ORIGINAL PAPER

DETERMINATION OF KINETIC PARAMETERS OF COAL PYROLYSIS TO SIMULATE THE PROCESS OF UNDERGROUND COAL GASIFICATION (UCG)

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ABSTRACT

Purpose	The aim of the research presented in this paper was to determine the values of the kinetic parameters of coal pyrolysis from two areas of the planned experiment, UCG, i.e. the Barbara Experimental Mine of the Central Mining Institute and the Wieczorek Mine.
Methods	The thermal decomposition of coal analysis used the thermogravimetric technique. The test was carried out in a temperature range of 298−1173 K in a nitrogen atmosphere for three fixed heating rates, β – 5, 10, and 15 K/min. A selection of sample heating rates of coal and reaction environments were designed to reflect the conditions seen during the process of underground coal gasification. The kinetic parameters were determined by using modified Coats-Redfern, Kissinger and Mianowski-Radko methods.
Results	The values of the activation energy, *E*, and the pre-exponential factor, *A*, were determined for a given model of the first order decomposition reaction of coal. The study successfully compared kinetic parameters of the tested coals.
Practical implications	Designated kinetic parameters may be used to model the process of pyrolysis and – as preliminary data – for installation design of pilot underground coal gasification.
Originality/ value	The devolatilization of a homogenous lump of coal is a complex issue. Currently, the CFD technique (*Computational Fluid Dynamics*) is commonly used for the multi-dimensional and multiphase phenomena modelling. The mathematical models, describing the kinetics of the decomposition of coal, proposed in the article can, therefore, be an integral part of models based on numerical fluid mechanics.

Keywords
underground coal gasification, pyrolysis of coal, thermogravimetric analysis, kinetic parameters

1. INTRODUCTION

The need for the optimum utilization of coal resources, while limiting the impact of combustion of this material on the environment, requires the use of innovative technological solutions. One of the most promising and complementary methods of obtaining energy from coal is through the use of underground coal gasification (UCG). This process takes place in a properly prepared coal seam, also known as a UCG reactor. When converting coal to synthesis gas, the fuel undergoes the process of drying, pyrolysis and gasification.

Pyrolysis is a key step in all coal conversion processes, including the underground coal gasification process (UCG). During the thermal conversion to synthesis gas, primary pyrolysis products such as char, gas and tar components are substrates for subsequent stages of the transformation, that is, combustion and gasification (Westmoreland, & Forrester, 1977; Ściążko, 2010). The pyrolysis process for the majority of solid fuel is completed when the typical temperature for the gasification reaction of char is reached (Łabojko, Kotyczka-Morańska, Plis, & Ściążko, 2012). The amount and composition of the thermal decomposition products depends on the physicochemical properties of coal and on process parameters (Kubica, 2003). Parameters which influence the pyrolysis process vary at different stages of the process and depending on the reactor space. Important factors influencing the course of pyrolysis in this technology include: temperature, pressure, heating rate, reaction atmosphere, particle size and the degree of comminution of coal. The technological process of underground coal gasification, due to the intensity of the overlap of the pyrolysis process, is divided into two stages: the first stage being – the synthesis gas production and, the second stage being – reactor shut down. In the first stage the reactor is filled with the UCG gasifying agent (oxy-

gen, oxygen with steam, oxygen-enriched air and cold or heated air), during the second phase a protective agent is added, mostly nitrogen. Due to the discontinuation of factors during the gasification reactor shut down and the administration of an inert substance, it is possible to identify the pyrolysis products (Urych, Kabiesz, & Iwaszenko, 2013). When designing an underground coal gasification reactor the knowledge of kinetic equations occurring in the chemical reactions is essential. The attempt taken in this article to designate the kinetic parameters of the thermal decomposition reaction of coal will constitute one of the stages of numerical modelling of the coal devolatilization in a UCG process.

