atoms by functional groups

Solubility (alcohol benzene blend)			
	COOH	C=O	OH
Initial coal	1,9	1	2,3
Activated coal (vibrating mill)	1,2	0,5	2,2
Activated coal (planetary mill)	1,7	0,4	1,7
Activated coal (vibrating mill + alkylation)	н.о	н.о	н.о
Activated coal (planetary mill + alkylation)	н.о	н.о	н.о

On exposure to mechanic action, chemical structure and a content of oxygen-containing functional groups in coal changed. On mechanical destruction of coal, C-C and C-O bonds disrupt and free radicals arise. Further free radicals take part in decomposition, displacement, additive, and disproportionate reactions, and etc. On mechanic exposure upon coal, the oxygen removes from coal as CO_2 and H_2O. Escape of CO_2 is due to decomposition of carboxyl group because of decarboxylation and dehydratation reactions. The conducted investigations shown that a content of oxygen-containing groups in coal decreased on mechanic activation of coal. After alkylation by isobutyl alcohol of mechanically activated coal in the presence of phosphoric acid, oxygen-containing groups were missed in coal samples.

Conclusions

From results obtained it may be deduced the followings.

1. Mechanic activation changes a composition and properties of coals. In response to mechanical activation reacting power of coal increases at the cost of formation of new pores and opening of inaccessible pores and arising of various defects in the coal structure. The preliminary mechanical activation of coals leads to decrease of a temperature of coal melting beginning to the temperatures 300-310 °C. Temperatures of the beginning of subliming ("ebullition") are shifted too and the step of subliming imposes upon the extended step of melting.

2. The process of coal alkylation by isobutyl alcohol in the presence of H_3PO_4 goes intensely in the case of preliminary mechanical processing of coal. The mechanic activation is more effective.

3. Alkylation of mechanically activated charcoal increases solubility of coal. Yield of coal extracts from modified (activation in vibrating mill + alkylation) coal is higher than from activated and initial coals. This is conditioned by the fact that coal solubility is mostly influenced by specific surface of material.

4. The regularities of changes in a structure and properties of coals under integrated impact of physical and chemical methods of activation can be used in processing of hard fuels.

References

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