UDC 662.743

Investigation of the Effect of Preliminary Mechanical and Mechanochemical Activation Treatment of the Material on the Thermolysis of Coal from the Tavantolgoy Deposit (Mongolia)

N. I. KOPYLOV[1], YU. D. KAMINSKIY[1], ZH. DUGARZHAV[2] and B. AVID[2]

[1]*Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Ul. Kutateladze 18, Novosibirsk 630128 (Russia)*

E-mail: kolyubov@narod.ru

[2]*Institute of Chemistry and Chemical Technology, Academy of Sciences of Mongolia, Ul. Mira 4, Ulaanbaatar 210351 (Mongolia)*

E-mail: dugar21mn@yahoo.com

(Received December 5, 2012)

Abstract

The results of experiments on DTGA of black coal from the Tavantolgoy deposit (Mongolia) are presented. It was discovered that intense voluminous expansion and at the same time agglomeration of coal material occur during thermal decomposition. This process is accompanied by the removal of gaseous, low melting and boiling components of coal. The effect of preliminary mechanical activation and its duration on the character of separation of thermolysis products was demonstrated. The suitability of coal without additional binding additives for briquetting was established.

Key words: black coal, Tavantolgoy deposit, thermal analysis, thermal decomposition, agglomeration, gaseous, low melting and volatile coal components, mechanochemical activation

INTRODUCTION

Dynamics and character of thermal decomposition of fossil coal are determined by their composition [1–4]. Depending on the chemical and phase composition, structure and type of coal, during heating it loses non-condensable gas fractions in a definite specific sequence, melting and sublimation of condensable products of thermolysis occur. Preliminary mechanical activation of the material brings its corrections into the dynamics of thermal decomposition.

It was demonstrated for coal from the Tuva deposit [2–4] that, depending on coal composition, short-term (within 1 min) mechanical activation may cause a decrease in melting and boiling temperature of the low melting component, broadening of temperature ranges of the endo effects of these transformations, shifts of explosion effects on DTA curves or their absence during thermal analysis.

Longer mechanical activation (3–10 min) is accompanied by deeper transformations in the sample material, such as changes in chemical composition, structure and physical properties. As a rule, the curves of thermal analysis exhibit only the relics of thermal effects of formation and boiling of readily melting phases. They are to a higher extent characteristic of experiments with mechanical activation for 3 min and to a less extent – with activation for 10 min. In this situation, DTA curves exhibit also low temperature effects due to absorption of the gas phase components (water vapour, oxygen, carbon dioxide *etc.*) by the activated material [4].

Fossil coal from the Tavantolgoy deposit in Mongolia belongs to black coal judging from the appearance; similarly to coal from the Tuva deposit; it may have complicated composition, specific physical and technological characteristics. When used as heat carrier, it may have similar hazardous effect on the environment. In this connection, in order to determine the possibility of coal briquetting, we carried out thermographic studies of coal decomposition and investigated the effect of preliminary mechanical and mechanochemical activation on the characteristics of coal.

EXPERIMENTAL

Black coal samples from the Tavantolgoy deposit (Mongolia) was the object of investigation. The coal samples were studied as averaged, finely ground (~0.02 mm) matter from coal bed VIII and a snap lump sample from coal bed IV.

Thermal analysis was carried out with the help of a MOM-1000 derivatograph (Paulic–Paulic–Erdey, Hungary). Temperature range was 650–700 °C. Heating rate was kept at the level of 10 °C/min. The weighted portion of the sample was ((1±0.2) g. Experiments were carried out in quartz crucibles. In order to eliminate the effect of the environment, the crucibles were closed with a cap made of foamed corundum which provided free diffusion of gas components formed during heating.

Mechanochemical activation of initial material was carried out using AGO-2 planetary mill with water cooling with time schedule 1 and 3–10 min.

RESULTS AND DISCUSSION

DTGA of coal sample from coal bed VIII

It was established (Table 1) that the results of experiments are almost identical. One can see (Fig. 1, *a*) that the start of thermal decomposition of the material is marked with a sharp explosion-like effect connected with the emission of gaseous components at 420–490 °C. Mass loss varies within the range 5–7 % at this stage. At the same time, low-melting fractions of coal are evolved, with the corresponding endo effect at the DTA curve with a maximum at 480–485 °C. The next stages of thermolysis have monotonous stepwise nature. The overall mass loss is 14–15 %. A sharp exothermal peak is observed on the DTA curve within temperature range 360–410 °C; its nature has not been established yet. This effect is in no way pronounced on TG and DTG curves, therefore, in this case we may speak of phase or structural transformation proceeding with heat evolution.