During the process of underground coal gasification, the rate of temperature increase in the lump of coal in the deeper layers, outside the zone of oxidation, does not exceed 12 K/min (Urych, Kabiesz, & Iwaszenko, 2013). A commonly available measurement technique – thermogravimetry, has been used to determine the kinetic parameters of the pyrolysis of coal. This technique can be used for the investigation of the devolatilization of coal in both inert and oxidizing atmospheres (Tomeczek, 1991). The thermogravimetrical analysis (TGA) measures weight loss rate with temperature changes. A TG curve shows the rate of mass loss versus temperature (T) or time (τ) (Szczepaniak, 1997). Non-isothermal kinetic analysis of thermal processes of solids can be affected by several methods, in which the reaction rate constant is described by classic Arrhenius equation, including the differential or integral method (Kissinger, 1957; Tiwari, 2007; Yang, & Wu, 2009), and by an alternative tri-parametric model presented by Mianowski (2000). These methods differ in the degree of curve fit of the model TG and DTG to the experimental data.

2. ASSUMPTION

The thermal decomposition of coal is too complex to be described by a single chemical reaction. Therefore, most researchers suggest the use of a simplified model based on a single, irreversible reaction of the thermal decomposition of coal for the description of the kinetics of pyrolysis (Mianowski, & Radko, 1993; Arenillas, Rubiera, Pevida, & Pis, 2001, Ściążko, 2010):

$$\text{Coal} \rightarrow x \text{ (volatiles)} + (1 - x) \text{ (char)}$$

where x – the fraction of volatiles.

It was found that for most coals tested, decomposition occurs evenly throughout the volume of the particles as first order reaction, and its course is determined by the chemical structure of coal (Jüntgen, 1983; Kubica, 2003; Ściążko, 2010). The rate of decomposition reaction is thus expressed as

$$\frac{d\alpha}{d\tau} = k(1-\alpha) \tag{1}$$

where:

α – degree of conversion of coal substance in time τ and the decomposition rate constant,

k – described by the Arrhenius equation

$$k = Ae^{-E/RT} \tag{2}$$

where:

E – activation energy, kJ/mol;

A – pre-exponential factor, 1/min;

R – universal gas constant, kJ/(mol·K);

T – absolute temperature, K;

m – mass of the sample, mg; (subscript: i – initial stage, f – final stage).

The pyrolysis process, in the thermogravimetric study, occurs at non-isothermal conditions at which temperature increases linearly with time, thus

$$T = \beta\tau + T_o \tag{3}$$

where β is the heating rate. Eqn (1) can be written as a function of temperature applying Eqn (3)

$$\frac{d\alpha}{dT} = \frac{Ae^{(-E/RT)}}{\beta}(1-\alpha) \tag{4}$$

where α – degree of conversion of coal substance in temperature T is defined as

$$\alpha = \frac{m_i - m(T)}{m_i - m_f}, \quad \alpha \in \langle 0,1 \rangle \tag{5}$$

3. EXPERIMENT

Thermogravimetric measurements were carried out on samples of coal from the Barbara Mine and the Wieczorek Mine. The samples were taken from the areas where the coal bed was made available for use by the underground gasification of coal, i.e. seam 310 of the Barbara Mine and seam 501 in the case of the Wieczorek Mine. The measurements used the Mettler Toledo TGA/DSC 1 STARe System thermo balance. The samples were placed in a crucible with a capacity of 70 ml, made of Al_2O_3, with about 20–30 mg aliquot in a nitrogen atmosphere (nitrogen 4.0), the flow rate was 60 ml/min. The thermobalance had a resolution of ±10 mg. The samples were heated in a temperature range of 298–1173 K at a linear increase in temperature in accordance with the programmed heating rate – 5, 10 and 15 K/min. The selection of the sample heating rates of coal and the inert environment was based on results from previous studies and was designed to reflect the conditions during the process of underground coal gasification (Urych, Kabiesz, & Iwaszenko, 2013). After completion of the pyrolysis, the samples were burned in order to clean the air of the cell. The specimens were tested in analytical conditions (air-dried and then ground to a grain size below 0.2 mm). The characteristics of the samples are given in Table 1.

