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Comparison of differential and integral methods for coal oxidation kinetic analysis

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Abstract. The influence of two different methods of kinetic analysis on obtained values of kinetic constants of coal oxidation process was studied. The oxidation of T-grade bituminous coal of Kuznetskiy deposit and 2B-grade lignite of Borodinskoe deposit was investigated by means of thermogravimetric analysis. All measurements were carried out with heating rates 2,5, 10, 25 and 40 K/min in temperature range 300-1100 K in air medium. The dependences of activation energy and frequency factor on conversion were obtained using two isoconversional methods: differential method of Freidman and integral method of Kissinger-Akahira-Sunose. The average values of activation energy which were obtained by KAS method were higher by 14.5 % for bituminous coal and 23.3 % for lignite in comparison with values obtained by Freidman method. The same relations were observed for frequency factor values.

1. Introduction

Energy consumption in the world is steadily increasing every year for the last 50 years [1]. More than 70 % of this energy comes from fossil fuels [1]. At the same time, it is the main source of greenhouse gas emissions into atmosphere [1]. The contribution of coal-fired energy production into total amount of emissions is one of the largest among other sources. Today it is impossible to completely avoid using coal as fuel. This is why improving ecological properties of solid fuel-based power generation has become a relevant problem nowadays [2].

Different methods may be applied to reduce pollution: from improving exploitation parameters [3] of existing equipment to completely new technologies like gasification [4, 5], and using of coal-water-slurry [5, 6] or chemical looping combustion [7]. To effectively apply these methods the precise information on coal conversion kinetics is needed. Many methods for defining kinetic parameters of conversion process are presented in literature [8]. They can be divided into two large groups: differential and integral methods. Both methods are widely used for description of coal combustion parameters [9-11]. Depending on the applied method, different values of kinetic parameters may be obtained. Differential methods were considered to be less precise due to difficulties in defining instant conversion rate at any temperature while the drawback of integral method is a significant error of integration of the so-called temperature integral [12].

The influence of kinetic analysis method on obtained values of kinetic constants was studied. The kinetic parameters of coal oxidation process were defined using two methods of kinetic analysis: methods of Freidman and Kissinger-Akahira-Sunose. The obtained dependences of activation energy and frequency factor on conversion were compared. The integral methods have resulted into higher values of both kinetic parameters.

2. Experimental section

2.1. Sample characterization

Two types of different coals were studied: T-grade bituminous coal of Kuznetskiy deposit and 2B-grade lignite of Borodinskiy deposit. Initial fuel was crushed to particles with a size of lass then 50 mm using a jaw crusher. Then it was further ground with a ball mill and sieved through the sieve with 80 μm mesh size to prevent influence of diffusional effects during thermal analysis.

The proximate analysis was carried out using standard methodology [13] while the ultimate analysis was performed using an elemental analyzer Euro 3000. The analysis results are presented in table 1.

Table 1. Proximate and ultimate analysis of samples

Sample	Proximate analysis[a], wt.%				Ultimate analysis[b], wt. %				
	Ash content	Moisture content	Volatile matter content	Fixed carbon content	C	H	N	S	O
T-grade	16,5	0,3	13,1	70,1	69,1	2,2	2,5	<1	14,3
2B-grade	4,5	1,0	39,8	54.7	51,1	4,6	1,5	<1	28,2

[a] Results are presented on working mass of fuel.
[b] Results are presented on dry mass of fuel.

The form and size of particles and structure of their surface was studied by means of scanning electron microscopy using SEM Jeol JSM-6460LV. Images of sample powders with different magnitudes are presented in figure 1.