Agglomeration over the whole sample volume and compaction of the material are observed in the experiments with this sample.

Coal material activated for 1 min starts to decompose according to the explosion mechanism within the range 400–500 °C, mass loss reaches 4.6–6.6 % (see Table 1) and is comparable with the mass loss by non-activated sample within this temperature range. Subsequent heating involves step-by-step decomposition with the removal of gaseous and low-boiling thermolysis products (see Fig. 1, *b*). Total mass loss may vary depending on the final temperature of experiment. For example, for heating to 600 °C, mass loss is within the range 11.3–12.1 %, while for heating to 680–700 °C it reaches 16.9–20.9 %. In all experiments, two clear exothermal effects appear on each DTA curve. The first exo effect appears before the start of decomposition and relates to the structural transformation in the material. The second exo effect can be explained by the thermal effect of combustion of sublimate products of thermolysis at the outlet of the crucible. Preliminary short-term activation of coal is likely to make this process more active. For example, it follows from the data shown in Fig. 1 that for non-activated initial sample, the exo effect (510–610–660 °C) is not clearly expressed; it is extended within temperature range, while activation of the material sharply intensifies combustion process and affects narrowing of its temperature ranges (530–545–600 °C).

DTGA of coal sample from coal bed IV

The sample was preliminarily crushed in a porcelain mortar till particle size ≤0.5 mm. Judg-

TABLE 1

Thermal decomposition of coal from the Tavantolgoy deposit (sample from coal bed VIII)

Stages	Initial sample						Mechanically activated sample							
	Experiment No.						Experiment No.							
	1		2		3		1		2		3		4	
	T, °C	Δm, %	T, °C	Δm, %	T, °C	Δm, %	T, °C	Δm, %	T, °C	Δm, %	T, °C	Δm, %	T, °C	Δm, %
1	300–420	0.9	20	–	20–450	–	20–400	–	20–465	–	300–500	1.1	20–510	1.0
2	420–480	4.9	490–510	4.7	450–480	7.5	400–460	4.6	465–510	4.9	500–510	6.6	510–520	5.4
3	480–530	2.7	510–550	5.7	480–600	7.1	460–620	9.1	510–600	7.2	510–700	13.3	520–600	4.9
4	530–700	4.9	550–700	4.8			620–680	3.2						
Σ	700	13.6	700	15.2	660	14.6	680	16.9	600	12.1	700	20.9	600	11.3

Note. Δm is mass loss with respect to the initial mass.

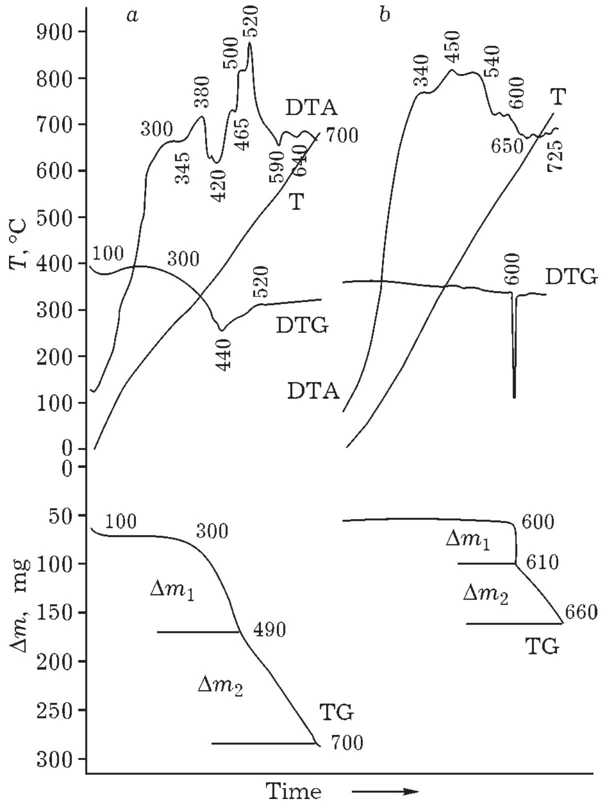

Fig. 1. DTGA of the sample from coal bed VIII: *a* – initial sample; *b* – after mechanical activation for 1 min.