Table 1. Technical analysis of taken coal samples

	The Barbara Mine	The Wieczorek Mine
As received		
Moisture W^r, %	9.45	8.69
Ash A^r, %	9.22	9.14
S Total S^r_t, %	0.68	1.26
Lower heating value Q^r_i, kJ/kg	25 602	25 054
Analytical		
Moisture W^a, %	3.71	3.89
Ash A^a, %	9.8	9.62
Volatile matter V^a, %	35.46	30.08
Lower heating value Q^a_i, kJ/kg	27 380	26 499
C^a_t, %	68.49	69.77
H^a, %	4.05	3.31
N^a, %	1.26	0.98
S^a_t, %	0.72	1.33
S^a_c, %	0.63	0.18
O^{a*}, %	12.06	12.25

[*] Oxygen calculated as: $(O^a)=100-(W^a)-(A^a)-(C^a)-(H^a)-(S_c^a)-(N^a)$, %.

Technical analysis of the coal was performed in an accredited laboratory in the Central Mining Institute, in accordance with current European Union standards. During the measurements the following curves were recorded: TG curves (weight loss), DTG (weight loss rate) and the DSC curve (thermal effect).

4. SCOPE OF THE ANALYSIS

The kinetic parameters of the decomposition reaction were evaluated by Coats and Redfern (1964), Mianowski and Radko (1995) and the method of Kissinger (1957). It was assumed, based on Mianowski and Radko, that the thermal decomposition of dry coal ($W^a = 0\%$) takes place in two stages. Non-linear mass loss as a function of temperature (the kinetic regime) is observed at the beginning of the process, it is then followed by linear mass loss (the diffusion regime). Under such conditions, it is possible to describe the pyrolysis process by using two different activation energy values, respectively, for the area of kinetics $E > 0$ and a diffusion area $E \rightarrow 0$ (Minkina, Zasusz-Zuberek, & Mianowski, 2006). As a consequence of characteristic peaks for the coal DTG curve, the pyrolysis process may be divided into separate stages. In a further study the analysis is limited to the characteristic temperature range $<T_i, T_f>$ in accordance with the DTG curve (Table 2). For comparative purposes, the temperature ranges $<T_i, T_f>$ were assumed to be between 633 to 1173 K.

Table 2. Characteristic temperatures of coal materials determined by TGA

	Temperature range in pyrolysis, K		Temperature at maximum mass loss, K
	T_i	T_f	T_p
Coal from the Barbara Mine			
5 K/min	633	1123	706
10 K/min	633	1173	720
15 K/min	633	1173	727
Coal from the Wieczorek Mine			
5 K/min	633	1123	713
10 K/min	633	1173	725
15 K/min	633	1173	732

5. KINETIC PARAMETERS ESTIMATION

In the temperature range $<T_i, T_f>$ there are two possible procedures for analyzing the pyrolysis process: the method of using one or several stages. When analyzing the whole process (one-step procedure), it is assumed that the conversion rate for $\alpha(T_i) = 0$ and for $\alpha(T_f) = 1$. The multistep procedure is carried out on the basis that the temperature range $<T_i, T_f>$ is divided into several consecutive steps so that the degree of conversion in each individual step is in the range of $<0,1>$ (Mianowski, & Radko, 1995). This analysis estimates the kinetic parameters of the decomposition reaction for two variants:

a. Analysing a whole pyrolysis process (one-step procedure), in which the individual stages consist of a single process for which the degree of conversion of $\alpha \in <0,1>$.

