STRUCTURAL AND CHEMICAL TRANSFORMATION OF LOW COAL DURING ACTIVATED CARBONIZATION PROCESS

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INTRODUCTION

It was earlier show [1] that additions of inorganic substances at pyrolysis of fuel combustible are able to increase the conversion of its organic mass (OM). But the yeild and composition of pyrolysis products being forming depends on specific feature of composition and structure of OM of the coal under study and process conditions[2]. The goal of the report was to estimate the inorganic substances influence on initial structure of coal, to show the transformation of mineral matter (MM) of coal and to exime the latter behaviour during pyrolysis.

EXPERIMENTAL

The characteristics of studies coals is presence at Tabl.1. The activation of a coals was carried out accoding to the method as follows. The sample of an coals (a fraction less than 0,5 mm) was treated by 1 M of KOH and HCL solutionn in weight ratio of 2:1 (solution-coal). The mixture obtained was left for 12 hours to react at 20 °C with a successive coal and coal having activators was carried out in autoclave , inert atmosphere, within temperature region of 400-700 °C. The heating rate was 10 °C/ min, the time of experimental was 1 hour. X-ray diffraction of initial a coal and coal with activators, as well as carbonized solid residues (CSR) of pyrolysis were performed on the diffractometer "DRON-1".

RESULTS AND DISCUSSION

Data of Tabl.2 illustrate the influence of activators on the restructurization of parent coal "Turow'. It is seen that (Tabl.2) alresdy on the coal preparation stage to be pyrolized the activators (KOH, HCL) have a considerable effect upon a brown coal structure. Thus a KOH addition can descrease the degree of interlayer ordering (h/l_{002}) of the initial coal cristallite in 2,8 times and HCL addition - 1,3 times, that testifies a different effect of activator on the coal structure. The change of other parameters (Lc, La, n) of the coal structure also takes place.

By X-ray diffraction it was established (on the coal "Turow') the MM transformation in the impregnation process of brown coal. The reflex (d_j) koalinite $Al_4[SiO_{10}](OH)_8$ were found (d=2,56; 3,56; 4,13 A°) hexahidrate $MgSO_4\ 6H_2O$ (d=2,49; 4,04; 5,50 A°) and glauberite $N_2SO_4\ CaSO_4$ (d=3,18; 6,00 A°). Piryte FeS_2 presence was eximined on reflex with d= 1,63; 2,12; 3,18 A°, halite NaCL with d=1,97; 4,25 A°.

At KOH impregnation in coal total content of MM is decreased all reflexare wider, this show degradation of mineral crystal phase. The reflex of $MgSO_4\ 6H_2O$, kaolinite and NaCL are absent. At HCL impregnation kaolinite, hexahidrate degrodated too, but formation of new mineral phases are observed. So ultramarine $Na_4Al_6Si_8O_{24}S_4$ (d=3,70 A°), pirrotine Fe_{1-x} (d=2,98 A°) with d=2,76; 3,10;,3,86 A°, concerning elemental sulfur, are found.

The results of activators effect upon the yeild of liquid products of brown coal pyrolysis are shown in Fig.1. It is seen from the Fig.1 that structural changes in coal at the stage of activation predetermine at considerable extent its behaviour during pyrolysis. The interaction between the volue of h/l_{002} parameter and the yeild of liquid products at 500 °C has been detected. It has been established that decrease of aromatic part of COM ordering allous to increase the yeild of pyrolysis liquid products. The highest yeild of liquid products takes place in coal activated by KOH that consist of 33 % of total COM conversion.

To evaluate changes taking place in the brown coal structure under effect of activators, the structure of CSR within 400-700 °C was studied. Data on changing the value of h/l_{002} parameter of initial coal and with KOH and HCL additions with pyrolysis temperature are given at Fig.2 It is seen (Fig.2) that at brown coal pyrolysis the change of its structural organization has a stage character. Temperature being increased up to 400 °C the value of h/l_{002} parameter for initial brown coal and coal with activators tends to be decreased that indicateds desordering of coal structure and simultaneous increase a decomposition of COM at pyrolysis. The lower value of h/l_{002} parameter - 0,56 for a coal activated by KOH could be considered as the most KOH effect upon COM decomposition as well as liquid pyrolysis products yeild (Fig.1).

