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Non-isothermal kinetic analysis of the thermal decomposition of spruce wood in air atmosphere

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Abstract

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Thermal decomposition of spruce wood (*Picea abies*) was studied using the thermogravimetric (TG) analysis in air atmosphere from 30°C to 600°C with the heating rates of 5, 10, 15, 20, 25 and 30°C·min^{-1}. The TG results show that the main decomposition region is in the temperature range of 250–360°C, where a total disintegration of hemicellulose and cellulose with partial lignin decomposition can be observed. The values of apparent activation energy for this process are between 168.6–196.5 kJ·mol^{-1}, 179.8–188.1 kJ·mol^{-1} and 179.1–187.7 kJ·mol^{-1} determined by the Friedman, Flynn-Wall-Ozawa and Kissinger-Akahira-Sunose methods, respectively.

Keywords: apparent activation energy; spruce wood; thermal decomposition; wood biomass

In many countries, forest biomass is, in comparison with other renewable energy sources, the best choice from the point of view of its potential. However, if forests are used as an energy source, then it is necessary to use it rationally and in a sustainable way to avoid a disruption of the bio-system balance. The reason for this is the fact that it takes several decades until the mass of wood reaches the desired level and can be used as fuel. To use biomass fuel rationally, the combustion process must be optimized in order to ensure an effective combustion. Kinetic analysis is a suitable tool to achieve such a goal.

Wood represents a complex heterogeneous system of components consisting mainly of hemicellulose, celluloses and lignin, with a small content of inorganic impurities (Harun, Afzal 2010; Shen et al. 2009; Mohan et al. 2006; Poletto et al. 2012). The content of these wood polymers in a typical wood biomass is 40–50% cellulose, 25–35%

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hemicellulose, and 10–40% of lignin (Mohan et al. 2006; Jin et al. 2013). The thermal decomposition of cellulose occurs in the temperature range of 240–350°C while the hemicelluloses decompose already in the temperature interval of 200–260°C. The thermal decomposition of the last major component, lignin, takes place between 280–500°C (Mohan et al. 2006).

Kinetics of thermal decomposition in inert and oxidative atmospheres are influenced by various factors such as heating rate, temperature, pressure, moisture content, particle size and chemical composition (Bilbao et al. 1997; Harun, Afzal 2010). The effects of these factors on the processes of the biomass decomposition have often been examined in an inert atmosphere. Therefore, there is still not enough available information related to an oxidative environment for different types of biomass. Moreover, information obtained from the studies of thermal decomposition of various kinds of wood biomass in an oxidative environment is important for the development of efficient biomass combustion applications (Shen et al. 2009).

The aim of this study is the kinetic analysis of the thermal decomposition of spruce wood (*Picea abies*) in an oxidative atmosphere. From the results of thermogravimetry (TG) under various heating rates, the values of apparent activation energy were determined by three isoconversional methods: Friedman (FR), Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS).

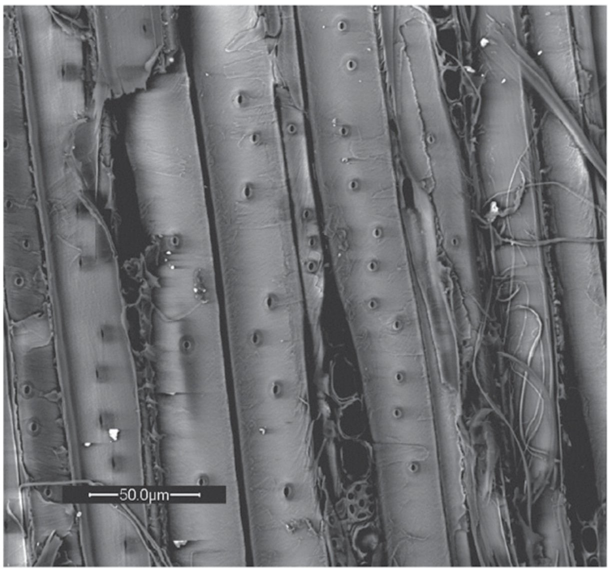

Fig. 1. SEM micrograph of spruce wood (SEM FEI Quanta TM FX200)

