

Thermal decomposition of sulfur brown coal

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Abstract. The influence of heating rate, temperature and particle size of sulfur brown coal from the Moscow region on the yield of coke residue and its elemental composition was studied. The results can be useful in choosing a rational way of using the presented coals from the energy and ecology point of view.

1 Introduction

Currently, coals and other solid combustible fossils remain one of the main sources of raw materials for the energy, chemical industry and metallurgy [1]. The explored reserves of coal significantly exceed the known reserves of oil and natural gas, so coal and other solid combustible minerals will be used in various industries for a long time [2]. On the other hand, coal is one of the “dirtiest” fuels. It is natural concentrator of sulfur, containing heavy metals, and when burned, significant amounts of ash and finely dispersed dust particles are formed [3-4]. The sulfur contained in coals is a harmful component both its impact on the environment and technological point of view [5]. As high-quality coals are produced, coal of poorer quality is increasingly being used, which will negatively affect the environmental situation [6]. Low-quality coals are characterized by a predominance of sulfide sulfur: mainly pyrite (FeS_2), as well as chalcopyrite (CuFeS_2) and marcasite (iron polysulfide, FeS_2) [7]. Organosulfur compounds are an integral part of the coal matrix and are thiol (R-H-S), sulfide (R-S-R'), disulfide (R-S-S-R), sulfoxide (R-S-O-R) and thiophene (heterocyclic) compounds [8-9]. In addition, sulfur presents in coal in elemental form.

A comprehensive solution to the problem of using low-quality coals is the development and implementation of modern eco-friendly thermal technologies for their processing [10-13]. To reduce the amount of sulfur before thermal processing of coal, various methods of sulfur removal are used: magnetic separation, gravitational separation, leaching, etc. [14-15]. Also, to improve the environmental characteristics of flue gases it is necessary to reduce the amount of exhausted carbon dioxide [16].

When coal is heated, it goes through a complex series of physical and chemical transformations. The chemical and physical changes that occur during coal pyrolysis depend primarily on the type of coal but are also significantly influenced by various other factors such as the temperature, heating rate, duration of exposure to high temperatures, pressure, surrounding gas composition, type of reactor used, amount of coal sample, coal

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particle size, and hydrodynamic conditions within the reactor [17-23]. These additional parameters can greatly modify the nature of the changes brought about by pyrolysis, despite coal type initially being the dominant determining factor.

The purpose of this work is to study the patterns of thermal decomposition of sulfur coal depending on temperature and heating regime. The subject of the study was sulfur content in solid products under various heat treatment regimes of sulfur brown coal. The main attention was paid to the processes of oxidative pyrolysis and coal gasification.

2 Methodology

The object of study was sulfur brown coal from the Moscow region - Tula coal from the Kimovsky open pit. Preliminary technical analysis of brown coal in accordance with GOST R 52911–2013 "Solid mineral fuel. Determination of total moisture", GOST R 55661–2013 "Solid mineral fuel. Determination of ash content", GOST R 55660–2013 "Solid mineral fuel. Determination of the yield of volatile compounds" showed that the moisture content of the coal was approximately 3%, the total yield of volatile products was 27% (tar yield ~10%), coke yield - 38%, ash content - 27%.

Experiments on the oxidation of brown coal particles were carried out in an SKV 15/12 electric muffle furnace (TU 3443-013-0151289328-2015), intended for heat treatment of products, materials and substances in an air environment up to a temperature of 1250°C. Two characteristic pyrolysis modes were studied, differing in the fuel heating rate: fast oxidative pyrolysis, with heating from 500 to 1200°C; gradual – from room temperature to 1200°C.

Coal samples were placed in quartz cuvettes and set up in the furnace. The weight of the samples was 25.0 g. The coal particles used had an average size of 1.5, 2.5 and 5.0 mm. During rapid heating, a sample of coal was placed in a furnace heated to a given temperature, ranging from 500 to 1200°C (every 100°C), and kept in the furnace for 15 s, which corresponds to the residence time of the particle in the high-temperature zone during gasification in filtration mode [24-26]. During gradual heating, the samples were simultaneously placed inside the furnace on eight quartz cuvettes, after which the furnace was turned on. Upon reaching the specified temperature, one of the samples was removed from the furnace. After the sample cooled, it was weighed and submitted for elemental analysis.

