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Non-isothermal kinetic study of bituminous coal and lignite conversion in air and in argon/air mixtures

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ABSTRACT

The exact characteristics of the pyrolysis and combustion kinetics for Siberian bituminous coals and lignites were studied for better understanding of the fuel conversion processes. The bituminous coal samples of Kuznetskiy deposit and lignite samples of Kansko-Achinsk deposit were investigated in argon and in argon/air gas mixtures. The pyrolysis and oxidation experiments were executed at four heating rates (5, 10, 20 and 30 °C/min) under TG/DSC analyses coupled with mass-spectrometry. The activation energy for bituminous coal and lignite samples was decreased with conversion degree during oxidation. The combustion products of highest oxidation degree (CO_2 and H_2O) were dominated in gases released in oxidizing atmosphere. Contrariwise, activation energy was increased during pyrolysis with high content of CO, CO_2, H_2O, CH_4, and H_2 in released gases.

The two isoconversional models were applied to determine the activation energy dependence on fuel samples conversion: Starink model and Ozawa iterative procedure. The mean arithmetic values of the resulted activation energy were 60 kJ/mole and 400 kJ/mole for oxidation and pyrolysis processes, respectively. These values are in good agreement with the results, presented previously for the other coals. The Starink model showed higher accuracy and lower activation energy values. The heating rate by non-isothermal oxidation and pyrolysis had the significant influence on the reaction rate because of evolution processes of the reactive surface and pore structure of the coal samples.

1. Introduction

A traditional coal energetics is one of the largest CO, CO_2, NO_x, SO_x, soot, ash and mercury suppliers to the environment [1,2]. The energy companies are encouraged to increase the fossil fuel burning efficiency and involve renewable energy sources for electricity and heat production [2]. New technologies are implemented to decrease the negative influence of the greenhouse gases on environment including fuel combustion in pure oxygen with the flue gas isolation [3], solid fuel gasification [4], CO_2 capturing [5], etc. Moreover, the technologies for solid fuel liquefaction are becoming more common to substitute the limited oil reserves. Since a ratio «energy return on investment» for oil recovery was decreasing for the last 13 years from 26 to 18, such technologies may become competitive even earlier than the dramatic depletion of oil reserves [6].

Coal is the cheapest one among fossil fuels. However, some features cause difficulties with its usage: relatively high solid inert ash content and/or high sulfur content [7]. Traditional coal technologies cause intense air pollution and require expensive equipment to provide the acceptably clean exhaust gases. Effective implementation of the environmental friendly technologies requires explicit knowledge about both fuel properties and burning process characteristics [2]. Taking into account the fact, that coal is used to produce about 30% of energy worldwide in 2012 [8], the need for modern energy-generating system implementation is obvious. The tendency in this field will be continued in future: in 2035 the coal combustion equipment would occupy more than 25% of energy in the world according to [8].

Pyrolysis is the thermochemical process of coal devolatilization and partial oxidation. It determines the influence of particle

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reactive surface, its structure and the fuel reactivity on the efficiency and properties of the whole conversion process [9].

Thermogravimetric (TG) analysis is considered to be precise and reliable method for the prediction of coal behavior in the conversion process, providing reaction kinetics data and being widely used for the solid fuel characteristics [10,11]. TG-based pyrolysis methods are well described in scientific literature [12]. Two ways of kinetics study are mostly in use: isothermal, conducted at a constant sample temperature during the experiment, and non-isothermal, when the sample temperature is gradually growing. Non-isothermal methods, being closer to the real pyrolytic conditions, are more precise and require fewer amounts of experiments. Usually, the experimental data are used to define the parameter of models describing the pyrolysis process: the frequency factor, the activation energy and the kinetic function. The various models result in different values of their parameters [12,13]. Two approaches are the most widespread in modeling: Starink and Ozawa models. In the present research both models were applied. The determination coefficient was used to assess the fit of calculated and experimental data [14].

Table 1
Characteristics of coal.

Characteristic	Coal			
	Bituminous		Lignite	
	#1	#2	#3	#4
Ash content, mass %	18	16	20	11
Humidity, mass %	5	6	9	7
Volatiles, mass %	20	31	39	36
Fixed carbon, mass %	57	47	32	46
Elemental composition[a], mass %				
C	71.0	67.9	63.1	66.0
N	<0.1	13.9	12.6	12.6
O	19.3	13.1	17.4	14.3
Al	2.0	0.9	0.1	0.8
Si	3.0	2.2	0.1	2.7
S	0.4	0.4	<0.1	0.2
Ca	2.6	1.1	6.5	1.8
K	0.6	0.5	<0.1	0.4
Fe	0.6	<0.1	<0.1	1.3
Na	0.1	<0.1	<0.1	<0.1
Mg	0.1	<0.1	0.2	<0.1
Ti	0.1	<0.1	<0.1	<0.1
Zr	0.2	<0.1	<0.1	<0.1

[a] Elemental composition is given for the samples dried at 105 °C for 2 h.

