



ISOTHERMAL KINETIC ANALYSIS OF THE THERMAL DECOMPOSITION OF SPRUCE WOOD

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Abstract

The thermal decomposition of pellets made from spruce wood (*Picea abies*) was studied under isothermal conditions by the thermogravimetric analysis. The Arrhenius parameters, i.e. apparent activation energy (E_a) and pre-exponential factor A , were determined from thermogravimetric experiments in the temperature range of (275–290) °C. Calculated values of E_a and A by a method based on the half-time of reaction are 151 kJ mol^{-1} and $8.09 \times 10^{10} \text{ s}^{-1}$, respectively.

Key words: apparent activation energy; thermal decomposition; woody biomass; spruce wood.

INTRODUCTION

Wood consisting mainly of hemicellulose, celluloses, and lignin, with a small content of inorganic impurities (Shen, et al., 2009; Harun & Afzal, 2010; Mohan, Pittman & Steele, 2006). During heating, in the temperature range of 200 °C – 260 °C and 240 °C – 350 °C, the thermal decomposition of the first and second component occurs, respectively. Lignin decomposition in wood was proposed to begin at 280 °C and continues to 450-500 °C (Mohan, Pittman & Steele, 2006; Brebu & Vasile, 2010). Generally, the thermal decomposition of woody biomass can be expressed as (Harun & Afzal, 2010; Slopiecka, Bartocci & Fantozzi, 2011)



where $k(T)$ is the rate constant and volatiles means the sum of the gas and tar. Besides that, it is believed, that the various factors, such as heating rate, temperature, moisture content, particle size, pressure, and chemical composition, have an influence on thermal decomposition kinetics under an inert and oxidative atmosphere (Hosoya, Kawamoto & Saka, 2007; Holubčík, Nosek & Jandačka, 2012; Ondro & Trník, 2017). In general, the reaction order reaction model ($f(\alpha)=(1-\alpha)^n$), where n is the reaction order, is often used to describe this process (Harun & Afzal, 2010; Slopiecka, Bartocci & Fantozzi, 2011). However, in (Liu, et al., 2002) the authors stated, that the best linear regression of the Arrhenius function is achieved when the first order ($f(\alpha)=(1-\alpha)$) reaction model is used. The aim of this study is the kinetic analysis of the thermal decomposition of pellets made from residual processing spruce wood (*Picea abies*). Thermogravimetric (TG) analysis was used to obtain data for kinetic analysis, from which the values of apparent activation energy, pre-exponential factor, and the most probable reaction model were determined.

MATERIAL AND METHODS

The experiments were performed on pellets made from residual processing spruce wood (*Picea abies*) originated in the locality Nitra-Horné Krškany, Slovakia. As was mentioned in Section 1, the particle size is one of the factors which have an influence on thermal decomposition kinetics. For this reason, an analytical sieve shaker Retsch AS200 was used for sieve analysis of sawdust, which was an input material for pelletizing. The 5-minute sieve shaking time with amplitude 2.0 mm g^{-1} was applied. For this analysis, the sieves with opening size 5, 2.5, 1.25, 1, 0.5, 0.2, 0.1 mm and a bottom pan (<0.1 mm) were used. Then, the material was screened to the sieve with the largest opening size. The measurements were carried out on thermogravimetric analyzer Mettler Toledo TGA/SDTA 851^e in a dynamic atmosphere of dry air with a flow rate of 50 ml min^{-1} . The heating rate of 50 °C min^{-1} was used to reach the isothermal temperatures from 275 °C to 290 °C, which corresponds to the major decomposition region.

Kinetic analysis

The rate of reaction can be described by the following equation (White, Catallo & Legendre, 2011; Vyazovkin, et al., 2011)



$$\frac{da}{dt} = k(T)f(\alpha) \quad (2)$$

where α is the degree of conversion, t is time, T is absolute temperature, and $f(\alpha)$ characterized the reaction model. The degree of conversion can be calculated from the TG measurements as (Vyazovkin, et al., 2011; Ondro, Hulan & Vitáček, 2017)

$$\alpha = \frac{m_i - m}{m_i - m_f} \quad (3)$$

where m is current, m_i is initial, and m_f is the final value of sample mass. Then, the state of the heterogeneous process is expressed by the single degree of conversion. Equation (1) is often used in its integral form, which for isothermal conditions becomes (Ptáček, et al., 2010)

$$g(\alpha) = k(T)t \quad (4)$$

where $g(\alpha)$ is the integral form of the reaction model. Then, the dependence of $g(\alpha)$ on time must give a straight line for proper reaction model. The temperature dependence of the reaction rate is typically parameterized through the Arrhenius equation (5) (Vyazovkin, et al., 2011; Obert & Trník, 2018)

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (5)$$

where A is the pre-exponential factor, E is the activation energy and R is the universal gas constant. In the case of thermal decomposition of woody biomass, the apparent activation energy E_a is the combination of the partial activation energies of different processes. The determination of A and E_a is based on the half-time of the reaction method ($t_{0.5}$) when the degree of conversion $\alpha = 0.5$. This method is based on the equation (6)

$$\ln t_{0.5} = \ln\left(\frac{g(\alpha)}{A}\right) + \frac{E_a}{RT} \quad (6)$$

The slope of the plot of the $\ln(t_{0.5})$ on T^{-1} must give a straight line, which corresponds to the E_a/R (Ptáček, et al., 2010).

