

DEPENDENCE OF PYROLYSIS RATE OF COAL ON TEMPERATURE

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Abstract. Pyrolysis process of coal has been researched to define kinetic constants which can be used for design and optimization of different processes of fuel transformation. The article considers anthracite powders and bituminous coal of Krasnogorsky mine with the use of non-isothermal thermogravimetric analysis with mass spectrometry. Spectroscanning microscopy and laser diffraction for definition of sizes and forms of particles distribution has been done. Other parameters – carbon content, ash and volatiles, density and moisture have been defined by standard methods. Energy of activation and pre-exponent with the use of models of Freedman, Starink and distributed activation energy model (DAEM), and also relative deviation of design data from experimental ones have been designed. The results of the analysis have shown the important influence of volatiles content and coal transformation degree on maximum reaction rate. Energy activation values received with the help of DAEM model are higher than with Freedman and Starink models. Process of pyrolysis of bituminous coal has a big rate in comparison with anthracite, and is better described by the above-mentioned models.

1 Introduction

World resources of carbonaceous gas and liquid fuels are limited. With the same existing speed of energy consumption growth and ease of access deposits depletion oil and gas extraction will become more and more expensive: values EROI (Energy Return On Investment – ratio of received energy to investments) of oil and natural gas extraction decreased from 26 to 18 for the last 6 years in the world, while it almost did not change for coal – not less than 50 [1]. This makes use of technologies of deep coal transformation more and more attractive. Accordingly for the last time interest to technologies using solid fuel has increased in scientific literature. Ecological problems and growth of costs on solid fuel led to necessity of its utilization efficiency growth [2], with less amounts of pollution and low disposal costs [3]. Understanding of processes which occur during fuel transformation is exceptionally important for fulfillment of these conditions.

Pyrolysis is thermochemical process of volatiles deletion from coal and partial oxidation which strongly influences final value of coal transformation degree and mass decrease rate [4]. A lot of chemical and physical processes occur at this stage: drying, volatiles output, cracking and burning. The same factors – temperature, pressure, oxidation environment content influence their efficiency differently, which makes the research process more difficult. Other parameters of pyrolysis are

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strongly influenced by parameters of burning, gasification and other transformational processes [5]. Nowadays apparatuses with chamber division for different processes have being worked out which makes study of these processes more important [6]: pyrolysis, gasification and burning.

Thermogravimetric analysis is one of the most spread methods of receiving pyrolysis process parameters. It allows receiving necessary data with precision and accuracy. There are a lot of mathematical models for description of such processes. The most famous models are Freedman and Starink models and distributed activation energy model (DAEM) based on Arrhenius equation:

$$v=A \exp(-E/RT), \quad (1)$$

where v – mass loss rate, mass.%/s; A – pre-exponent (frequency factor), mass.%/s; E –energy activation, J/mole; R – gas coefficient, J/(mole·K); T – temperature, K.

Analysis of pyrolysis processes of Kuznetsky anthracite and bituminous coal in argon atmosphere was made with the help of differential thermal analysis. Three groups of kinetic constants have been defined for three non-isothermal models – Freedman, Starink and DAEM. Conclusions on models adequacy have been made on the basis of comparison of values presented in literature.

2 Experimental part

2.1 Preparation of samples and characteristics

Coal powders of Krasnogorsky mine, Kemerovo region have been researched. Powders have been received as a result of coal grinding and its screening through screen plate with the size of cells 315, 150 and 80 mkm. Bulk and volumetric densities have been defined with the help of pycnometry with five parallel changes as long as it strongly influences pyrolysis rate [7, 8]. Relative measuring inaccuracy of density did not exceed 0.5%. Moisture, ash and volatiles output have been defined by standard methods according to ISO 1171-81, 602-83 and 562-81 (table 1). Values of both ash content and moisture are relatively low while volatiles content in bituminous coal is higher than in anthracite.

Table 1. Main characteristics of researched samples of solid fuel

Characteristics	Unit of measurement	Value*		Way of definition
		A	K	
Relative density	kg/m ³	1753	1927	ISO 1171-81
Bulk density		339	340	
Ash content	mass %	10.5	10.8	ISO 602-83
Moisture		1.6	2.5	ISO 1171-81
Volatiles content		4.2	29.3	ISO 562-81
Carbon content		83.7	56.4	TG-analysis
Average size of particles	mkm	82.2	69.31	ISO 13320
Parameter X ₁₀		1.89	6.45	
Parameter X ₅₀		20.9	31.58	
Parameter X ₉₀		71.05	75.33	

*A relates to anthracite, K – to bituminous coal.

