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Thermoanalytical investigation of selected fuel during isothermal heating

I. Vitázek[1,*], T. Ondro[2], I. Sunitrová[3], R. Majdan[1] and M. Šotnar[2]

[1]Slovak University of Agriculture in Nitra, Faculty of Engineering, Department of Transport and Handling, Tr. A. Hlinku 2, SK949 76 Nitra, Slovakia
[2]Mendel University in Brno, Faculty of Agronomy, Department of Agricultural, Food and Environmental Engineering, Zemědělská 1, CZ61300 Brno, Czech Republic
[3]Constantine the Philosopher University in Nitra, Faculty of Natural Sciences, Department of Physics, Tr. A. Hlinku 1, SK94974 Nitra, Slovakia
[*]Correspondence: ivan.vitazek@uniag.sk

Abstract. The thermal decomposition of woody biomass was studied using pellets made from residual processing spruce wood (*Picea abies*). The samples were studied using thermogravimetric analysis in the isothermal regime at the temperatures 275 °C, 300 °C, 325 °C, and 350 °C, which corresponds to the main decomposition region. The results show that the main decomposition region can be described as a volatilisation of the main constituents at a temperature higher than 300 °C. Otherwise, the results indicate, that the lignin does not decompose at lower temperatures. Therefore, it can be concluded that the heating rate is one of the most important parameters that affect the thermal decomposition of lignin and could lead to different interpretations if non-isothermal measurements are used.

Key words: woody biomass, thermogravimetric analysis, spruce wood.

INTRODUCTION

Wood represents a complex heterogeneous system of various chemical constituents, such as cellulose, hemicellulose, and lignin, along with a small content of inorganic material (Shen et al., 2009; Poletto et al., 2012). According to Mohan et al. (2006), the content of cellulose is ~40–50 wt.%, hemicelluloses ~25–35 wt.% of dry wood. However, softwood comprises ~28 wt.% of hemicelluloses. The content of the last major component, lignin, is 23 wt.%–33 wt.% of softwood.

During heating, in the temperature range of 240 °C–350 °C, the thermal decomposition of cellulose occurs, whereas the hemicelluloses decompose already in the temperature interval of 200 °C–260 °C. The thermal decomposition of lignin takes place between 280 °C–500 °C. However, there is disagreement in the interpretation of the measurements. Orfao et al. (1999), Safi et al. (2004) and Ondro et al. (2018) all stated that the first step of the main decomposition region can be described as a combination of total hemicellulose and cellulose decomposition with partial lignin decomposition. The second step corresponds to the decomposition of the remaining lignin and the combustion of char residues. On the other hand, Bilbao et al. (1997) stated that the first

observed step is attributed to the volatilisation of the main constituents, while the second step is assigned to the combustion of char residue. The same explanation for the measured curves was given by both Liu et al. (2002) and Fang et al. (2006). However, some studies show that under certain conditions there should be an interaction between components (Hosoya et al., 2007a; 2007b; 2007c).

These interpretations of the decomposition process could be caused by various factors, such as heating rate, temperature, particle size, pressure, and chemical composition. For the development of efficient biomass combustion applications, it is therefore important to study the thermal decomposition of various kinds of woody biomass.

The aim of this study is to study the main decomposition region using thermogravimetric (TG) analysis during isothermal heating at different temperatures. Based on these results, interpretation about the decomposition of woody biomass that best explains the measured curves can be decided. This paper is a continuation of studies (Ondro et al., 2018; Vitázek & Tkáč, 2019).

MATERIALS AND METHODS

The experiments were carried out using pellets (see Fig. 1) made from the residual processing spruce wood (*Picea abies*) which originated in the locality of Nitra-Horné Krškany, Slovakia. The procedure for producing the wood pellets can be found, for example, in the paper by Holubcik et al. (2012). Due to the influence of particle size on thermal decomposition, an analytical sieve shaker Retsch AS200 was used for sieve analysis. An amplitude of 2.0 mm g^{-1} during the five-minute sieve shaking was applied on sawdust, which was used as the input material for pelletizing. For this analysis, the sieves with opening sizes of 5, 2.5, 1.25, 1, 0.5, 0.2, and 0.1 mm and a bottom pan were used. The material was then put on the sieve with the largest opening size.

Figure 1. Pellets made from the residual processing spruce wood.

The measurements were carried out by a thermogravimetric analyser Mettler Toledo TGA/SDTA 851^e under a dynamic atmosphere of dry air with a flow rate of 50 mL min^{-1} on samples with a mass of ~12 mg.

The decomposition process was described using the non-isothermal measurement in the temperature range of 25 °C–600 °C, with a heating rate of 50 °C min^{-1}. The heating rate of 50 °C min^{-1} was also used to reach the isothermal temperatures from 275 °C to 350 °C. This heating rate ensures that the heat transfer within the sample leads to delay in decomposition, which is needed to decompose as little material as possible. For each isothermal temperature, three or more measurements

were carried out and compared in order to ensure the reproducibility of obtained results. The blank measurements with empty crucible were used to subtract the influence of the apparatus on the measurements.

