

KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA COLLECTED FROM BIGGER SAMPLES

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Results for microcrystalline cellulose pyrolysis are presented, which includes thermogravimetric measurements and kinetic analysis of experimental data. The effect of sample mass size and heating rate on estimated values of activation energy and pre-exponential factor is demonstrated and a simple modification of procedure is proposed that allows for the correct values of kinetic parameters regardless of the experimental conditions. The efficiency of the proposed method is confirmed for two endothermic chemical reactions. A method of nonlinear regression is used for calculation of kinetic parameters for a single or TG curve or several curves simultaneously.

Keywords: thermogravimetry, kinetics, thermal lag, cellulose pyrolysis, metal oxide reduction

1. INTRODUCTION

Development and optimisation of technological processes is usually assisted by modelling, which can only be effective if a reliable physico-chemical data are available. In the case of chemical reactors knowledge of the kinetics of a process is the most important thing. Kinetics of many solid only or gas-solid reactions can be easily obtained through the use of thermogravimetric methods (Galwey and Brown, 1998; Vyazovkin and Wight, 1998). The weight loss (TG) or the rate of weight loss (DTG) versus time curves are recorded by heating a small sample of a solid material in a precisely controlled temperature and atmosphere. These curves are then used to evaluate a kinetic model. There are many kinetic models for solid state reactions and methods available in the literature that can be used for estimating kinetic parameters based on TG or DTG curves (Galwey and Brown, 1998; Vyazovkin and Wight, 1998).

Depending on way a sample is heated during measurement, kinetic analysis methods are divided into static and dynamic categories. During the static thermal analysis the sample's temperature is raised rapidly to a proper temperature and maintained at that level until the reaction is complete. However, dynamic analysis is more common, whereby the temperature is increasing or decreasing. The disadvantage of measurements carried out in dynamic conditions is the difficulty in avoiding the temperature gradient inside the sample due to a small thermal conductivity of the reacting substances. In addition, the temperature distribution in the sample can be affected by the heating effect of by undergoing chemical reactions. The existence of heat transfer resistance between the test sample and the environment affects the rate of chemical reactions. In practice, this can be observed as a shift of TG and DTG curves towards higher temperatures. To minimise the impact of this phenomena, it is recommended that the kinetic measurements of the initial sample mass do not exceed 2-5 mg and the measurements are carried out at low heating rates (below 5 K / min) (Cabellero et al., 1995; Conesa et

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al., 2001; Di Blasi, 1998; Gronli et al., 1999). The accuracy and sensitivity of the currently constructed thermobalance allows a study of small samples with sufficient precision, but only for material of homogeneous composition. For heterogeneous materials, like fossil fuels, solid waste and sewage sludge too small a sample may not be representative of the composition (Cabellero et al., 1995), therefore the initial sample mass should be larger.

Notably in thermogravimetry a direct measurement of the temperature inside the sample is not possible because the sample is very small. Instead, the sample temperature is estimated based on the temperature measured in the environment of the sample (reference temperature). Therefore, it is necessary to calibrate the temperature measurement system. Calibration is done mostly on the basis of melting temperatures of selected metals or salts. Correctly determined temperatures are not without error, because the use of materials from varying sources might somewhat modify their physical properties.

A strong influence of temperature on the rate of a chemical reaction can be attributed to any inaccuracies in the evaluation of kinetic parameters if the calibrated temperature is slightly off. Narayan and Antal (Narayan and Antal, 1996) studied the effect of thermal lag, which is the difference between the reference temperature and the real sample temperature, on estimated values of the apparent activation energy and pre-exponential factor for the endothermic pyrolysis process of cellulose. In many studies kinetic parameters were dependent on heating rates and to avoid this only the data obtained using one heating rate were used (Conesa et al., 2001).

Using a mathematical model of the process occurring in the sample based on the mass and heat balance equations it is possible to separate the heat transfer effects from the reaction kinetics (Babu and Chaurasia, 2004; Hagge et al., 2002; Jang, 1995; Pyle and Zaror, 1984; Stenseng et al., 2001). In this approach a sample was usually assumed as an infinitely long cylinder, allowing the problem to be described by a two-dimension model. Despite this simplification the solution of the balance equations is complicated and time-consuming regardless of whether a numerical method or simplified analytical solution was used (Pidubniak, 2011). In this study a simple approach is proposed which helps to eliminate the heat transfer effects and to obtain the correct kinetic parameters from thermogravimetric data collected from bigger samples.