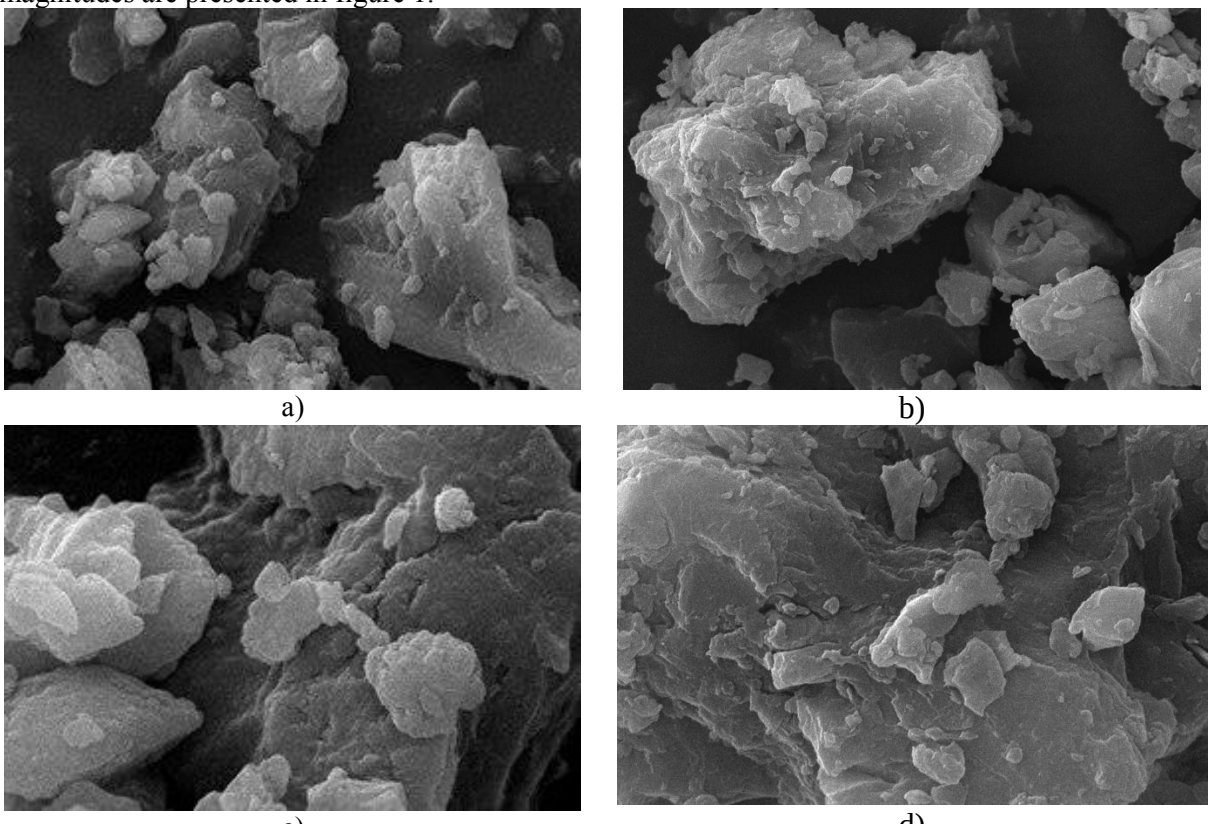


Figure 1. SEM images of bituminous coal (a, c) and lignite (b, d) samples with magnitude x3000 (a, b) and x10000 (c, d).

Particles of bituminous coal power has irregular form with the size of largest particles close to 35 μm. Particles of lignite are larger (~60 μm) and have an elongated form. The surface of both samples is represented by quite smooth surface with small cracks and small flake-like brows. The surface of large particles is covered with small stuck particles.

2.2. Thermal and kinetic analysis.

Thermal analysis of coal samples was carried out using simultaneous thermal analyser Netzsch STA 449 F3 Jupiter in the temperature range 320-1200 K with heating rates of 2.5, 10, 25 and 40 K/min. The air flow rate was 250 ml/min with purge gas flow rate of 10 ml/min. Argon was used as purge gas. Mass of fuel sample hinge was equal to ~25 mg. The sample was evenly distributed into thin layer across the bottom of the crucible to avoid diffusional resistance of the layer.

The dependence of coal oxidation kinetic parameters on conversion process was determined using Freidman and Kissinger-Akahira-Sunose methods [8, 12]. Freidman method is based on the following equation:

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = \ln\left[f(\alpha)\cdot A_{\alpha} \right] - \frac{E_{\alpha}}{R\cdot T_{\alpha,i}} \quad (1)$$

α is the conversion; t is the time, s; i is the heating rate of experiment, K/min; $f(\alpha)$ is the kinetic function (in current work the Mampel function $f(\alpha)=(1-\alpha)$ was used); A_{α} is the frequency factor at given conversion α, 1/s; E_{α} is the activation energy at given conversion α, J/mole; R is the universal gas constant, J/(mole K); and $T_{\alpha,i}$ is the temperature at given conversion and heating rate, K.