MATERIALS AND METHODS

Materials. The spruce wood used in this study is a residual processing wood originated in the locality Nitra-Horné Krškany, Slovakia. The SEM micrograph of used spruce wood is shown in Fig. 1. It shows the bordered pits arranged on the wood surface. For the TG analysis wood chips with a diameter ~5 mm were crushed to obtain smaller pieces with a diameter less than ~2 mm.

Experimental methods. TG analysis of spruce wood was carried out by a thermogravimetric analyser TGA/SDTA 851^e (Mettler Toledo, Czech Republic) on samples with masses ~5 mg in a dynamic atmosphere of dry air with flow rate 40 ml·min^{-1}. The measurements were carried out in the temperature range of 30–600°C with the heating rates of 5, 10, 15, 20, 25, and 30°C·min^{-1}. Blank measurement with an empty crucible was carried out prior to each heating program in order to subtract the influence of the apparatus on the measurement.

Kinetic methods. The rate of the reaction is commonly described by the equation (Vyazovkin et al. 2011; White et al. 2011):

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = f(\alpha)\, A \exp\left(-\frac{E}{RT}\right) \tag{1}$$

where: α – the reaction extent; t – time; T – the absolute temperature; $f(\alpha)$ – a reaction model; R – the universal gas constant; A and E – the Arrhenius parameters (pre-exponential factor and activation energy)

The basic idea of the isoconversional methods can be easily understood from the equation:

$$\left[\frac{\partial \ln(\mathrm{d}\alpha/\mathrm{d}t)}{\partial T^{-1}}\right]_\alpha = -\frac{E_\alpha}{R} \tag{2}$$

This equation states that the reaction rate at a constant degree of conversion is only a function of temperature (Sbirrazzuoli et al. 2009).

The first method that was employed for the determination of E_α was the differential isoconversional method proposed by Friedman (Friedman 1964). It is based on the logarithmic form of the Eq. (1):

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\alpha,i} = \ln\left[f(\alpha)A_\alpha\right] - \frac{E_\alpha}{RT_{\alpha,i}} \tag{3}$$

where: i – identifies an individual heating rate

The apparent activation energy is determined from the slope of the plot $\ln(\mathrm{d}\alpha/\mathrm{d}t)_{\alpha,i}$ vs. $T_{\alpha,i}^{-1}$ for various degrees of conversion.

Using a linear heating rate $\beta = \mathrm{d}T/\mathrm{d}t$, Eq. (1) may be written as:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right) f(\alpha) \qquad (4)$$

Integration of Eq. (4) leads to:

$$g(\alpha) = \int_0^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^{T} \exp\left(-\frac{E}{RT}\right)\mathrm{d}T \qquad (5)$$

The temperature integral on the right-hand side of Eq. (5) does not have an exact analytical solution. For this reason, there are many integral isoconversional methods differing in their approximations. By using Doyle's approximation a linear Flynn-Wall-Ozawa equation (Ozawa 1965; Flynn, Wall 1966) is obtained:

$$\ln\left(\beta_i\right) = \text{const} - 1.052\left(\frac{E_\alpha}{RT_{\alpha,i}}\right) \qquad (6)$$

The apparent activation energy is determined from the slope of the left-hand side of Eq. (6) vs. $T_{\alpha,i}^{-1}$ for different values of degree of conversion.