The elemental analysis of coal and pyrolysis products was determined using the equipment of the Federal Research Center of Problems of Chemical Physics and Medicinal Chemistry RAS (CHNS/O analyzer "Vario Micro cube"), and low heating value presented in Table 1. The lower heating value was calculated using the Mendeleev formula.

Table 1. Elemental composition and low heating value of brown coal and pyrolysis products (wt.%).

Product	C	H	O	N	S	Ash	Q, MJ/kg
Coal	42.57	3.82	23.13	0.78	2.70	27.00	13.0
Tars	75.36	6.76	10.70	1.17	2.90	3.11	33.0
Solid residue	0.14	0.08	--	0	1.18	98.60	--

The chemical composition of ash was determined by analysis on a *Zeiss LEO SUPRA 25* scanning field emission electron microscope and on an *ARL PERFORM'X* Sequential XRF X-ray fluorescence spectrometer (Thermo Fisher Scientific).

An analysis performed on an electron microscope showed that the mineral part of coal ash (in terms of oxides) consisted of: 46.0% Al_2O_3 , 32.3% SiO_2 , 2.1% CaO , 18.8% Fe_2O_3 , the content of other components totaled 0.8%. X-ray fluorescence analysis of coal ash

showed a similar result: 45.0% Al_2O_3 , 34.6% SiO_2 , 16.1% Fe_2O_3 , 2.2% CaO and 2.1% Na_2O .

3 Results and discussion

Fast heating. Fast heating is characterized by low mass loss, and the size of coal particles had virtually no effect on the characteristics of its pyrolysis.

At 500°C, only drying can occur in 15 s; since the original coal we used was almost dry, the weight loss was only 1.5%. At a temperature of 600°C, coal darkens and individual particles begin to ignite. The weight of the sample is reduced to 97% of the original, however, starting at a temperature of 700°C, the pyrolysis and oxidation of coal begins to become more active. The yield of solid residue at a temperature of 700°C is approximately 91%, and at 1100 and 1200°C – 79 and 76%, respectively (Table 2).

The carbon content remains almost unchanged over the entire temperature range from 500 to 1200°C; the hydrogen and oxygen content changes more noticeably, which is apparently associated with the formation of water (Table 2). The concentration of sulfur in the solid residue increases in proportion to the increase of ash content due to the combustion of organic substances that do not contain sulfur. Consequently, sulfur-containing compounds remain in the solid residue.

Table 2. Composition of the original coal and the solid residue derived during fast heating (wt.%).

Temperature, °C	C	H	O (differential)	N	S	Ash	Solid residue
20	42.62	3.82	23.13	0.78	2.70	26.95	100
1100	42.33	3.04	16.27	0.84	3.51	34.01	79
1200	41.67	2.49	15.80	0.89	3.80	35.35	76

Gradual heating. The temperature regime for heating the samples (curve 1) and the change in the relative mass of the solid coal residue (curve 2) are shown in Figure 1.

As with fast pyrolysis, with gradual heating the particle size did not affect the change in the relative mass of the sample.

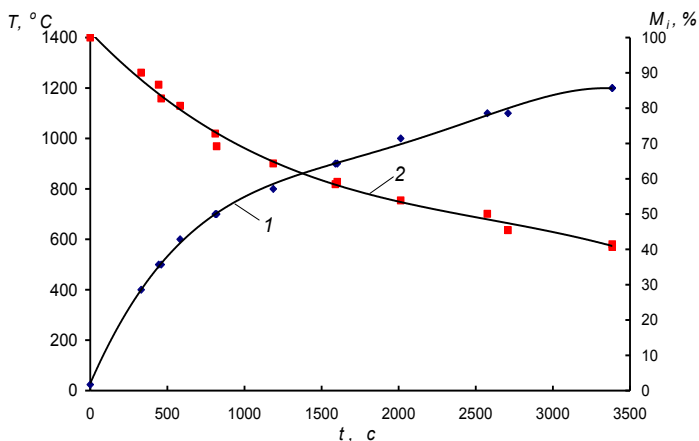


Fig. 1. Temperature heating regime (1) and the corresponding change in the relative mass of the solid coal residue (2).