b. The various stages of pyrolysis are considered separately, that is, for the kinetics area $\alpha_K \in <0,1>$ and the diffusion area $\alpha_D \in <0,1>$.
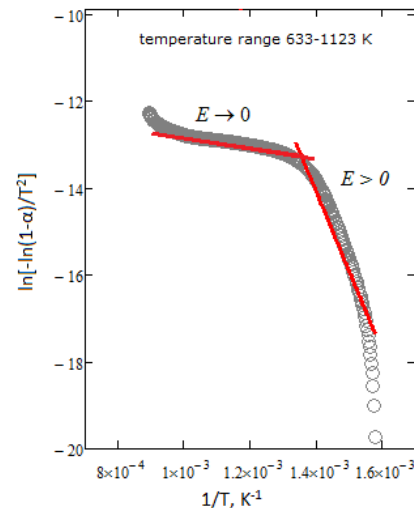
Ad a. The method of Coats and Redfern (1964) has been used to estimate the kinetic parameters of the decomposition reaction of selected samples of the raw material. This method, by integrating the equation (4) gives

$$\int_0^\alpha \frac{d\alpha}{1-\alpha} = \frac{A}{\beta} \int_0^T e^{\frac{-E}{RT}} dT \qquad (6)$$

After transformations and taking the logarithm on both sides into account the following equation was obtained

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \left(\frac{E}{RT}\right) \qquad (7)$$

Since in general $2RT/E \ll 1$ and it exhibits a small variation with T, for practical considerations it is assumed that the term $(1-2RT/E)$ is approximately constant and equal to unity (Urbanovici, Popescu, & Segal, 1999). The values of E and A for a given stage is calculated based on equation (7), plotting a straight line in the system $\ln(-\ln(1 - \alpha)/T^2) = f(1/T)$. Analysis of the pyrolysis process as a whole (one-step integral method) shows that the activation energy E at the beginning of the process reaches a value greater than 0 kJ/mol, and then assumes a value close to zero (Fig. 1). Kinetic parameters of the selected coal samples are summarized in Table 3.

Fig. 1. Plots of $\ln(-\ln(1 - \alpha)/T^2)$ vs $f(1/T)$ of a sample of coal from the Barbara Mine, pyrolysis calculated by a one-step integral method, with a heating rate of 5 K/min

Table 3. The kinetic parameters for the pyrolysis of coal samples from the Barbara Mine and the Wieczorek Mine

	$T_i – T_f$ K	Range α	E kJ/mol	A 1/min	R^a
The Barbara Mine					
5 K/min	633–751	0–0.61	161.4	5.5E+10	–0.96
10 K/min	633–757	0–0.56	159.6	5.4E+10	–0.96
15 K/min	633–760	0–0.55	157.6	1.6E+10	–0.97
The Wieczorek Mine					
5 K/min	633–753	0–0.38	149.8	3.6E+09	–0.95
10 K/min	633–759	0–0.39	146.2	3.1E+09	–0.96
15 K/min	633–760	0–0.36	143.6	2.5E+09	–0.96

R^a – correlation coefficient.

Ad b. A two-step kinetic model introduced by Mianowski and Radko (1995) assumes that in the temperature range $<T_i, T_f>$, the pyrolysis process is more complex and involves the rapid physical-chemical conversion of coal occurring in the kinetic area and then proceeds to a slower diffusion area. The kinetic equation becomes:

- for the kinetic area

$$-\ln(1-\alpha_K) = \frac{A_K R T^2}{\beta E} e^{-E/RT} \,, \quad \alpha_K \in \langle 0,1 \rangle \qquad (8)$$

where $\alpha_K = \dfrac{m_{K,i} - m(T)}{m_{K,i} - m_{K,f}}$

- for the area of diffusion, assuming that in the equation (4) $E \cong 0$

$$-\ln(1-\alpha_D) = \frac{A_D}{\beta} \Delta T \,, \quad \Delta T = T - T_{D,i} \text{ and } \alpha_D \in \langle 0,1 \rangle \qquad (9)$$