The research is focused on studying the properties of coal derived from Kuznetskiy and Kansko-Achinskiy coal deposits (West Siberia, Russia). The majority of research works on the coal from the West Siberia were carried out in the second half of 20th century and recently. The combustion properties were described by Scholler [15], nuclear-magnetic resonance research was made by Djafarov et al. [16], calorimetric behavior was given by Ivanov et al. [17]. Despite a considerable amount of publications, the majority of them are mostly dedicated to the classical fuel applications: direct combustion in boilers and metallurgical furnaces. In the present work we are focused on the pyrolytic and oxidative characteristics of the Kuznetskiy and Kansko-Achinskiy coal deposits.

In this work the four coals of different composition typical for these deposits were investigated as the most widespread in energetics and having the average characteristics in this class of fuels. TG and mass-spectrometry (MS) data on less than 80 μm coal powder pyrolysis in argon and air are presented. Activation energy dependencies on coal conversion were also determined.

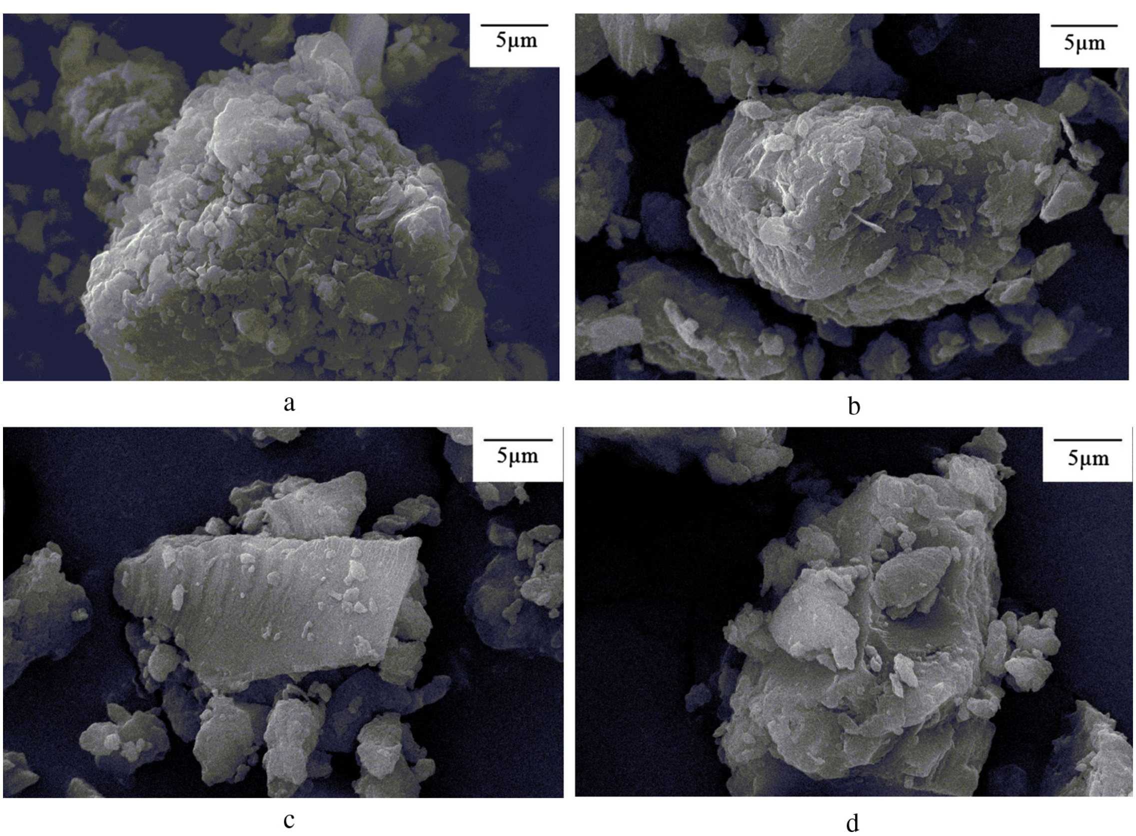

Fig. 1. SEM images of bituminous coal samples # 1 (a, × 3000), # 2 (b, × 3000) and lignite samples # 3 (c, × 3000), # 4 (d, × 3000).