The more accurate approximation by Murray and White leads to the equation that is often called the Kissinger-Akahira-Sunose (Kissinger 1957; Akahira, Sunose 1971) equation:

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = \text{const} - \left(\frac{E_\alpha}{RT_{\alpha,i}}\right) \qquad (7)$$

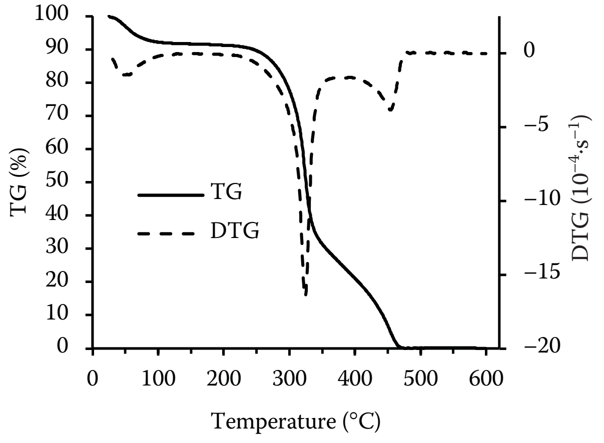

Fig. 2. Thermogravimetric (TG) and DTG curves for the heating rate of 5°C·min^{-1}

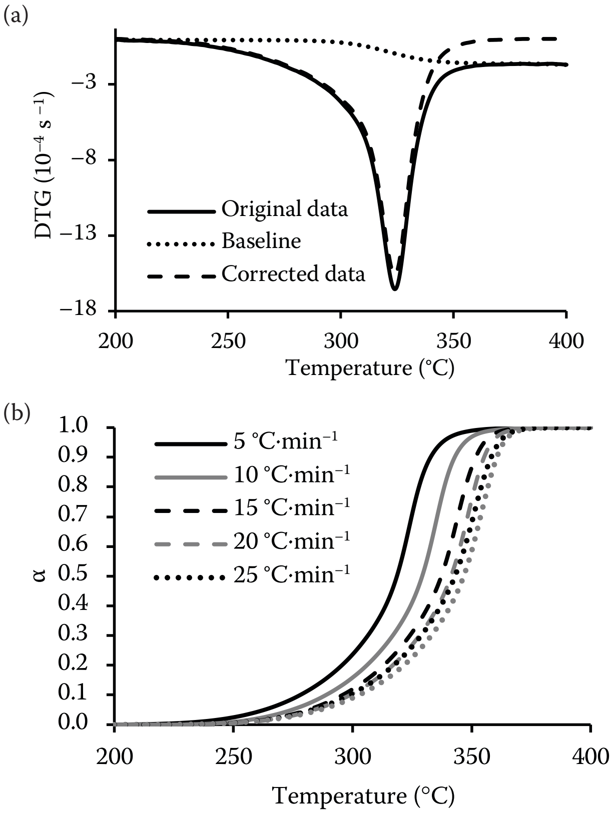

Fig. 3. An example of the baseline subtraction for the heating rate of 5°C·min^{-1} (a) and the dependence of degree of conversion on the temperature for different heating rates (b)

In this case, the apparent activation energy is determined from the slope of the plot $\ln(\beta_i/T_{\alpha,i}^2)$ vs. $T_{\alpha,i}^{-1}$ for different values of degree of conversion.

RESULTS AND DISCUSSION

The TG curve and its derivative (DTG) for the heating rate of 5°C·min^{-1} are shown in Fig. 2. The DTG curve reveals that the thermal decomposition of the spruce wood proceeds in several steps.

The first step, between temperatures of 30–120°C, corresponds to the release of the moisture and adsorbed water. The second step (main decomposition region) is in the range approximately from 250°C to 360°C with a significant mass loss of ~60%. The last step occurs in the temperature interval of 360–500°C.