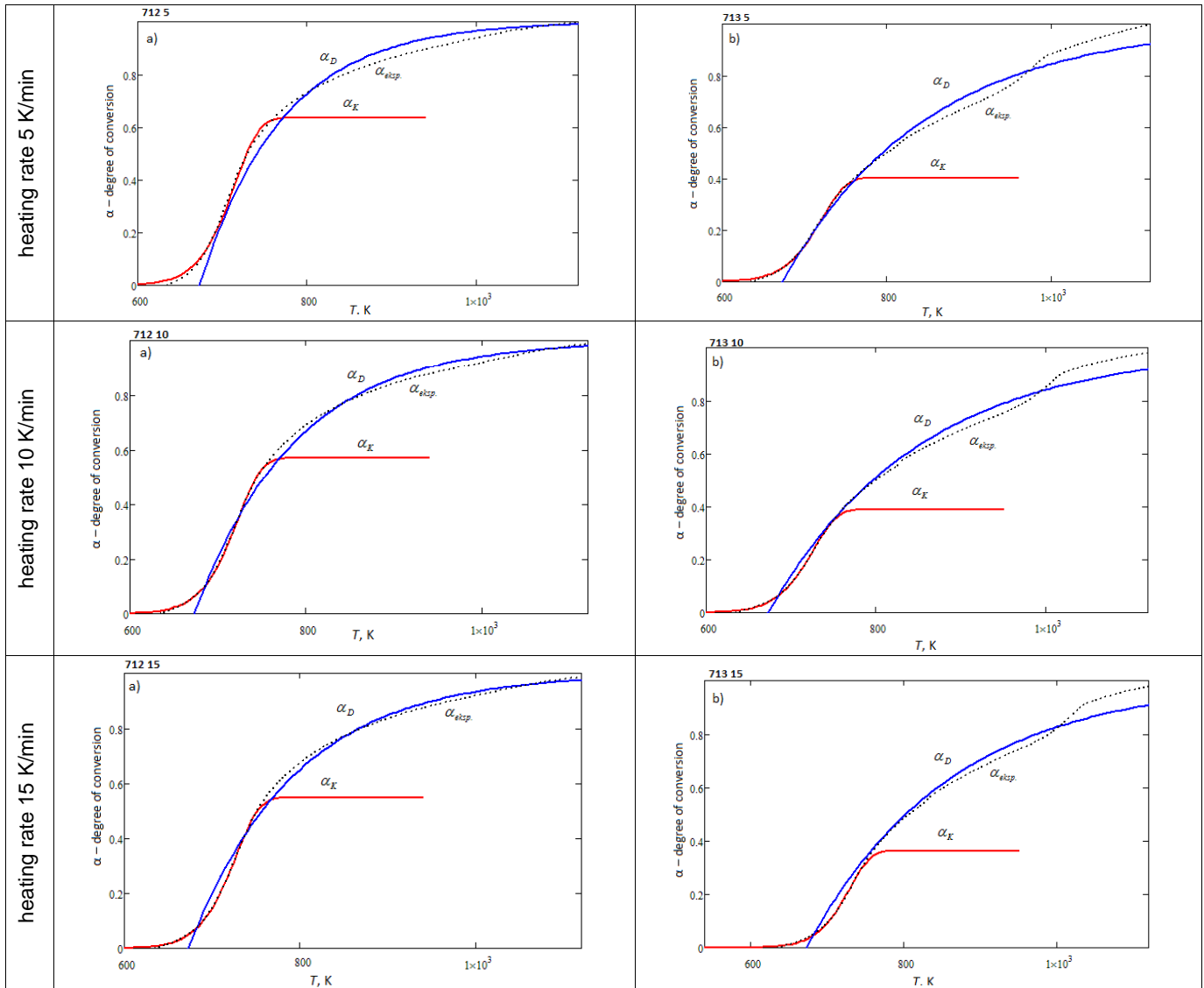where $\alpha_D = \dfrac{m_{D,i} - m(T)}{m_{D,i} - m_{D,f}}$

Estimates of the parameters E, A_K and A_D performed using the Levenberg-Marquardt algorithm, minimizing the error between the experimental data and the proposed function (Table 4).