Kissinger-Akahira-Sunose method is based on following equation:

$$\ln\left(\frac{i}{T_{\alpha,i}^{2}}\right) = \ln\left(\frac{R\cdot A_{\alpha}}{E}\right) - \frac{E_{\alpha}}{R\cdot T_{\alpha,i}} \quad (2)$$

3. Results and discussion

3.1. Thermal analysis

Experimental TG and DTG-curves for samples of bituminous coal and lignite at all heating rates are presented in figure 2.

The oxidation process is represented by two stages for samples of bituminous coal and lignite. The first stage is related to the drying of samples and takes place in the temperature range of 320-500 K for both samples at all heating rates. The second stage is related to complex processes of simultaneous oxidation and release of volatile matter. It begins after the drying stage and ends at 1200 K for bituminous coal and at 1100 K for lignite. Mass loss at the first and second stage is ~5 and 80 wt.% for bituminous coal while for lignite it is ~3 and 90 wt.%, respectively.

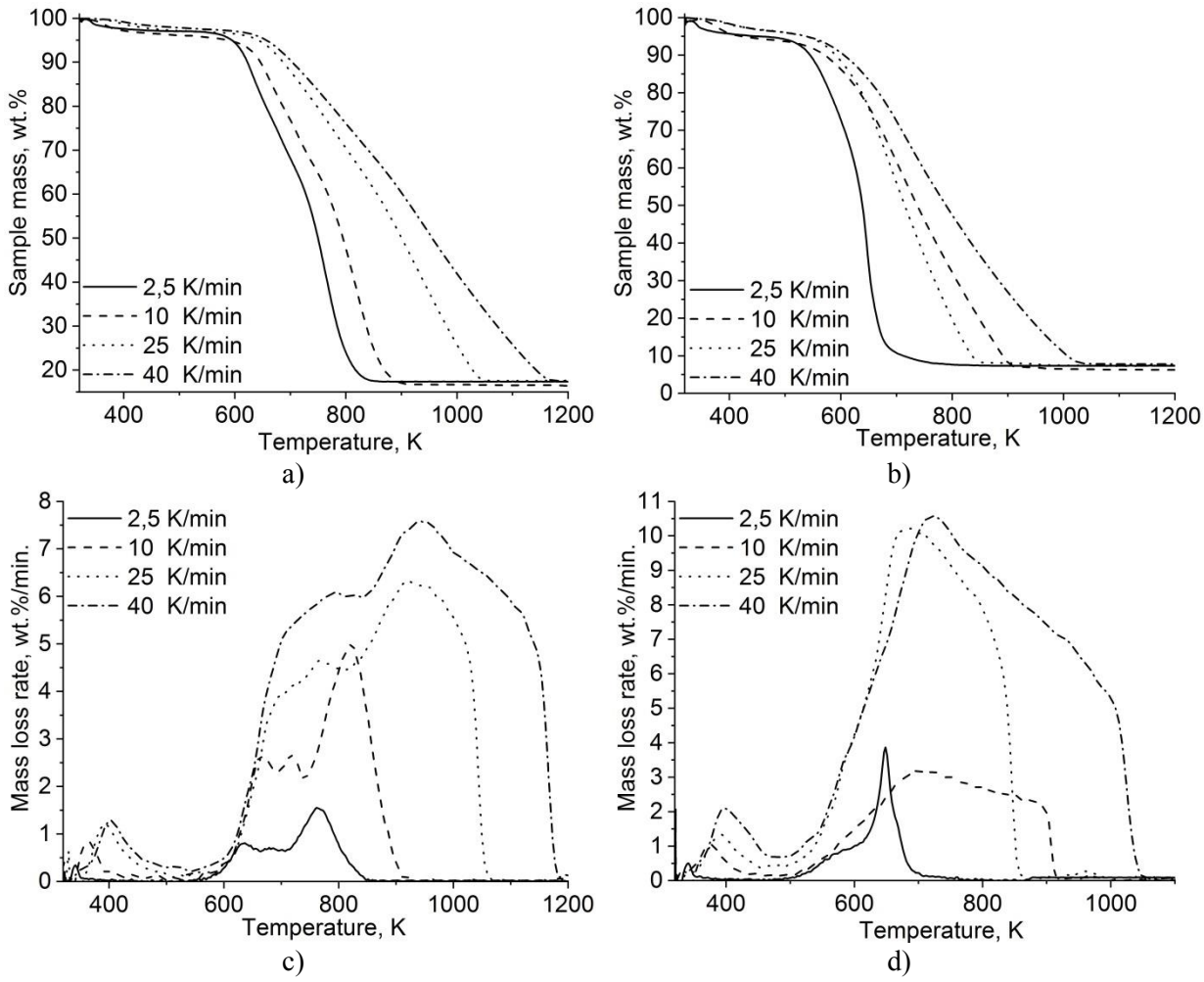


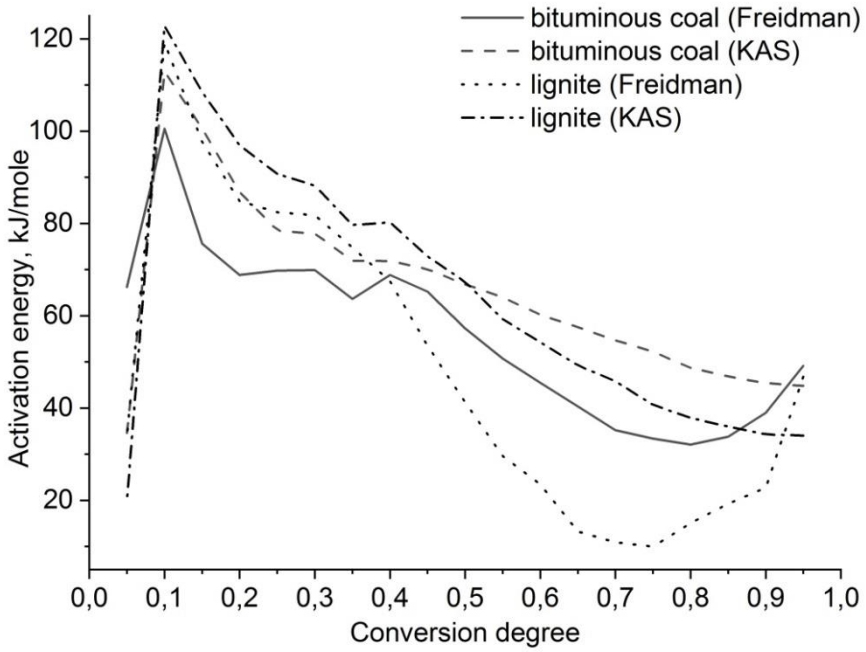
Figure 2. Experimental mass and mass loss rate curves at different heating rates for samples of bituminous coal (a, c) and lignite (b, d).

An increase in the heating rate results in an increase in the maximal mass loss rate from 1.5 wt.%/min at 2.5 K/min to 7.5 wt.%/min at 40 K/min for bituminous coal and from 3.85 wt.%/min to 10.6 wt.%/min for lignite. Peak temperature is also in the area of higher temperatures: from 763 and 646 K to 943 and 717 K for bituminous coal and lignite, respectively. The burnout temperatures also increase while temperature of the beginning of the second stage doesn't change.