2. EXPERIMENTAL

All of the kinetic experiments were performed in a thermobalance (Mettler-Toledo type TGA/SDTA851 LF) The samples (2, 10 i 50 mg) were inserted into 0.150 cm³ crucible made of Al₂O₃ and were heated up with a constant heating rate $\beta = 5, 10$ or 20 K/min.

Microcrystalline cellulose PH-101 Vivapur (J. Rettenmaier and Söhne, Rosenberg, Germany) with a particle size of less than 65 μm were used for the pyrolysis tests. The pyrolysis process was carried out under inert conditions of argon gas flowing around the sample at a rate of 50 cm³ /min. Due to the small size samples used in the experiments, all of them were repeated with the same amount of ground quartz glass instead of cellulose. Results obtained in this way were then used to correct the TG curves recorded during pyrolysis to reduce errors associated with the buoyancy effect.

3. RESULTS AND DISCUSSION

The rate of weight loss represented by DTG curves recorded during the pyrolysis of cellulose at different heating rates and sample masses (2 and 50 mg) is shown in Figure 1. Thermal decomposition of cellulose occurred at a temperature range from 500 to 750 K with a maximum rate at 600-630 K, depending on the heating rate and sample mass. The numbers given in the figure define the position of

each peak on the temperature scale. It is clear from these values, that the maximum rate of reaction for the bigger samples is significantly shifted towards higher temperatures, which is an illustration of the problems described in the introduction.

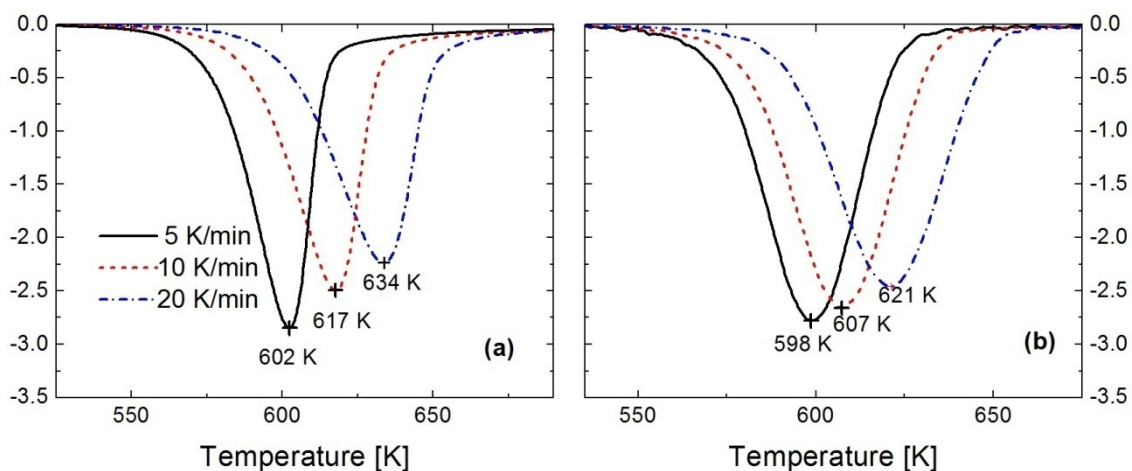


Fig. 1. DTG profiles recorded during heating of the crystalline cellulose under atmosphere of argon for different sample mass: 50 mg (a) and 2 mg (b) at different heating rates