RESULTS AND DISCUSSION

The results of the sieve analysis (see Table 1) show, that only a small amount of material (less than 10 wt.%) was captured by the sieves with opening sizes of 2.5 mm, 1.25 mm, 1 mm and 0.1 mm. On the other hand, more than 30 wt.% of the material was captured by sieves with opening sizes of 0.5 mm and 0.2 mm. Furthermore, the material contains ~7.6 wt.% of particles, with sizes of < 0.1 mm.

Table 1. Sieve analysis of sawdust

Grain size (mm)	Retained (%)
< 5, 2.5)	0.19
< 2.5, 1.25)	6.20
< 1.25, 1)	7.93
< 1, 0.5)	33.99
< 0.5, 0.2)	34.20
< 0.2, 0.1)	9.85
lower than 0.1	7.64

The TG curve and its derivative (dTG) for a heating rate of 50 °C min^{-1} are shown in Fig. 2. The first process, which occurs in the temperature range of 40 °C–150 °C, corresponds to the release of the moisture and adsorbed water, during which the mass loss is ~8%. The second process (250 °C–400 °C) can be characterised as the main decomposition region and is accompanied by a mass loss of ~60%. The last process occurs in the temperature range of 400 °C–570 °C. Similar curves (see Fig. 2) can be found in the study by Cui et al. (2019), where the authors used the nitrogen and oxygen in ratio 8:2 for studying feedstock, which includes the powder of *Chlorella Vulgaris* and apple tree sawdust.

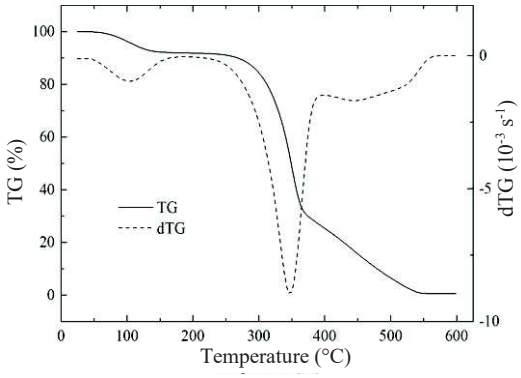

Figure 2. TG and dTG curves for heating rate 50 °C min^{-1}.

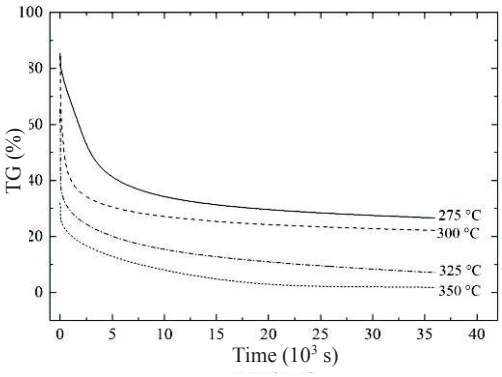

Figure 3. Results of TG analysis under isothermal heating.

The results of the isothermal TG analysis are shown in Fig. 3. The time $t = 0$ corresponds to the point when the isothermal heating began. Temperatures of 275 °C, 300 °C, 325 °C, and 350 °C were chosen due to their correspondence to the main decomposition region. The TG curves show that if higher temperatures are used, then

a higher mass loss is observed. In addition, the results show, that the decomposition process is not complete even if the sample is heated at 350 °C for ten hours.

The results show that if the temperature of the isothermal regime is 275 °C and 300 °C, then the total mass loss is ~73% and 78%, respectively. However, if temperatures 325 °C and 350 °C were used, which still correspond to the main decomposition region, the total mass loss is higher (93% and 98%, respectively). As mentioned in Section 1, the softwood contains 23 wt.%–33 wt.% of lignin, which can indicate that the lignin has already decomposed. Therefore, it can be concluded that the main decomposition region can be described as volatilisation of the main constituents if temperatures higher than 300 °C are used. Otherwise, the results indicate, that the lignin does not decompose at lower temperatures. The same interpretation of non-isothermal measurements was also used by Bilbao et al. (1997), Liu et al. (2002) and Fang et al. (2006). On the other hand, non-isothermal measurements could lead to different interpretations. Based on the results in this work, it can be also concluded that the heating rate is, along with the content (Gottipati & Mishra, 2011), one of the most important parameters that affect the thermal decomposition of lignin.

In a recently published article, Vitázek & Tkáč (2019) studied the region between the temperatures of 275 °C and 290 °C. Compared to these results, the region which corresponds to the beginning of the main decomposition region can be described as a first-order reaction model. However, a determined reaction model cannot be used to describe the whole process.

CONCLUSIONS

The thermal decomposition of pellets made from spruce wood (*Picea abies*) was studied using thermogravimetric analysis under the dynamic atmosphere of dry air. As there are different interpretations of the main decomposition region in the literature, the woody biomass was studied under isothermal conditions at temperatures of 275 °C, 300 °C, 325 °C and 350 °C over the course of ten hours. Based on the results it can be concluded, that the possible explanation for the main decomposition region seems to be the volatilisation of the main constituents. Otherwise, the results indicate that lignin does not decompose at temperatures lower than 300 °C. Therefore, it can be concluded that the heating rate is one of the most important parameters that affect the thermal decomposition of lignin and could lead to different interpretations if non-isothermal measurements are used.

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