Table 4. The kinetic parameters for the pyrolysis of coal samples from the Barbara Mine and the Wieczorek Mine

	$T_{K,i}$ K	$T_{K,f}$ K	$T_{D,i}$ K	$T_{D,f}$ K	E kJ/mol	A_K 1/min	SSE[a]	A_D 1/min	SSE[a]
The Barbara Mine									
5 K/min	633	751	673	1123	157.5	6.1E+10	2.1E−04	0.051	9.9E−04
10 K/min	633	757	673	1173	160.7	1.4E+11	4.0E−05	0.087	3.9E−04
15 K/min	633	760	673	1173	161.9	2.2E+11	5.6E−05	0.124	4.1E−04
The Wieczorek Mine									
5 K/min	633	753	673	1123	153.5	2.5E+10	8.1E−05	0.029	1.4E−03
10 K/min	633	759	673	1173	155.0	4.7E+10	7.7E−05	0.056	1.3E−03
15 K/min	633	760	673	1173	157.3	9.3E+10	1.8E−04	0.080	1.6E−03

SEE^a – sum of squared errors.

The Levenberg-Marquardt algorithm is one of the most commonly used algorithms for nonlinear optimization, in the case of applying the criterion of least squares (Lourakis, & Argyros, 2005). Minerr Solve Block program MathCad 14 has been used for the calculations. Figures 2a, 2b, 3a and 3b illustrate the results of models for TG and DTG curves of the coal pyrolysis of the Barbara Mine and the Wieczorek Mine with the selected heating rates and experimental data.

Fig. 2. Thermal decomposition of coal samples divided into kinetic and diffusion area with a constant heating rate of 5, 10, 15 K/min with:
a – The Barbara Mine, b – The Wieczorek Mine

The method of Kissinger (1957), which is the non-linear weight loss of the sample depending on the temperature to determine the kinetic parameters of the decomposition reaction, may be used for the kinetic area as well as the above-mentioned Mianowski and Radko method (1995). According to the Kissinger equation the correctness criterion of developed experimental data is linear correlation

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E}{RT_p} + \ln\left(\frac{AR}{E}\right) \tag{10}$$

where T_p – corresponds to the temperature at the maximum weight loss rates of coal materials.