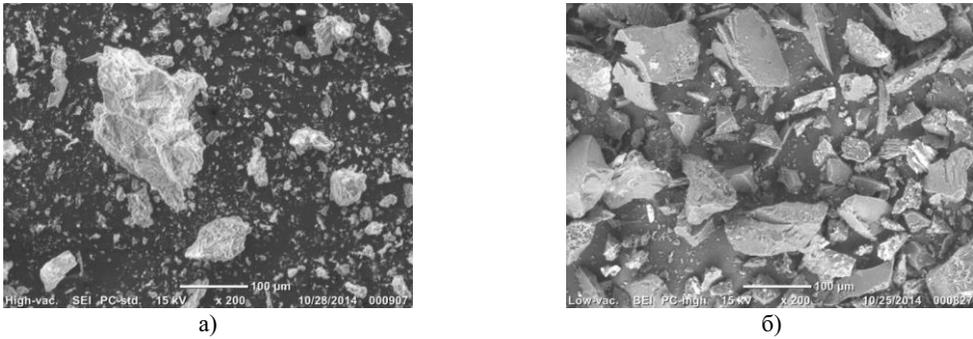


Figure 1. Micro photographs with 200-multiple approaching of anthracite (a) and thin coal (b).

Most models have hypotheses in relation to the form of particle and powder. Stereo scanning microscopy has been made for definition of this form with the help of raster type scanning microscope JEOL 6000 C (fig.1). Large particles of bituminous coal powder do not have a correct form, anthracite – spherical. The form of small particles is spherical for both samples. Analysis of particles distribution has been made with the help of laser diffraction HELOS in accordance with ISO 13320. Average size of particles and some other values – X_{10} , X_{50} , X_{90} – are presented in table 1.

2.2 TG- analysis and mass spectrometry

TG-analysis was made with the help of synchronous differential thermal analyzer Netzsch STA 449 C (Germany) at heating rate 10K/min in the range of temperatures from 323 to 1273 K. Argon of high refinement degree B was used as blowout gas for the process of pyrolysis. During the experiment for excluding the possibility of chemical reactions appearance with residual air in chamber TG, it was blown out with argon with volume flow rate 250 ml/min during 1 hour. After the beginning of the experiment volume flow rate made 50 ml/min. Mass spectrometry was made with Netzsch QMS 403 D Aëolos. Inaccuracy of mass decrease and temperature made less than 0.5 mass.% and 1 K, accordingly.

2.3 Kinetic models

Non-isothermal kinetic research of burning and pyrolysis processes problems is extremely difficult because of a large amount of components and their parallel and successive reactions [9]. At kinetic analysis of solid fuels process rate is usually expressed as follows:

$$d\alpha/dt=A/\beta \exp(-E/(RT)) f(\alpha) \quad (2)$$

where $\alpha=(m(t)-m_a)/(m_0-m_a)$ – coal transformation degree; $m(t)$, m_0 and m_a – mass of samples in a moment of time t , initial moment of time and after the pyrolysis process, g ; β – sample heating rate, K/min; $f(\alpha)$ – dependence of transformation rate on transformation degree (function of reaction rate distribution considering change of properties and structure of fuel particles during the process).

Energy activation (E), pre-exponent (A) and function of reaction rate distribution [$f(\alpha)$] – kinetic triplet. Non-isothermal kinetic methods of Freedman, Starink and DAEM were used for getting energy activation of burning processes and pyrolysis reaction.

Freedman model can be expressed with the equation [9]:

$$\ln(\beta d\alpha/dT)=\ln[A f(\alpha)] - E/(RT) \quad (3)$$

Starink equation is as follows:

$$\ln(\beta/T^{1.92})=A-1.0008 E/(RT) \quad (4)$$

Simplified model DAEM is as follows:

$$\ln(\beta/T^2) = \ln(AR/E) - 0.6075 - E/(RT) \quad (5)$$

At similar transformation degree at different heating rates, energy activation can be defined according to decline of dependence curve $\ln(\beta \, d\alpha/dT)$ for Freedman $\ln(\beta/T^{1.92})$ for Starink and for DAEM method $\ln(\beta/T^2)$ from $1/T$. DAEM model is thought to be the most accurate among the above-mentioned ones but use of simplified integral approximation for temperature can cause a substantial mistake.

3 Results and their discussion

3.1 Parameters of pyrolysis

Dependences of mass and its decrease rate on ambient temperature are in fig. 2 a, b.

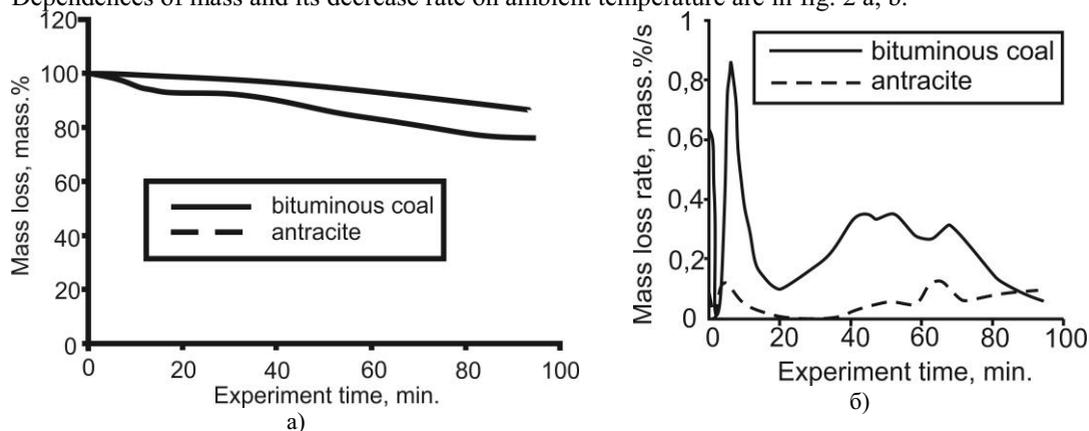


Figure 2. TG data (a) and dependence of coal samples pyrolysis rate (b) on time in argon atmosphere at temperature 1000 °C