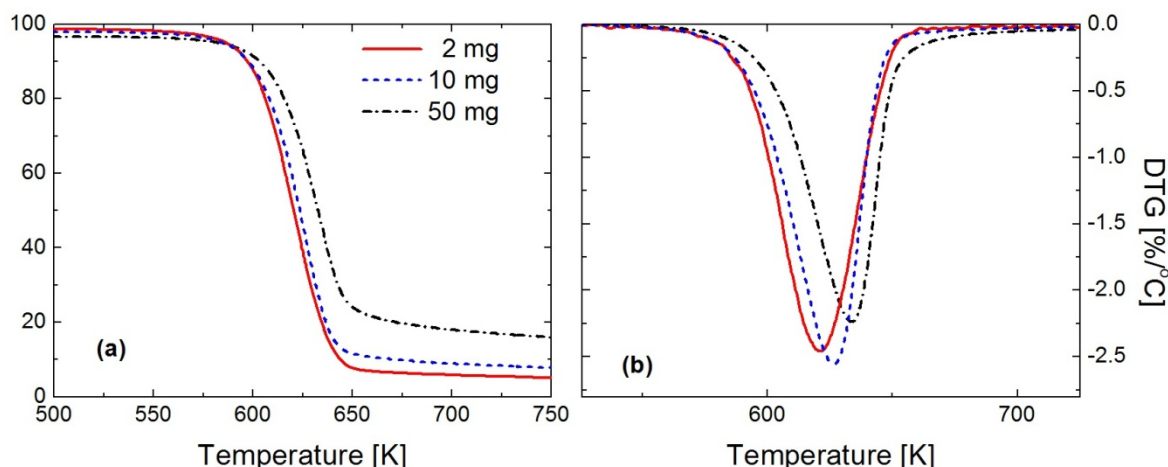


Fig. 2. TG (a) and DTG (b) profiles recorded during heating of crystalline cellulose in an inert atmosphere of argon for different initial sample masses (heating rate 20 K/min)

The effect of sample mass on the position of DTG peaks is also presented in Figure 2b, which compares the curves obtained for three initial sample weights (2, 10 and 50 mg)). Figure 2a shows TG profiles for cellulose pyrolysis. As can be seen from these figure the sample mass has a large impact on the yield of solid reaction product, which is called pyrolysis coke or char. For a small sample (2 mg) the yield of char was only 2.3% of the initial sample mass, whereas the highest yield of 12.5% was obtained for a sample weighing 50 mg. Char is formed in secondary reactions of primary volatile decomposition products, as they are transported through the particle and the reaction environment (Di Blasi, 2009), therefore bigger samples allow for mores formation of char (Völker and Rieckmann, 2002).

4. MODELLING

Pyrolysis of cellulose is a complex chemical reaction, but usually for kinetic modelling it is regarded as a one stage process, where the overall rate may be described by the first-order reaction rate equation

(Gronli et al., 1999). Experimental TG and DTG curves presented in Figure 1 and 2 suggest that this assumption applies to this case. Two methods were used to determine the kinetic parameters of the rate equation: method ASTM E689 and nonlinear regression method. At the beginning, the calculations were performed for the experimental data collected on smaller samples, which appear to be free from thermal lag.

The ASTM E689 procedure based on the theoretical work of Kissinger (Kissinger, 1956) belongs to the methods of using the position of characteristic points on TG or DTG curves. The method consists of searching for the temperature, at which the reaction rate is the highest. Performing measurements using linearly increasing temperature for several measurements of the sample heating rate β from a diagram drawn based on the Kissinger equation:

$$\ln\left(\frac{\beta_j}{T_{max,j}^2}\right) = \ln\left(\frac{R \cdot k_0}{E}\right) - \frac{E}{R \cdot T_{max,j}} \quad (1)$$

where activation energy E and pre-exponential factor k_0 (index j corresponds to a given heating rate of the sample) can be found. More details on how to use the equation can be found in the literature (Stolarek, 2006). The application of the ASTM E689 method to experimental data is shown in Figure 3 g, and the values of the kinetic parameters E , k_0 obtained on the basis of this chart are given in Table 1. The activation energy is determined to be 180.6 kJ/mol, which is significantly below the values reported in the literature (234-263 kJ/mol (Gronli et al., 1999)). A comparison of the experimental TG profiles with those predicted using the parameters values from the Kissinger method demonstrates a lack of compatibility between the model and the experimental data. The reason for this discrepancy will be explained later.