ing from the appearance of DTA curves (Fig. 2, *a*), complicated transformation processes occur in the material. These processes are observed in the DTA curve as clear thermal effects: exo effects at 380, 500 and 520 °C, endo effects at 420, 590 and 640 °C. This is connected with the fact that during heating at definite stages several processes take place either simultaneously or sequentially: low temperature structural transformation, melting of the low-melting hydrocarbon component, evaporation of the gaseous fraction, boiling and sublimation of the hydrocarbon component and its inflammation at the outlet of the crucible (exo effect at 500–520 °C). The behaviour of the curves showing the changes of sample mass (TG and DTG) shows a small mass loss at 90–100 °C (~0.8 %), possibly due to the loss of sorbed water. A smooth mass loss appears at 300 °C; its intensity increases gradually to 440–480 °C and becomes uniform with further temperature rise to 700 °C. At the first stage of decomposition (Table 2 and Fig. 2, *a*) mass loss is 11.3 %, at

TABLE 2

Thermal decomposition of coal from the Tavantolgoy deposit (sample from coal bed IV)

Stages	Initial sample		Mechanically activated sample					
			Experiment No.					
			1		2		3*	
	T, °C	Δm, %	T, °C	Δm, %	T, °C	Δm, %	T, °C	Δm, %
1	20–90	0.8	20–600	–	20–500	–	20–480	–
2	300–480	11.3	600–610	4.5	500–600	0.6	480–520	4.2
3	480–700	13.7	610–660	5.4	600–800	8.3	520–600	6.6
Σ	700	25.8	660	9.7	800	8.9	600	10.8

* Exposure for 40 min at 350 °C.

the next stage it is 13.7 %. Total mass loss to 700 °C reaches 25.8 % of the mass of initial weighted portion, which is much higher than mass loss in experiment with coal sample from coal bed VIII. This may be connected with the initial aggregative state of samples: coal sample from bed IV was prepared from lump material, while sample from coal bed VIII is crushed powdered material from which a substantial part of gaseous components could diffuse outward due to the large surface of contact with the environment.

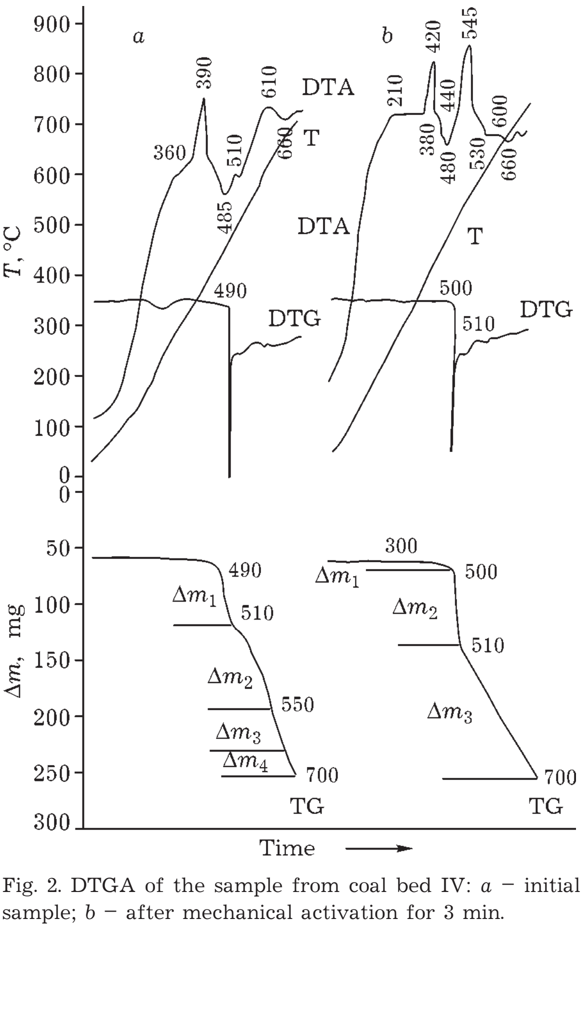

Fig. 2. DTGA of the sample from coal bed IV: a – initial sample; b – after mechanical activation for 3 min.