The mass loss in the second step is ascribed to the combination of a total hemicellulose and cellulose decomposition with partial lignin decomposition. The third step corresponds to the decomposition of remaining lignin and the combustion of char resi-

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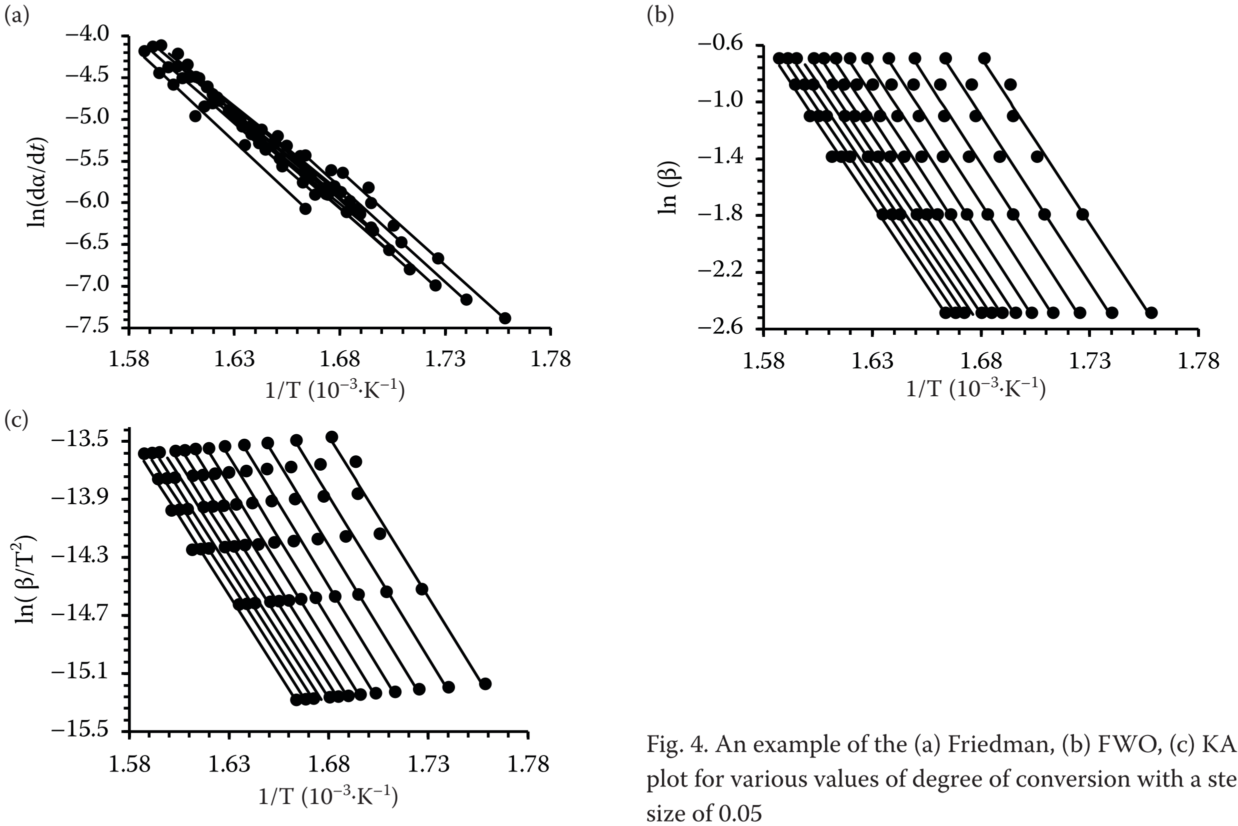

Fig. 4. An example of the (a) Friedman, (b) FWO, (c) KAS plot for various values of degree of conversion with a step size of 0.05

dues (Orfao et al. 1999; Strezov et al. 2003; Safi et al. 2004).