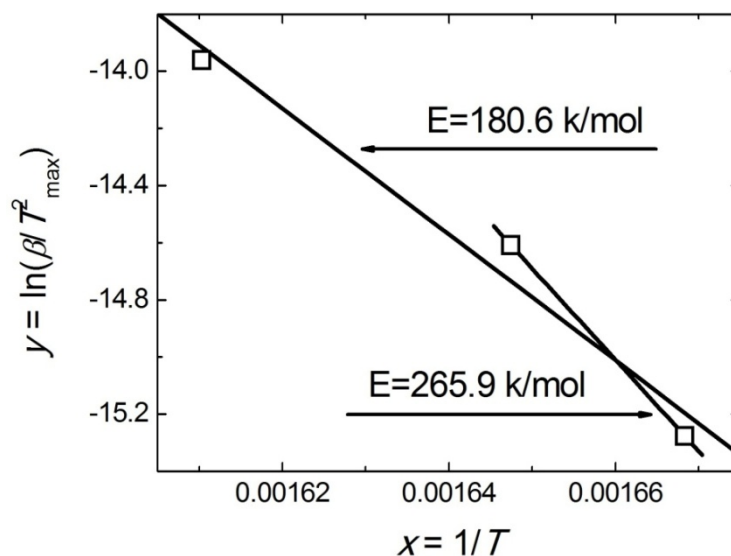


Fig. 3. Application of the Kissinger chart to determine the activation energy and preexponential factor for pyrolysis of crystalline cellulose

ASTM E689 method is very simple to use, but it does not use due information contained in the whole DTG curve. Significantly greater possibilities to analyse experimental data can be expected of those methods, which will use the entire TG (or DTG) profiles and not only the selected points. One of such methods commonly used in thermal analysis is a method of nonlinear regression. This method is used to find the kinetic parameters that minimise the value of the approved model quality index. The quality index can take various forms (Stolarek, 2006). In this study it was defined as:

$$J(k_0, E) = \sum_{j=1}^S \sum_{k=1}^N \left[\frac{m_{j,k}^{exp}}{m_{0,j}} - \frac{m_{j,k}^{cal}}{m_{0,j}} \right]^2 \quad (2)$$

where m^{exp} means the sample mass directly measured at temperature T , while m^{cal} is the mass of the sample calculated by integration of the following mass balance equation:

$$\frac{d\alpha}{d\tau} = A \cdot \exp\left(-\frac{E}{R \cdot T(\tau)}\right) (1 - \alpha), \quad \alpha(\tau = 0) = 0 \quad (3)$$

where $\alpha(\tau)$ is a conversion degree defined by

$$\alpha(\tau) = \frac{m_0 - m(\tau)}{m_0 - m_\infty} \quad (4)$$

and relationship between α and the relative sample mass used in Equation (2) is as follows:

$$\frac{m}{m_0} = 1 - \alpha \left(\frac{m_0 - m_\infty}{m_0} \right) \quad (5)$$

Under conditions of a constant heating rate of the sample instantaneous temperature T temperature is related to time by the expression

$$T = T_0 + \beta \cdot \tau \quad (6)$$

The method of nonlinear regression can be performed for a single experiment ($S = 1$ in Equation 2) or for some experiments performed at different heating rates (multivariate regression) The compliance kinetic model with experimental data obtained for individual scans of temperature and non-compliance for a series of experiments performed at different heating rates shows the influence of heat transport phenomena on the process. In rare cases, this discrepancy may be due to an improper form of a kinetic model (Conesa, 2001).

Table 1. Kinetic parameters for pyrolysis of microcrystalline cellulose

Calculation Method	Experimental data	A , 1/s	$\log(A)$, 1/s	E , kJ/mol
Kissinger	$m_0 = 2$ mg, $\beta = 5; 10; 20$ K/min	$3.25 \cdot 10^{13}$	13.73	180.6
Kissinger	$m_0 = 50$ mg, $\beta = 5; 10; 20$ K/min	$3.79 \cdot 10^8$	8.58	127.2
Nonlinear regression	$m_0 = 2$ mg, $\beta = 5$ K/min	$1.03 \cdot 10^{21}$	21.01	266.7
Nonlinear regression	$m_0 = 2$ mg, $\beta = 10$ K/min	$1.01 \cdot 10^{21}$	21.00	266.2
Nonlinear regression	$m_0 = 2$ mg, $\beta = 210$ K/min	$2.90 \cdot 10^{16}$	16.6	214.2
Kissinger	$m_0 = 2$ mg, $\beta = 5; 10$ K/min	$1.09 \cdot 10^{21}$	21.04	265.9
Nonlinear regression with a correction of the temperature	$m_0 = 50$ mg, $\beta = 5; 10; 20$ K/min	$1.38 \cdot 10^{21}$	21.14	267.2

Kinetic parameters obtained using the nonlinear regression method for individual tests carried out with the sample mass of 2 mg are given in Table 1. As can be seen, both parameters E , k_0 calculated for smaller scanning rates (5 and 10 K/min) are very similar, whereas the kinetic parameters for a scan of

20 K/min differ significantly. This discrepancy clearly shows that the heat transport phenomena can occur even for such a small sample at higher heating rates. Moreover, the Arrhenius equation parameters determined using the Kissinger method, based on experimental data for $\beta = 2$ and 5 K/min agree very well with the values obtained from nonlinear regression (Table 1) and all these values match literature data.