In the case of tight packing of the material in the crucible, expansion with volume increase occurs at a temperature within the range 450–480 °C, which is explained by the formation of viscous binding mass in the material. Subsequent cooling leads to the formation of rather hard porous column.

The data of thermal analysis of sample material mechanically activated for 3 min differ substantially from the results obtained for initial samples: only relicts of thermal effects observed in thermograms of initial samples appear in DTA curve; mass loss observed in TG curve starts only from a temperature approximately equal to 600 °C (see Table 2 and Fig. 2, b) and has clearly pronounced explosion-like appearance. However, agglomeration was not observed in this case. Subsequent experiment with thermolysis of mechanically activated material, exposed for 40 min at 300–350 °C and then heated, has shown that a sharp decrease in the mass of the material shifts to lower temperature range (about 480 °C).

The mass loss by the activated sample occurs in two stages: at 480–520 °C it is 4.2 %, while within temperature range 520–600 °C it is 6.6 %. Total mass loss reached 10.8 %, and this is more than 2 times lower than the total mass loss for the initial sample in thermal analysis. So, short-term mechanical activation (within 1 min) activates the material but does not change its major phase composition (experiments with coal sample from coal bed VIII), but with an increase in activation time (up to 3 min and more) deeper transformations occur in the activated material.

In particular, the concentrations of gaseous, low melting and readily volatile components in the material decrease sharply. It appears that a substantial part of the gaseous component diffuses out of the material as early as at the stage of activation. Long-term mechanical activation is accompanied by an increase in the concentrations of oxygenated phases and substantial changes of the phase composition of coal matter.

CONCLUSION

Results of thermographic studies of black coal samples from two coal beds (VIII and IV) showed that thermolysis causes evaporation of the gaseous component from coal, while solid hydrocarbons undergo subsequent melting and sublimation. The depth and quantitative characteristics of the thermal decomposition of coal during heating are to a high extent determined by the initial aggregative state of coal (particle size, preliminary treatment, heating mode, and the final temperature of the experiment).

Thus, fine ground initial sample from coal bed VIII studied by means of DTA with heating to 660–700 °C is characterized by relatively low mass loss – within 13–15 %. After its short-term activation (for 1 min) the mass loss somewhat increases; the higher is the limiting temperature of experiment, the larger is mass loss. For example, for the final temperature equal to 600 °C, mass loss was nearly 12 %, while for the temperature of 680 °C the mass loss was 16.9 %, and at 700 °C it was 20.9 %.

The initial lump monolith matter from coal bed IV subjected to DTGA exhibits somewhat different behaviour of thermal decomposition. The DTA curve more sharply shows the thermal effects of gas component sublimation, melting, sublimation and combustion of hydrocarbon solid phases at the outlet of the crucible. The mass loss by coal during heating reaches 26 %. It was established that an increase in the time of preliminary mechanical activation of the sample to 3 min and more causes substantial removal of the gas component of the matter, which causes decreased mass loss by the coal sample during thermographic studies (within the temperature range up to 800 °C) to 9–11 %.

A comparison between the data of thermal analysis of the initial fine ground sample from coal bed VIII and initial coarse-lump sample from coal bed IV points to the sharp difference in gas component content – almost by a factor of 2. This is likely due to the more favourable storage conditions for the diffusion of the gas component of coal and depletion of the fine ground product of coal bed VIII than for the lump material of sample from coal bed IV.

REFERENCES

1 Gornaya Entsiklopediya, Moscow, 1991, vol. 5, pp. 227.
2 Kaminskiy Yu. D., Kopylov N. I., Kulikova M. P., Nauchnye Yrudy TuvIKOPR SO RAN (Treatises), Kyzyl, 2005, issue 8, pp. 123–128.
3 Kopylov N. I., Kaminskiy Yu. D., Kulikova M. P., *Khim. Tekhnol.*, 9, 4 (2008) 168.
4 Kopylov N. I., Kaminskiy Yu. D., *Chem. Sustain. Dev.*, 21, 3 (2013) 319. URL: http://www.sibran.ru/en/journals/KhUR