Some peaks can be noted in the graphs: in the range of temperatures 330 - 375 K with maximum rate 0.138 mass. %/s and 0.868 mass.%/s for antracite and bituminous coal accordingly and at 750-780 K with 0.132 mass.%/s and 0.362 mass.%/s. The first peak can be connected with adsorbed moisture deletion – this can be proved with corresponding peaks in graphs of mass spectroscopy. Mass decrease rate increase does not have a sharply defined peak for the second time and has a bimodal character for thin coal. It is probably connected with some chemical reactions behavior such as hydrogen containing elements output (hydrogen, methane, hydrocarbon etc.), and also compounds of full and partial oxidation of sulfur, nitrogen and carbon. Oxidizing of substances of solid phase arises as a result of elements interaction in solid phase – sulfur, carbon – with oxygen in composition of adsorbed gases, and also air inflow is also possible into the chamber of differential chamber analysis analyzer. Mass spectrometric analysis shows the presence of a lot of compounds which can be the result of oxidation reactions or adsorbed gas output.

3.2 Pyrolysis kinetics constants

Fig. 3 illustrates dependence of energy activation on coal transformation for different samples and kinetic models. Let us consider that energy activation calculated with DAEM model is linearly dependent on transformation while it is close to constant for equations of Freedman and Starink.

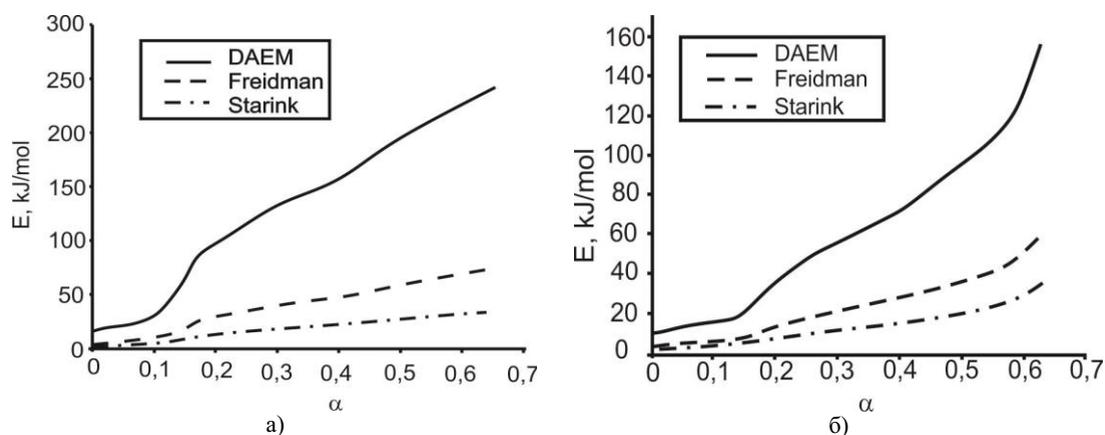


Figure 3. Dependence of energy activation calculated with different models on transformation degree for anthracite (a) and bituminous coal (b).

At design with formula 1, fixed value of energy activation reaction is often used $E = \text{const}$. In this case the most accurate result will be achieved at reaction constant use defined by Starink model as its change at different values α is the lowest one for both anthracite and thin coal. Average values of energy activation and pre-exponents are presented in table 2.

Table 2. Average values of kinetic constants of pyrolysis process samples

Constant \ Model	Anthracite			Bituminous coal		
	Friedman	Starink	DAEM	Friedman	Starink	DAEM
Pre-exponent $\ln A$	9.74	8.32	2.76	7.85	12.86	13.6
Energy activation E	35	15	125	30	15	80

It is clear from the table that use of DAEM model gives the highest values of energy activation, and Starink model – the lowest ones. Pre-exponent values for each bituminous coal increase at energy activation growth, and for anthracite – decrease. It is connected with both a bigger intensiveness on the whole and with influence increase of porous structure of fuel particles on process kinetics. The received data are coordinated with values presented in literature for analogous coals [4-6].

4 Conclusion

Energy activation values for pyrolysis process of anthracite and bituminous coal of Krasnoborodsky mine have been defined as a result of the research, two main phases of coal pyrolysis process and maximum values of mass decrease for each of them have been defined. Energy activation values of two coals with the use of three kinetic models have been defined. For DAEM model decline angle is far bigger than for Freedman and Starink models. Starink model is the most preferable for design with the use of energy activation constant value.

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