In Figure 4 the experimental TG data for the initial sample of a mass of 2 mg are compared with the mass loss curves calculated on the basis of kinetic parameters obtained for the sample heating rate $\beta = 5$ K/min. As can be seen from this figure, the calculated curves fit very well the experimental data obtained for smaller heating rates, while the data for $\beta = 20$ K/min are shifted towards higher temperatures. That means that at a higher heating rate the real sample's temperature was lower than that recorded by the thermobalance. A similar comparison for a sample weighing 50 mg is shown in Figure 5.

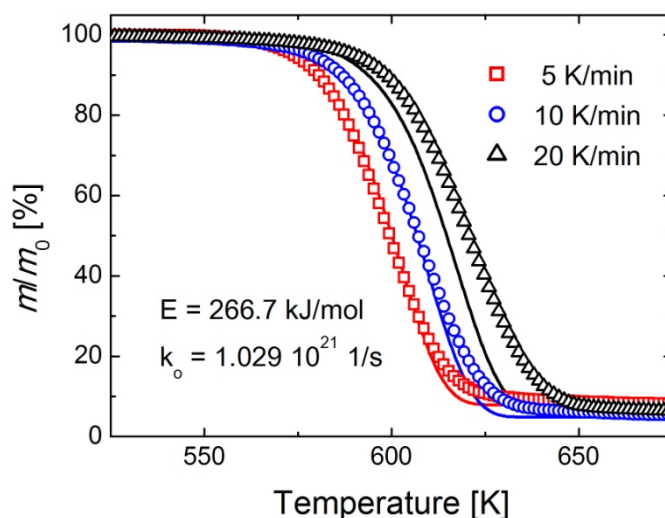


Fig. 4. Comparison of experimental data collected during pyrolysis of cellulose with predicted TG profiles using Arrhenius parameters obtained for small heating rates (initial sample mass of 2 mg)

Assuming that the kinetic parameters determined from thermogravimetric measurements carried out with small samples (2 mg) at low heating rates (5 or 10 K/min) are not affected by the heat transport phenomena, the graphs in Figure 6 highlight the trends of the thermal phenomena occurring during the pyrolysis of samples with a bigger mass of cellulose. As might be expected, the experimental curves are again shifted towards higher temperatures and this shift is the greater the higher the heating rate. A small effect of conversion on the shift can be also noticed.

Taking into account the above observations, a modification of the procedure was proposed to allow for obtaining more reliable values of kinetic parameters based on thermogravimetric measurements with larger samples. This modification relates to Equation (4). Which was rearranged to the following form:

$$T = T_0 + \beta\tau - a\beta[1 + \alpha(\tau)] \quad (7)$$

where $\alpha(\tau)$ is the degree of conversion defined by Eq. (4) and a is an additional parameter, whose value is determined simultaneously with the activation energy and pre-exponential factor.

Using the modified version of the model, parameters were determined for three tests performed with samples weighing 50 mg. The results of these calculations are given in Table 1 and are shown graphically in Figure 6. In this case the Arrhenius parameters are consistent with those obtained for small samples. The optimum value of the parameter a is 0.745. As can be seen from Figure 6, the calculated TG profiles fit the experimental data well in nearly the entire range of conversion, regardless of the heating rate of the sample.