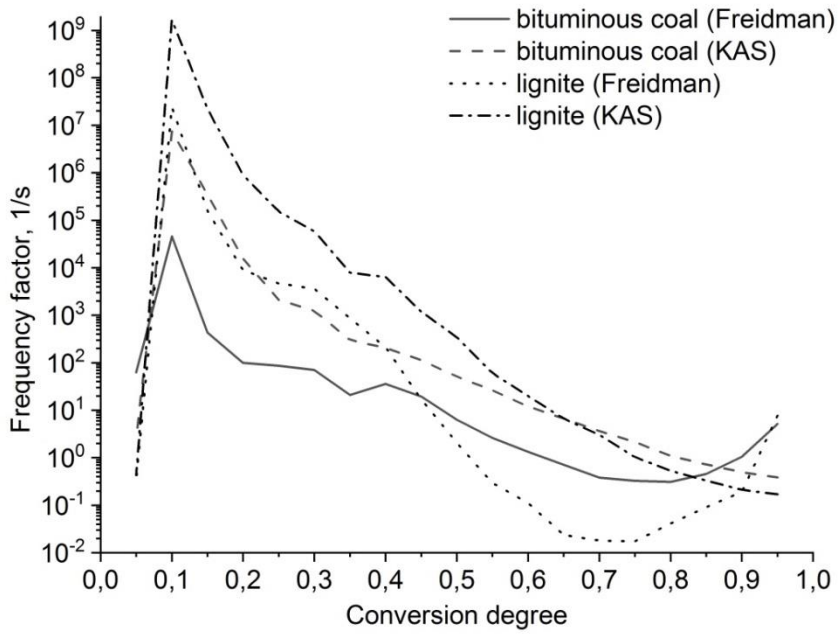
Total mass loss for lignite (93 wt.%) is higher in comparison with bituminous coal (85 wt.%). This is connected to higher ash content of the latter. The maximal mass loss rate for lignite is also higher. That may be connected to the higher content of volatile matter.

3.2. Kinetic constants

Dependences of activation energy and frequency factor on conversion degree defined by different methods are presented in figure 3.



a)



b)

Figure 3. Dependences of activation energy (a) and frequency factor (b) on conversion degree.

Values of kinetic constants decrease with conversion degree. The form of dependences of activation energy and logarithm of frequency factor on conversion degree is nearly identical. The first peak of kinetic parameters is observed at conversion degree vales of 0.1-0.15. At larger conversion degree kinetic parameters decrease. For parameters defined by Freidman method the minimum is observed at conversion degree values of 0.75 for bituminous coal and 0.7 for lignite. For KAS method the decrease is constant, and the minimal value may be observed at maximal conversion degree. At the same values of conversion degree kinetic parameter values from KAS method are lager. The average

difference between activation energy values for samples of bituminous coal is ~20 % while maximal relative difference – about 35 % – is observed at conversion degree value of 0.75. For lignite the average difference is higher (28 %) as well as maximal difference – 75 %. For lignite, the maximal difference is situated at the same conversion degree values – 0.65-0.75. Higher differences may be explained by higher absolute values of activation energy (obtained by Freidman method) for bituminous coal – 56 kJ/mole – in comparison with lignite – 48 kJ/mole. For these values defined by KAS method the difference is not so significant – 66 and 64 kJ/mole for bituminous coal and lignite, respectively. Using kinetic parameter values obtained by KAS method for calculation of high temperature conversion process would result in higher values of reaction rate for both samples.

4. Conclusion

Oxidation of bituminous coal and lignite samples in air medium was studied by means of thermogravimetric analysis. Experiments were carried out in the temperature range of 320-1200 K at four different heating rates – 2.5, 10, 25 and 40 K/min. Activation energy and frequency factor dependences on conversion degree were defined using methods of Freidman and Kissinger-Akahira-Sunose.

An increase in heating rate results in higher mass loss rate and burnout temperatures for all samples. Temperature of maximum mass loss rate also shifts to the area of higher temperatures. The form of DGT-curve changes from monomodal with one clear peak to more complex with less clear maximum.

Dependences of activation energy and frequency factor have one clear peak in conversion degree range of 0.05-0.20 and decrease in conversion degree range of 0.25-0.95. Average activation values defined by Freidman method for bituminous coal were 56 kJ/mole and 48 kJ/mole for lignite. For KAS method average values were close to each other – 66 and 64 kJ/mole. The form of activation energy dependence on conversion degree is close to the form of frequency factor if defined by same method. The activation energy values defined by KAS method were higher by 20 % for bituminous coal and by 28 % for lignite. The same relations could be observed for the values of frequency factor.

Acknowledgments

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