Influence of atmosphere composition on thermal decomposition of coal-bitumen composite materials

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Abstract. The gas products yield for the thermal decomposition of coal-bitumen composite materials was experimentally studied. The effect of temperature change on the product distribution was investigated using FTIR spectroscopy. The influence of atmosphere composition on the release of different gaseous products was analysed at different temperatures.

1. Introduction
Compaction of combustible materials for fuel production is a technology widely used in many countries. The use of briquettes from combustible materials as a fuel is an attractive approach which can solve several problems such as the utilization of bio-waste products and industrial waste, effective use of fine coal dust and low-grade coals, etc. [1-3]. However, the prediction of yield and product distribution in coal-containing materials as a result of chemical processes during heating is difficult because highly complex chemical processes complicate the accurate thermodynamic analysis. On the other hand, to provide for the stable and continuous work of the power plants with high efficiency it is necessary to develop models for analysis of combustion of coal composite materials [4].

Investigation of thermal processes in carbonaceous materials is very important for the development of qualitative and quantitative kinetic models to describe chemical reactions occurring during combustion [5, 6].

In the present work we have experimentally studied the influence of the gas medium composition and the temperature on the product distribution during thermal decomposition of coal-bitumen composite materials based on Pavlovskiy brown coal. Our previous studies [7] have shown that the briquette of a coal and tar (bitumen) mixture have the low total moisture content of approximately 0.4%. It is well-known [8, 9] that water can influence pyrolysis, gasification and combustion processes. To avoid the influence of absorbed moisture, the samples with the lowest moisture content were used for experimental studies on the influence of the atmosphere content on thermal decomposition of composite materials.

2. Experimental part
The briquette of a composite material was based on Pavlovskiy brown coal with the addition of tar in the ratio 81 mass%:19 mass %, respectively. The coal was previously crushed and sieved till the grains size of 0÷7.5 mm. Both constituents of briquettes were dried at about 130°C before forming. Then they were mixed and compacted into briquettes at a pressure of 160 kN for 3 minutes.
IR spectra of gas products thermal decomposition were recorded using the Nicolet iS10 FT-IR Spectrometer (Thermo Electron Corporation, USA). For this purpose, this equipment has a special gas-cuvette for gas product sampling and the temperature-maintaining unit. The experiments were performed in an air-nitrogen atmosphere (with a volume ratio of 3:1 and 1:1) and in a carbon dioxide-nitrogen atmosphere (volume ratio of 3:1) at atmospheric pressure. The flow rate of gases was constant for all experiments and amounted to 400 cm³/min. For experiments in gas chamber the briquette was divided into small pieces with approximately the same size and weight of about 1 gram. A sample was placed into a small basket in the chamber and was heated up to 800 ºC with the heating rate of 5 ºC /min. The maximum temperature was maintained for 1.5 hours. Gases from the chamber came out into a separate gas line heated up to 200 ºC which was connected to the spectrometer. IR spectra were recorded every 5 seconds during the experiment.

3. Results and discussion

The coal pyrolysis (the thermal decomposition in inert atmosphere) was studied by many researchers [8, 10]. Generally, the process of pyrolysis can be divided into three main stages. The first stage takes place below 300 ºC with slow thermal decomposition. The yield of volatiles is small at this stage. The second stage occurs in the temperature range from 350 to 550 ºC. The decomposition reactions are fast and approximately 75% of all possible volatile matter is released at this stage. The main products of the second stage are light hydrocarbon gases and a great variety of organic condensable compounds that form tar.

![Figure 1. FTIR spectroscopy of the decomposition products obtained during coal-bitumen composite material heating under air-nitrogen atmosphere in a ratio of 3:1.](image)

The third stage occurs at temperatures above 550 ºC and involves the secondary devolatilization associated with char transformation. Typical products of this stage are hydrogen (main product) and
non-condensable gases such as CO, CO$_2$, CH$_4$, C$_2$H$_6$, C$_2$H$_4$, and NH$_3$ [8]. The distribution of different gas components depends on coal type and can differ from the composition described above.

Decomposition products released during coal-bitumen composite material heating under different atmospheres by Fourier-transform infrared (FTIR) spectroscopy (Figures 1-3) were studied. Unfortunately, FTIR spectroscopy has some limitations. So, if the concentration of released molecules is low it is not possible to detect them as well as molecules with covalent bond, for instance hydrogen. As it is mentioned above the heating of samples was performed in range from room temperature to 800°C and then samples were kept for some time at the same conditions at 800°C. Thus, in Figures 1-3 the last spectrum marked as 800°C (1h) was registered after 1 hour since the temperature in the chamber had reached 800°C.

