Catalytic influence of native minerals on thermochemical conversion of salty coals

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Abstract – The possibility of involvement of salty coal (SC) into the fuel base of Ukraine is considered. SC has high fuel indexes, but has an abnormal level of alkali metals in its composition. The changes of ash content and elemental composition of coal after water extraction are shown. The influence of alkali and alkaline earth metals salts on thermochemical conversion of salty coal at different temperatures and particle size of coal is determined.

Key words – salty coal, mineral matter, thermolysis, catalytic action, gaseous products, burning rate

Introduction

Coal with high content of alkali and alkaline earth metals (salty coal) occupies its definite place in an energy reserve, not only in Ukraine but also in many other countries, including China, USA, Russia, Germany and Australia. The deposits of salty coals in Ukraine are located in the Western and Northern Donbas, total explored reserves of ~ 12-25 billion tons.

Compounds of alkaline metals (alkali, salts) are universal catalysts (reagents) in many processes of thermal conversion of fossil fuels and biomass [1]. This applies to artificially introduced reagents and natural minerals, which are component parts of fossil fuels.

Salty coal (SC) stands out among other fuels not only by problems at traditional combustion (slagging, corrosion), but also that it contains a natural catalytic complex - alkali and alkaline earth metals salts, iron sulfides [2] and some of catalytically active trace elements in significant amounts. In our works [3] it is established that in salty coal of different deposits of Ukraine there are not only sodium chloride, but also sodium and calcium sulfates in significant amounts, which were clearly identified from aqueous extracts.

The purpose of this work was to determine the role of natural water soluble compounds in the processes of thermolysis of the salty coal of Bogdanovsk deposit (Northern Donbas) (table 1). It has a different content of sodium chloride (compared to Novomoskovsk SC) and another composition of water-soluble minerals, but not more attractive energy characteristics.

Table 1 – Characteristics of salty coal of Bogdanovsk and Novomoskovsk deposits

Deposit	Heat of combustion Q^{daf}, kcal/kg	Ash A^d, %	Volatiles V^{daf}, %	Na_2O in ash, %	Chloride Cl, %	Sulfur S, %
Novomoskovsk	7200-7500	10,1-15,0	44,0-47,3	0,6-1,0	0,6-0,9	2,1
Bogdanovsk	7020-7580	12,6-14,6	41,2-42,6	0,5-0,7	0,3-0,6	1,6-2,1

Experimental

Experiments were carried out at the Coal Energy Technologies Institute of the National Academy of Sciences of Ukraine at the facility of «Pyrolysis M». This equipment is designed to study the dynamics of gas evolution and combustion of the coke during thermal contact pyrolysis of coal in a fluidized bed at atmospheric pressure.

Samples of salted and desalted coal are crushed and dispersed to three fractions of particle size of 0.2-0.63, 0.63-1 and 1-1.6 mm. Extraction of salts from coal was carried out according to the parameters optimized in previous studies [4]: time (5-10 minutes), temperature (20 ^{o}C) and the ratio of solid phase to liquid (T:P=1:3). It should be noted that desalting resulted in some changes in the elemental composition (dry mass) of samples of salty coal (fig.1). As a result of desalting there was a decrease in the concentration of oxygen (a decrease in content by about 2-3%), a less significant reduction of hydrogen (about 1%) and nitrogen (by ~ 0.5%). Loss of sulfur content did not exceed 0.25%, and ash content was reduced by 0.5-2%. At the same time, carbon content increased substantially from 74 to 80%. Losses of oxygen, nitrogen and hydrogen can be explained by extraction during water desalting, so-called fulvic acids - water-soluble organo-mineral compounds. The reduction of the total sulfur content may be due to the presence of sulfates in the water-soluble salts of minerals and their removal by aqueous extraction.

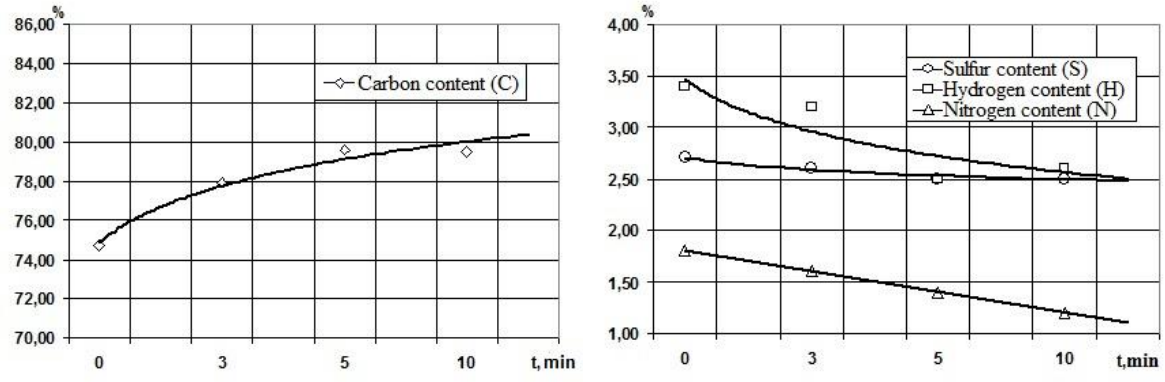

Fig.1. The content of macroelements in organic mass of coal depending on the time of desalination

The study of thermolysis was carried out at the temperatures of the fluidized layer of inert material (sand) at 550, 650, 750 and 850 ° C. As a result of the study, it was determined that the yield of gases (H_2, CO, CO_2) during combustion of salty coal is much more intense than that of combustion of desalted coal, as at the characteristic time (5 vs. 10-15 seconds) of the first stage of pyrolysis, and at the maximum yield of H_2, CO, CO_2 (Fig. 2). This is true for all particle size fractions studied.