Kinetic analysis

The apparent activation energy values of the main decomposition region determined by the FR, FWO and KAS methods were calculated according to equations (3), (6) and (7) for various values of degree of conversion. To construct the conversion curves, a suitable sigmoidal baseline was subtracted from the experimental data. An example of this step is shown in Fig. 3a for the heating rate of 5°C·min^{-1}. From the corrected curves the conversion curves were constructed as a ratio between the partial area to the total area of the peak for the temperature interval of 200–400°C. Fig. 3b shows the dependence of the degree of conversion on the temperature for different heating rates. Because there is no significant change of the weight at the beginning and at the end of the reaction, the val-

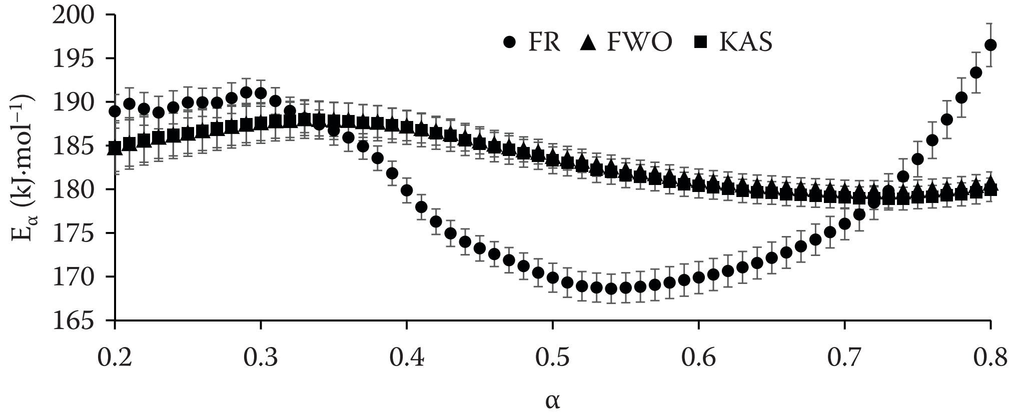

Fig. 5. The apparent activation energy as a function of degree of conversion (α)

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ues of apparent activation energy are not accurate at these points. Therefore E_α was calculated only for the conversion degree in the interval of 0.2–0.8 with a step size of 0.01.

The Friedman plot $\ln(d\alpha/dt)_{\alpha,i}$ vs. $T_{\alpha,i}^{-1}$ for various values of degree of conversion is shown in Fig. 4a. The FWO plot $\ln(\beta_i)$ vs. $T_{\alpha,i}^{-1}$ for various values of degree of conversion is shown in Fig. 4b and the KAS plot $\ln(\beta_i/T_{\alpha,i}^{2})$ vs. $T_{\alpha,i}^{-1}$ for various values of degree of conversion is given in Fig. 4c.

The values of E_α are in the range of 168.6 to 196.5 kJ·mol^{-1}, 179.8–188.1 kJ·mol^{-1} and 179.1 to 187.7 kJ·mol^{-1}, determined by the FR, FWO and KAS methods, respectively. Practically identical results were obtained using the FWO and KAS methods. The results show (Fig. 5) that the apparent activation energy depends on the degree of conversion. Nevertheless, the results obtained with the FR method show a more significant dependence of E_α on the degree of conversion than the results obtained with the integral methods. The change of E_α can be attributed to the complex composition of spruce wood and subsequently to the complex reactions ongoing during the heating.

CONCLUSION

The thermal decomposition of spruce wood was studied using the thermogravimetric analysis in air atmosphere and the dependence of the apparent activation energy on the degree of conversion was determined. The summary of the results is as follows:

The results of TG and DTG show that during the heating, there are three significant reactions. According to the literature survey, the first reaction corresponds to the release of the moisture and adsorbed water, the second corresponds to the total hemicellulose and cellulose decomposition with partial lignin decomposition. The third reaction corresponds to the decomposition of remaining lignin and combustion of char residues.

The values of E_α for the main decomposition region are in intervals of 168.6–196.5 kJ·mol^{-1}, 179.8–188.1 kJ·mol^{-1} and 179.1–187.7 kJ·mol^{-1}, determined by the FR, FWO and KAS methods, respectively.

The degree of conversion dependence of the apparent activation energy of the studied process determined by these methods shows that the mechanism of the reaction changes over the entire decomposition process.

In this study, the missing data regarding the kinetics of spruce wood thermal decomposition was determined. These results can be used for the development and optimization of biomass combustion applications.

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