Figure 1 demonstrates changes in the decomposition product compositions with the change of temperature during the sample heating in an air-nitrogen atmosphere (ratio of 3:1). Under such conditions the estimated volume concentrations of oxygen and carbon dioxide are about 15% and 0.02-0.03%, respectively. All observed peaks (Fig. 1-3) were analysed using integrated Thermo scientific FTIR spectral libraries. Both peaks in the ranges of 2250-2400 cm$^{-1}$ and 600-750 cm$^{-1}$ are assigned to vibrations in carbon dioxide [11]. Two low-intensity peaks in the range of 2050-2250 cm$^{-1}$ are assigned to vibrations in carbon monoxide [12]. Peaks at about 3000 cm$^{-1}$ were assigned to methane [11, 12]. For all spectra sets of absorption bands were observed between 3400 and 3800 cm$^{-1}$ and between 1500 and 1900 cm$^{-1}$. These bands correspond to H-O stretching and H-O-H bending in water molecules. Additionally, Figure 1 demonstrates peaks at about 950 cm$^{-1}$ and 2900 cm$^{-1}$ for 400 and 450°C. These peaks can be assigned to vibrational bands of ethylene vapor [13]. At last, the small peak at 1020 cm$^{-1}$, which appeared also at 400 and 450°C, can be related to methanol [14].

![Figure 2](image-url)  

**Figure 2.** FTIR spectroscopy of the decomposition products obtained during coal-bitumen composite material heating under air-nitrogen atmosphere in a ratio of 1:1
Thus, in accordance with data from Fig. 1 a release of methane is detected in temperature range of 400-550°C. Carbon monoxide can be found in a wider range of temperatures from 300 to 650°C. Carbon dioxide and the presence of water are detected on all FTIR spectra. As it can be seen from peak intensities the largest quantity of volatile matter is released at 450°C.

Figure 2 shows changes of the decomposition products compositions with temperature during sample heating in an air-nitrogen atmosphere with the ratio of 1:1. Under such conditions the estimated volume concentrations of oxygen and carbon dioxide are about 10% and 0.01-0.02%, respectively.

Traces of methane were detected in the spectrum at a temperature of 500°C. They were observed until 750 °C. The maximum absorption was at a temperature of 650°C. Traces of carbon monoxide were observed starting from 500°C, with the maximum at 750°C. Traces of carbon monoxide were observed even after 1-hour sample treatment at 800°C. An increase of carbon dioxide and water content was detected up to 450°C with further decrease at temperatures above 550°C.

![Figure 3](image.png)

**Figure 3.** FTIR spectroscopy of the decomposition products obtained during coal-bitumen composite material heating under carbon dioxide-nitrogen atmosphere in a ratio of 3:1.

Figure 3 demonstrates results for sample decomposition in a carbon dioxide-nitrogen atmosphere with ratio of 3:1. The volume concentration of carbon dioxide is 75%. As discussed above peaks related to carbon dioxide and water present in all spectra. At 200-250°C the peak intensities of carbon dioxide and water rapidly increase with the maximum at 250°C. Further their decrease is observed in the temperature range from 300 to 800°C. As it can be seen from Fig. 3 traces of methane are detected at 200 and 250°C. The traces of carbon monoxide also appear at 200°C.
4. Conclusions
The results of this work demonstrate that the atmosphere composition has a significant influence on the thermal decomposition of coal-containing composite materials. The decrease of oxygen concentration from 15 vol.% to 10 vol.% shifted the temperature of methane and carbon monoxide formation to the higher temperatures for about 100° (from 400 to 500°C) and for about 200° (from 300 to 500°C), respectively. It is also demonstrated that the presence of CO₂ decreases the yield of volatiles in a good agreement with data presented in [15, 16]. In our work it was possible to detect formation of methane and carbon monoxide during sample decomposition at lower temperatures (200-250°C) in the carbon dioxide-nitrogen atmosphere. This could result due to the large content of aliphatic structures [8] in studied composite materials.

The results of experimental measurements of product distributions observed during the decomposition of coal-bitumen composite material are of interest in development and validation of kinetic models composite materials of pyrolysis and combustion. We believe that the knowledge of product compositions may be useful for developing technological procedures of composite fuel briquettes combustion.

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