A straight line has been plotted in $\ln(\beta/T_p^2) = f(1/T_p)$ (Fig. 4) for each elementary curve and subsequent rates of heating on the basis of the coordinates of the peaks (Table 2).
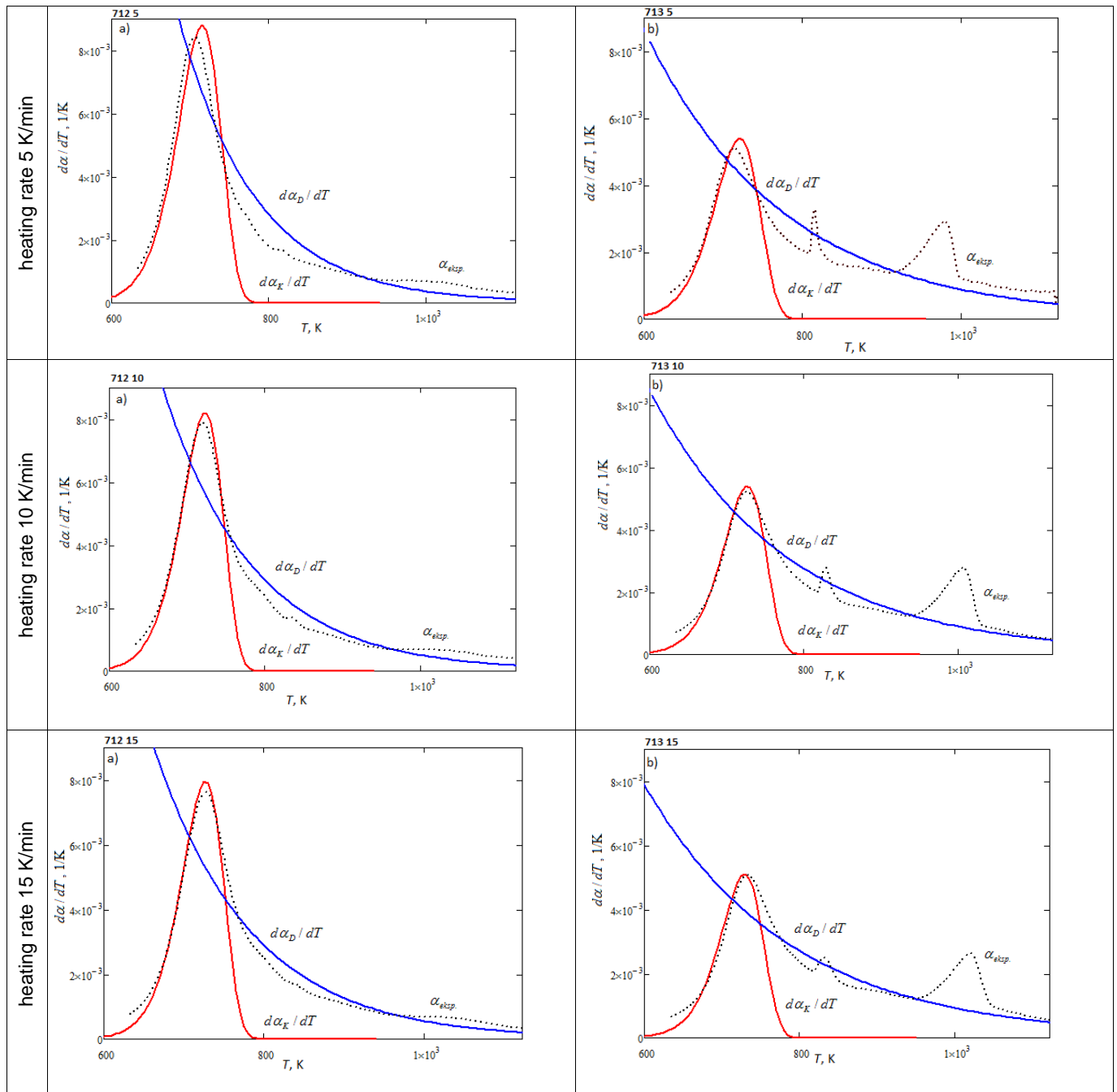

Fig. 3. DTG graph with a model derived for the selected heating rate of 5, 10, 15 K/min with: a – The Barbara Mine, b – The Wieczorek Mine
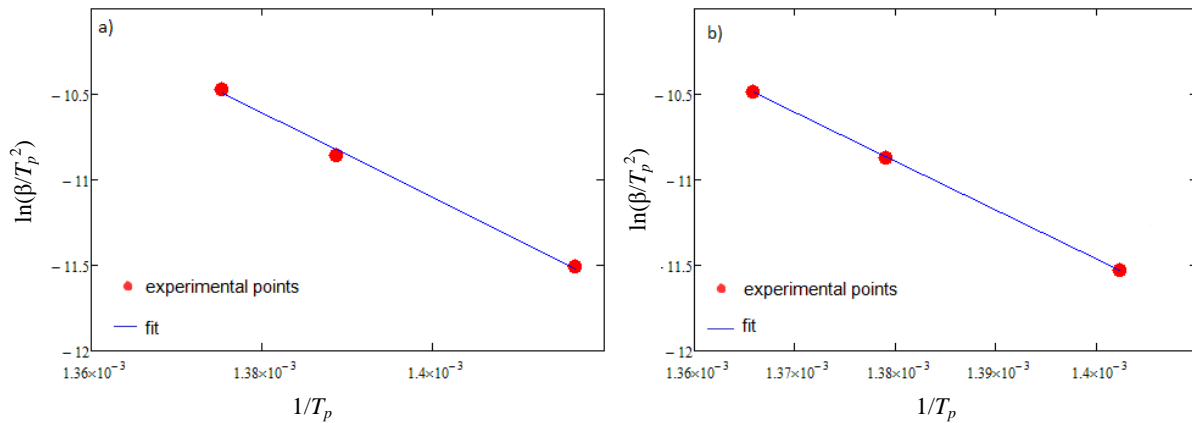
Fig. 4. Determination of the activation energy E and the pre-exponential factor A, Kissinger method for coal samples: a – The Barbara Mine, b – The Wieczorek Mine