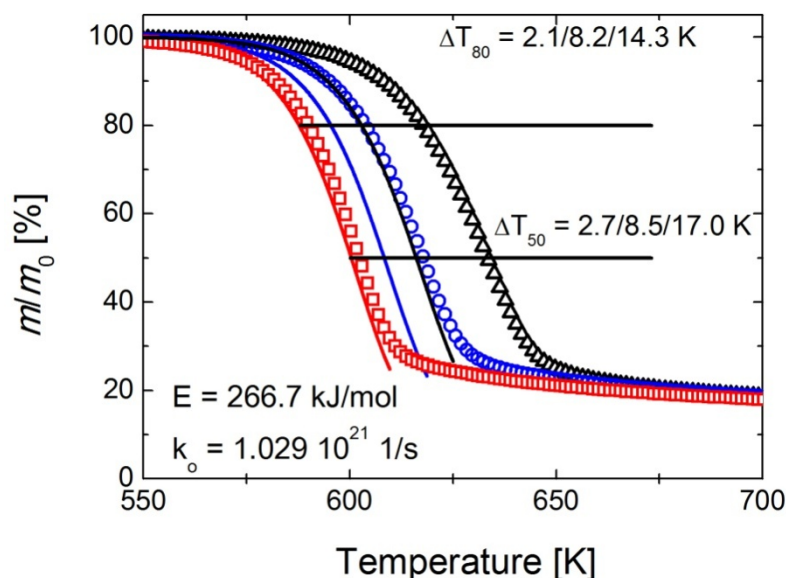


Fig. 5. Comparison of experimental data collected during pyrolysis of cellulose with predicted TG profiles using Arrhenius parameters obtained for small heating rates (initial sample mass of 50 mg)

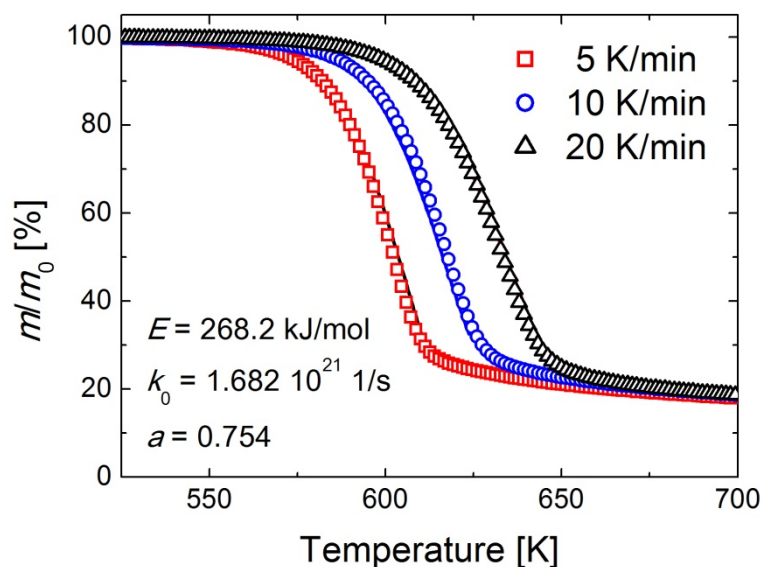


Fig. 6. Comparison of experimental data collected during pyrolysis of cellulose with predicted TG profiles using model parameters obtained from nonlinear regression method applied to three experimental data sets for sample mass of 50 mg

Parameter a has no strict physical meaning. It reflects dynamic properties of the measuring system, the properties of the sample material and the reaction occurring inside the sample. We can expect that its value will depend on the initial sample mass and other experimental conditions.

To verify the effectiveness of the proposed method, it was also used to determine kinetic parameters for reduction of pure copper (II) oxide (CuO) with hydrogen. The thermogravimetric data for this reaction were published in the literature (Ledakowicz, 2003). The initial mass of the sample in these experiments was 25 mg and the authors encountered a common problem with obtaining a single set of kinetic parameters that could describe all the experimental data. To achieve these parameters it was assumed that the rate of the process is partially limited by diffusion of hydrogen in the reaction zone.

The reduction of CuO with hydrogen gas occurs in two stages:



The differential mass balance equations describing the total mass loss due to the reaction progress can be found in the literature (Ledakowicz, 2003). The rate of each reaction was expressed by kinetic equations of n -th order, with respect to unreacted solid reagent. The results of the calculation performed by using the nonlinear regression method and Equation (7) for the reaction temperature are shown in Figure 7. It is clear from the TG and DTG profiles presented in the figure, that a small sample temperature correction using Equation (7) leads to a consistent description of the process, regardless of the operating conditions. The values of kinetic parameters that minimise the quality index are given in Figure 7.