The h/l_{002} value for all coal samples is maximum that consists for initial coal, having KOH and HCL 2,68; 2,53; 3,70, respectivety within 400-500 °C. It was suggested that within this temperature region structuring reactions are being intensively started together with a COM decomposition and maximum pyrolysis liquid products yeild. It is seen that the greatest package structuring rate (Lc) is typical for a coal activated by HCL and the h/l_{002} value consist 3,70 nm.Further in-

creasing of pyrolysis temperature up to 700 °C does not lead to the increasing of hll_{002} value but vice versa even to some its decrease down to 2,08; 2,04; 3,09 nm that suggests the completion of cristallite package (Lc) formation by vertical.

CONCLUSION

It has been shown that KOH and HCL change coal structure already at the activation stage. The interaction between the yeild of pyrolysis liquid products at 500 °C and h/l_{002} parameter of initial coal and coal with activators has been detected.

It has been established that at pyrolysis the change of reorganization of coal structure has a stage character. The interaction between the change of structural parameters h/l_{002} of a brown coal in temperature region 400 - 700 °C and the direction of activated pyrolysis has been found.

REFFERENCES

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[2] Shevkoplyas VN., Saranchuk VI. The generalities for activated pyrolysis of different rank coals. Extended Absrracts, Eurucarbon'98, on Science and Technology of Carbon. Strasbourg (France): 1998; 1, 193-194.

Table1 Characteristics of studied coals

Coal	C^{daf}	H/C	O+N	V^{daf}	R_o	d_{002}	Lc	La	h/l_{002}
Brown Ukraine	65,4	1,12	28,5	63,2	0,35	0,370	2,03	5,0	0,80
Brown Turow Poland	71,0	0,81	20,9	59,1	0,38	0,387	1,42	2,3	0,97
Salty Ukraine	74,9	0,79	19,2	45,2	0,45	0,370	1,98	4,7	0,89

Table 2. The effect of activators on the change of X-ray parameters of a initial brown coal

Activator	d_{002} nm	d_{yl} nm	Lc nm	La nm	Lc/La	h/l_{002} nm	h/l_{yl} nm	n
initial	0,387	0,520	1,42	2,3	0,61	0,97	1,00	4,7
KOH	0,387	0,520	0,94	3,0	0,31	0,35	0,24	3,4
HCL	0,387	0,520	1,35	2,9	0,47	0,80	0,74	4,5

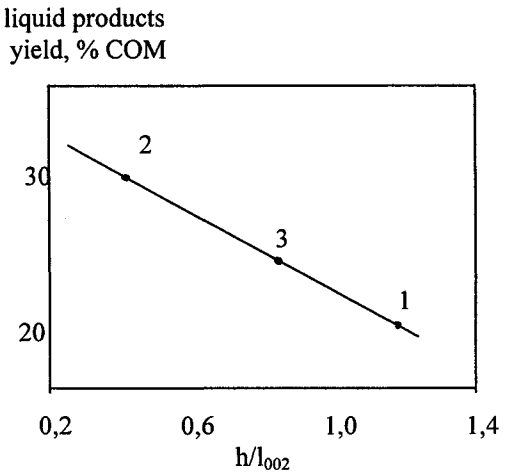

Fig.1 The dependence of liquid products yeild of a brown coal pyrolysis on h/l_{002} parameter: 1 - initial coal; 2 - activated by KOH; 3 - HCL

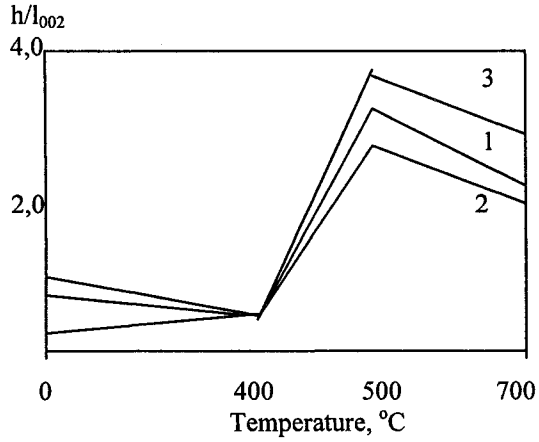

Fig.1 Changing of h/l_{002} parameter of a brown coal against a pyrolysis temperature: 1 - initial coal; 2 - activated by KOH; 3 - HCL