Curves plotted on the basis of equation (10) are used to determine the activation energy E and the pre-exponential factor A_K. This method, in instances of strong correlation, requires at least three experiments with the heating rates. The advantage of the method is the fast estimation of kinetic parameters. The summary of the kinetic parameters of the decomposition reaction of coal samples tested are shown in Table 5.

Table 5. The kinetic parameters for the pyrolysis of coal samples from the Barbara Mine and the Wieczorek Mine

	T_i–T_f K	Range α_K	E kJ/mol	A 1/min	R^a
The Barbara Mine	633–760	0–1	206.9	5.0E+14	–0.999
The Wieczorek Mine	633–760	0–1	238.9	8.8E+16	–1.000

R^a – correlation coefficient.

6. CONCLUSION

- Pyrolysis is a key process in underground coal gasification. The products of devolatilization are substrates for further UCG process steps, i.e. combustion and gasification.
- Thermal Gravimetric Analysis (TGA) is a fast and effective tool to determine the kinetic parameters of coal pyrolysis.
- The kinetic parameters of the Arrhenius equation increase while using the Mianowski and Radko model (1995) connected with the Levenberg-Marquardt algorithm when increasing the rate of heating β. Higher values of kinetic parameters (E, A_K, A_D), for coal from the Barbara Mine were obtained in the temperature range 633–760 K.
- Higher values, than in the case of other models, of the activation energy E and the pre-exponential factor A_K were obtained in the temperature range 633–760 K by the Kissinger method. Using this model, higher values of kinetic parameters for the Wieczorek Mine were achieved.
- The values of the activation energy E and the pre-exponential factor A are similar to those given in the literature (Mianowski, & Radko, 1995; Ledakowicz, & Stolarek, 2000; Mianowski, Butuzova, Radko, & Turchanina, 2005; Cai, Wang, Zhou, & Huang, 2008; Minkina, Zasusz-Zuberek, & Mianowski, 2006).
- The advantage of the Mianowski-Radko model (1995) connected to the Levenberg-Marquardt algorithm is the satisfactory fit of the model, both in the presence of non-linear mass loss (kinetic area) and linear mass loss (diffusion area).
- Designated kinetic parameters may be used to model the process of pyrolysis and – as preliminary data – for the installation design of pilot underground coal gasification projects.

The notations

A – pre-exponential factor, 1/min;
e – Euler's number, $e = 2.718...$;
E – activation energy, kJ/mol;
k – reaction rate constant, 1/min;
m – mass of the sample, mg;
R – gas constant, $R = 0.008314$ kJ/(mol·K);
β – heating rate, K/min;
τ – time, min;
T – temperature, K;
α – degree of conversion, $\alpha \in \langle 0,1 \rangle$.

Subscripts

i – initial stage,
f – final stage,
o – the initial value,
p – refers to temperature, which at the rate of weight loss is at maximum,
$eksp.$ – experimental data,
K – refers to the area of kinetics,
D – refers to the area of diffusion.

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