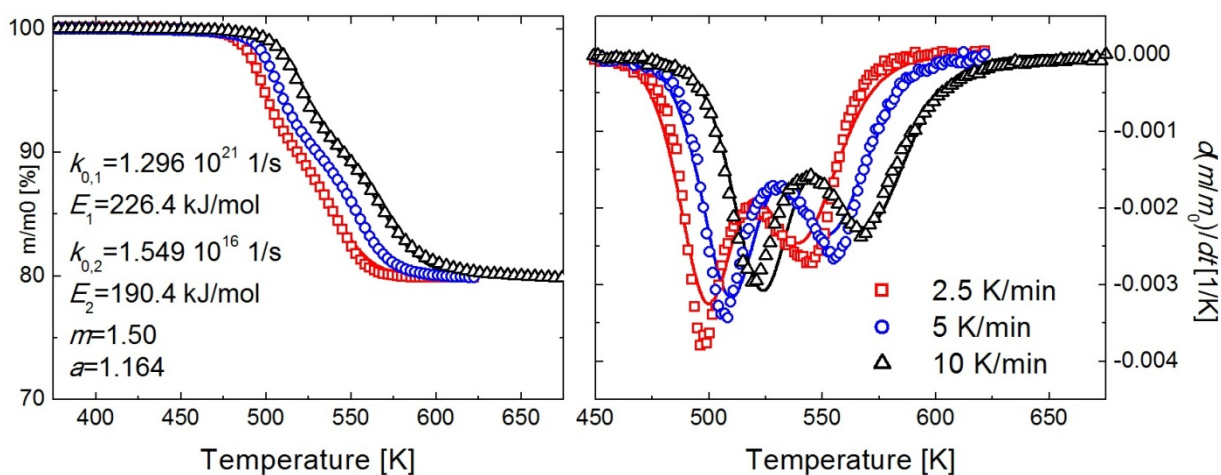


Fig. 7. Comparison of the experimental TG and DTG curves for the reduction of copper (II) oxide (dots) with the curves calculated on the basis of the model (lines)

5. CONCLUSIONS

Thermogravimetry is a simple and fast method for obtaining information on solid state chemical reactions. However, a kinetic analysis of experimental TG data can be difficult due to the nonuniform temperature distribution within the sample and consequent errors caused by indirect measurement of average sample temperature. To avoid the problems a small sample should be used, but this may be a source of error in the case of heterogeneous sample material. Slow heating rates of a sample are also recommended, but the exact values depend on the type of material and reaction rate.

The analysis of TG data collected of microcrystalline cellulose pyrolysis showed that for a 2 mg sample size heating rates of less than 10 K/min the experimental results are not affected by thermal phenomena in the sample and errors in assessing the actual sample temperature. Based on these data correct values of Arrhenius parameters can be obtained by using both the simple ASTM E689 method and the more accurate method of nonlinear regression.

The “true” value of kinetic parameters can also be obtained for measurements with samples of larger mass using the proposed method for sample temperature correction. This requires an inclusion of an additional parameter in the model where the value must be determined together with the values of kinetic parameters. The additional parameter has no exact physical meaning, but it reflects the thermal lag and other thermal effects influencing TG results.

The proposed form of the equation for correcting the sample temperature (Equation 7) was the result of the kinetic analysis of the experimental results, but to some extent it is inspired by the work of Narayan and Antal (Narayan R., Antal, 1996) and their fusion model.

This study confirmed that the rate of cellulose pyrolysis can be modeled with the first order reaction rate equation, but only for the conversion of less than about 80%. The reason for this discrepancy in the final stage of the process might be due to the excessive simplification of the kinetic model, change in reaction mechanism and diffusion limitations (Conesa et al., 2001).

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SYMBOLS

a	parameter in Eq. 7
A	pre-exponential factor, s^{-1}
E	activation energy, kJ/mol
N	number of measuring points in a scan
n	reaction order
m	mass of sample, g
R	universal gas constant, $J\ mol^{-1}\ K^{-1}$
S	number of scans
T	absolute temperature, K
TG	thermo gravimetric curve (m/m_0 vs. T)
DTG	first derivative of thermogravimetric curve

Greek symbols

α	degree of conversion
β	heating rate, $K\ min^{-1}$
τ	time, s

Superscripts and subscripts

j	scan index
k	measuring point index
exp	experimental value of sample mass
cal	calculated value of sample mass
max	refers to a maximum value
0	initial value
∞	final value

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