With gradual heating, noticeable thermal decomposition of coal begins when the temperature reaches 300°C, and at 350°C a noticeable release of volatile substances is

already observed. In the temperature range from 500 to 900°C, coal pyrolysis occurs predominantly with a gradually decreasing rate of decomposition. As a result of gradual heating to 900°C, the content of carbon in the solid residue (compared to the original) decreased by about a third, nitrogen by 2 times, and hydrogen and oxygen by 7–10 times (Figure 2). The sulfur content in the solid residue decreased by ~40%.

In the temperature range of 1000-1200°C, oxidation of coke residue occurs. The constant rate of oxidation of the solid residue at high temperatures (approximately 12 mg/s) suggests that at these temperatures the limiting stage is the oxidizer supply. Basically, carbon is oxidized; the content of other elements in the solid residue (with the exception of small quantities of nitrogen) changes relatively little. In particular, the sulfur content (from the original) decreases from ~60 to 50% (Figure 2).

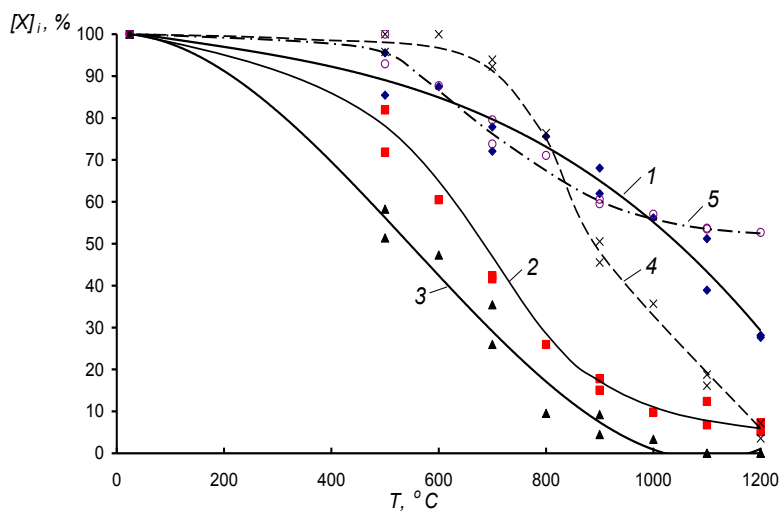


Fig. 2. Relative change in the proportion of carbon (1), hydrogen (2), oxygen (3), nitrogen (4) and sulfur (5) during the pyrolysis of brown coal.

With complete combustion of coal, all the iron sulfides at high temperatures must oxidize to iron oxides and remain in the ash, and be released in the form of sulfur oxides into the gas phase. However, analysis of coal ash (Table 1) showed the presence of sulfur in it, which is approximately 12% of its original content in coal. Apparently, part of the sulfur contained in coal interacted with other ash components (for example, CaO and Na₂O), whose sulfides and sulfates were decomposed at higher temperatures than iron compounds.

Thus, the optimal temperature regime for the thermal processing of this coal seems to be the range of 1000-1200°C, at which the process of carbon oxidation is limited by the stage of supplying the oxidizer (hence, the process efficiency linearly depends on the consumption of the oxidizer), sufficiently complete combustion of carbon is ensured, but does not lead to complete combustion of sulfur-containing compounds.

4 Conclusion

Experiments have shown that during the fast pyrolysis of Tula coal, the processes of dehydration and carbonization mainly occur. The sulfur contained in coal remains almost entirely in the solid residue. With gradual heating from 300 to 900°C, pyrolysis processes predominantly occur, accompanied by intense release of volatile substances. At a temperature of 900°C, the carbonization process is almost completed. In the temperature

range from 900 to 1200°C, coke residue is predominantly oxidized, occurring at a constant rate. The sulfur content in solid combustion products is determined by the temperature and intensity of oxidation of the organic mass of coal. It has been shown that the optimal temperature regime for thermal processing of this coal is in the range of 1000-1200°C. This temperature regime of coal combustion ensures fairly complete combustion of the carbon contained in it, but does not lead to complete combustion of the sulfur-containing compounds contained.

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