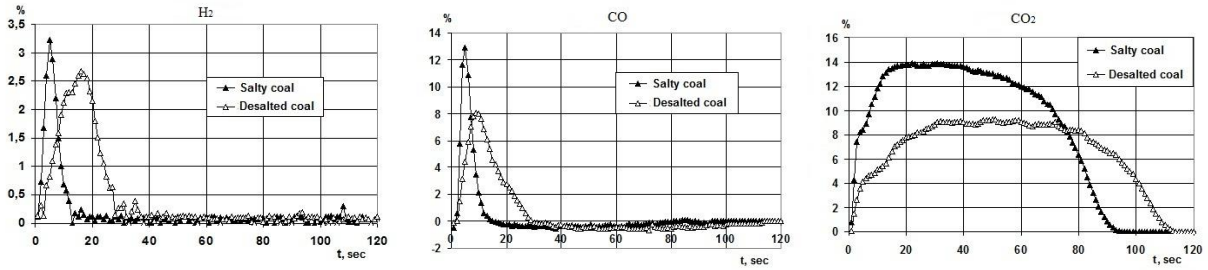

Fig. 2. The yield of gaseous products H_2, CO, CO_2 depending on the time of thermolysis (coal weight 0.5 g, temperature 750 ^{o}C, particle size 0,63-1 mm)

Particularly clearly, the difference can be seen at lower temperatures where the emission zones of volatile and combustion of coke are identified. It can be to claime that water-soluble minerals of salty coal (sodium chloride, sodium and calcium sulfates) give the process of formation and conversion (combustion) of volatile substances a significant catalytic effect. The same effect was observed in manuscript [5]. Native water soluble minerals have strong influence on decarboxylation reactions too (Fig.2).

On the other hand, as we see from Fig. 3, in the range of burning temperature 550-850 ^{o}C, the combustion rate (lnW) of coke residue (after devolatization) of salty coals (the main reaction $C + O_2 = CO_2$) is insignificantly different from the samples that ones were desalted by water washing.

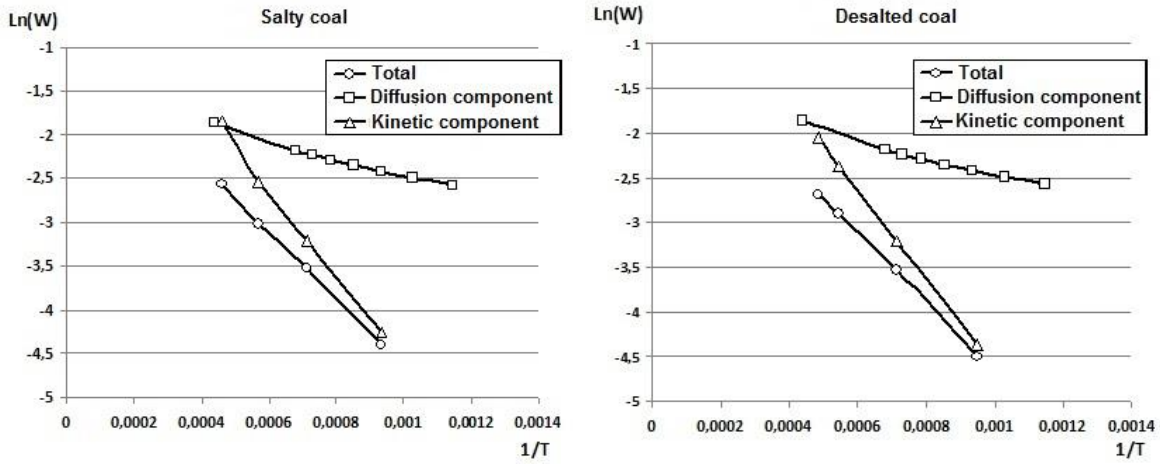

Fig. 3. Dependence of the carbon burning rate on the process temperature

Conclusions

1. The catalytic action of native salts is more pronounced in the stage of gas formation and is less significant at increasing the temperature of thermolysis.
2. The ratio of H_2/CO for initial salty coal at the maximal yield consist of from 0.36 to 0.40, while for desalinated coal it is 0.25 - 0.34. This indicates a more significant influence of alkaline salts on dehydration reaction than on the process of decarbonilation.
3. Native water soluble minerals have strong influence on decarboxylation reactions.
4. The presence of a natural catalytic complex in the composition of salty coal gives a certain perspective for the use of salty coal in a blends with other coal, which does not contain an catalytic alkaline additions and is characterized by more refractory ash.

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