RESULTS AND DISCUSSION

The results of sieve analysis (Fig. 1) show, that the more than 30 % of the material was retained on sieves with opening sizes 0.5 and 0.2 mm. Minimum of material (less than 10 %) were captured by the sieves with opening sizes 2.5 mm, 1.25 mm, 1 mm, and 0.1 mm. Further, the material contains ~7.6 % of particles with sizes less than 0.1 mm. On the other hand, the material did not contain particles >5 mm.

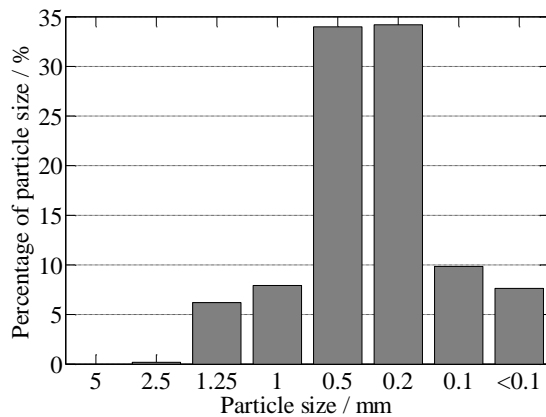


Fig. 1 Particle size distribution.

The isothermal measurements were carried out in temperatures from 275 °C to 290 °C, which correspond to the beginning of the main decomposition region. However, these results also show, that the decomposition process is not complete even if the sample is heated at 290 °C for 10 hours. Based on these measurements, the most probable mechanism of the process was determined from the dependence of $g(\alpha)$ on time for a degree of conversion in the range of 0.1 – 0.7. The results of linear regression show,



that the best model for this process is the first order reaction (F1), which is consistent with Liu et al. (2002).

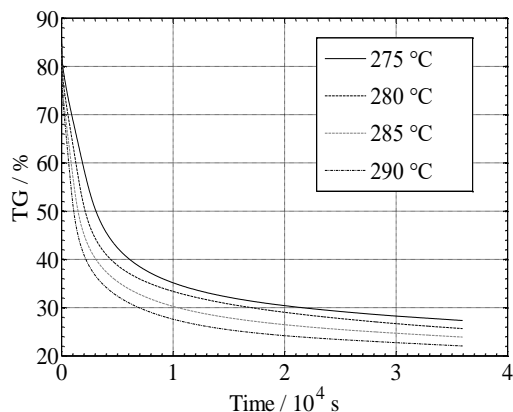


Fig. 2 Results of TG analysis for different isothermal regimes.

Tab. 1 Determined values of $t_{0.5}$.

Temperature °C	$t_{0.5}$ s
275	2220
280	1628
285	1184
290	925

From the experimental data, the values of $t_{0.5}$ were determined (see Tab. 1). Pertinent kinetic parameters (E_a and A) were determined graphically using the half-time of the reaction method (see Fig. 2). The determined value of E_a by a method based on the half-time of reaction is 151 kJ mol^{-1} . Using the determined reaction model (F1), the calculated value of A is $8.09 \times 10^{10} \text{ s}^{-1}$. The value of E_a is similar to the results obtained by non-isothermal TG analysis (Ondro et al., 2018), where the Friedman, Flynn-Wall-Ozawa and Kissinger-Akahira-Sunose methods were used for kinetic analysis. However, in the aforementioned work, the reaction model was not determined.

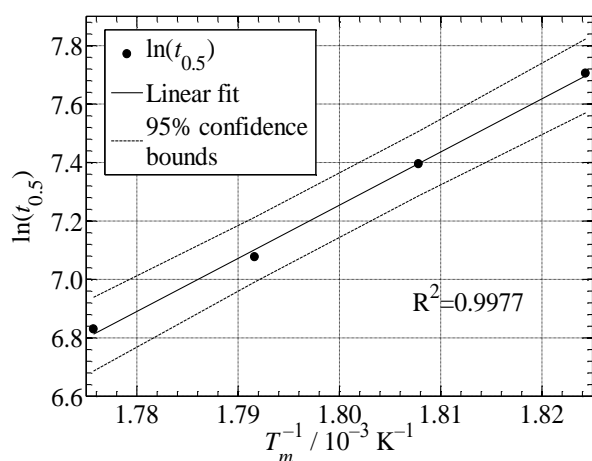


Fig. 3 The $\ln(t_{0.5})$ vs T^{-1} dependence.

CONCLUSIONS

The thermal decomposition of pellets made from spruce wood was studied by the thermogravimetric analysis in an oxidative atmosphere. The reaction model, apparent activation energy (E_a) and pre-exponential factor (A), were determined from thermogravimetric experiments in the temperature range of



(275–290) °C. The results show, that the most probable mechanism of the reaction is the first order reaction (F1). Besides that, the determined value of E_a by a method based on the half-time of reaction is 151 kJ mol⁻¹. Using the determined reaction model (F1), the calculated value of A is 8.09×10^{10} s⁻¹.

ACKNOWLEDGMENT

This study was supported by the Ministry of Education of the Slovak Republic, Project VEGA 1/0464/17 "Monitoring of the impact of ecological fuels obtained from the agricultural production and additives in hydrocarbon fuels to technical and environmental performance of internal combustion engines used in agricultural and transport technique".

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