DTA EVALUATION OF SPRUCE WOOD DEGRADATION PROCESS

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Abstract

The decomposition stages of spruce wood sawdust were analyzed by means of sequential differential calorimetry. Two stages of decomposition were identified and activation energy of one stage was calculated using the Kissinger method. The DTA was conducted by means of SEDEX safety calorimeter. Sample was analyzed under three heating rates of 10, 20 and 45 °C/h in temperature range from room temperature to 400 °C. The calculated activation energy for the last and most clear decomposition peak was 122.63 KJ/mol. The results are comparable with the data calculated by J.V. Rissanen et al., who calculated activation energy for Spruce hemicellulose as 120 KJ/mol.

Key words

Spruce wood, DTA, activation energy

INTRODUCTION

Lignocellulosic materials are naturally designed composites that play crucial roles in the survival of plants. Considering their broad availability, there is a general agreement on the replacement of major part of fossil-derived fuels and chemicals with lignocellulosic products. Additionally, some products are solely prepared from lignocelluloses and have no fossil-based equivalent (5).

The low-temperature heating of lignocellulosic materials (wood) causes changes in the physical, structural and chemical properties of wood. These changes are caused by temperature above 100 °C. Changes are also affected by other factors, such as time, atmosphere, pressure, and the amount of water content. Under certain conditions, changes in wood structure can be observed at temperatures up to 100 °C, for example, with increased humidity or reduced pressure. At temperatures range from 200 to 280 ˚C wood mass loss occurs (4).

Thermogravimetry has been widely applied to the study of wood and cellulose materials. There is a general agreement that decomposition of hemicellulose, cellulose, and ligning take place in a relatively narrow range of temperature, partially overlapping. There is no a definitive demonstration of which thermal feature corresponds to each component (9).

Previous studies have showed that biomass pyrolysis can be divided into four individual stages: moisture evolution, hemicellulose decomposition, cellulose decomposition and lignin decomposition (7, 10, 11). According to various publications, hemicellulose pyrolysis can occur in wide range of temperatures between 197-380 °C (11, 1). The pyrolysis of cellulose occurs mainly between 250–400 °C (1, 9). However, the lignin decomposition occurs throughout the range of temperatures: 150–900 °C (1, 11, 2).

Activation energy is one of the most important parameter, which describes the energy needed for the decomposition start to occur. Most methods for calculation of the activation energy of decomposition are based on the Arrhenius equation:

$$k = A.e^{\frac{-E_a}{RT}} , \qquad [1]$$

where k is the rate constant, A is the pre-exponential factor (min^{-1}), E_a is activation energy ($J.mol^{-1}$), R is universal gas constant ($8.314\ J.K^{-1}.mol^{-1}$), and T is thermodynamic temperature (K).

One of the major methods used today to calculate the activation energy of thermal decomposition of substances is the Kissinger method. It is assumed that the change in the heating rate of the sample leads to the changes of temperature at which the rate of mass loss is maximal (6). Kissinger also assumes that this change is dependent only on the activation energy. The modified form of this equation is currently most commonly presented in the form:

$$ln\left(\frac{\phi}{T_m^2}\right) = ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_m} , \qquad [2]$$

where ϕ is the heating rate ($K.min^{-1}$), and T_m is temperature at maximal mass loss.

MATERIALS AND METHODS

Sample of spruce wood was subjected to differential thermal analysis by the means of the SEDEX safety calorimeter (*Fig. 1*). This device was developed for quick assessment of materials behavior under elevated temperatures, and focuses on the safety aspects of such conditions. The apparatus is capable of operating under isothermal conditions, heating with specific heating rate and it can also operate under adiabatic conditions. Because of its variability and large heating oven, the SEDEX is suitable for analysis of larger samples with customizable storage of sample, or the aid of additional equipment. The heating range of the device is from room temperature up to 400 °C.
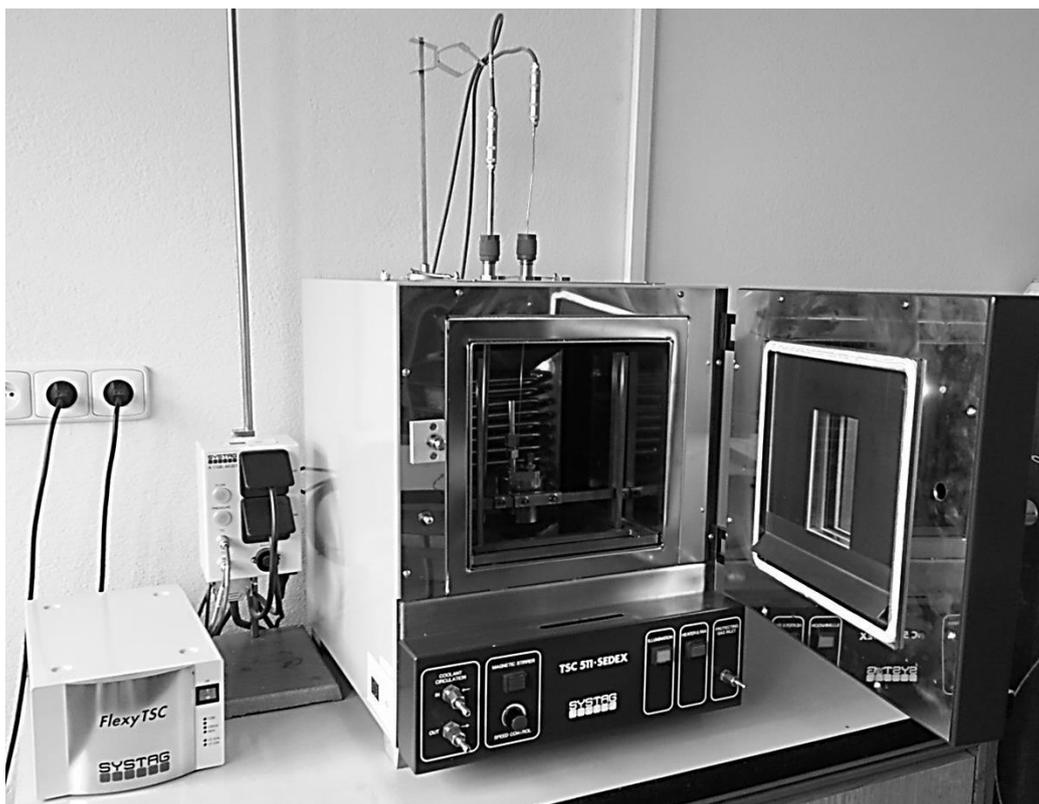
Fig. 1 SEDEX Safety calorimeter with standard sample vessel

This adiabatic calorimeter can collect a lot of useful and practical information on the reactions taking place in a substance, e.g. the safe upper temperature limit, gas production and heat production from the reaction. The acquired data can be used to predict the behaviour of a substance or mixture of substances in larger quantities, thereby avoiding potentially dangerous situations (3).
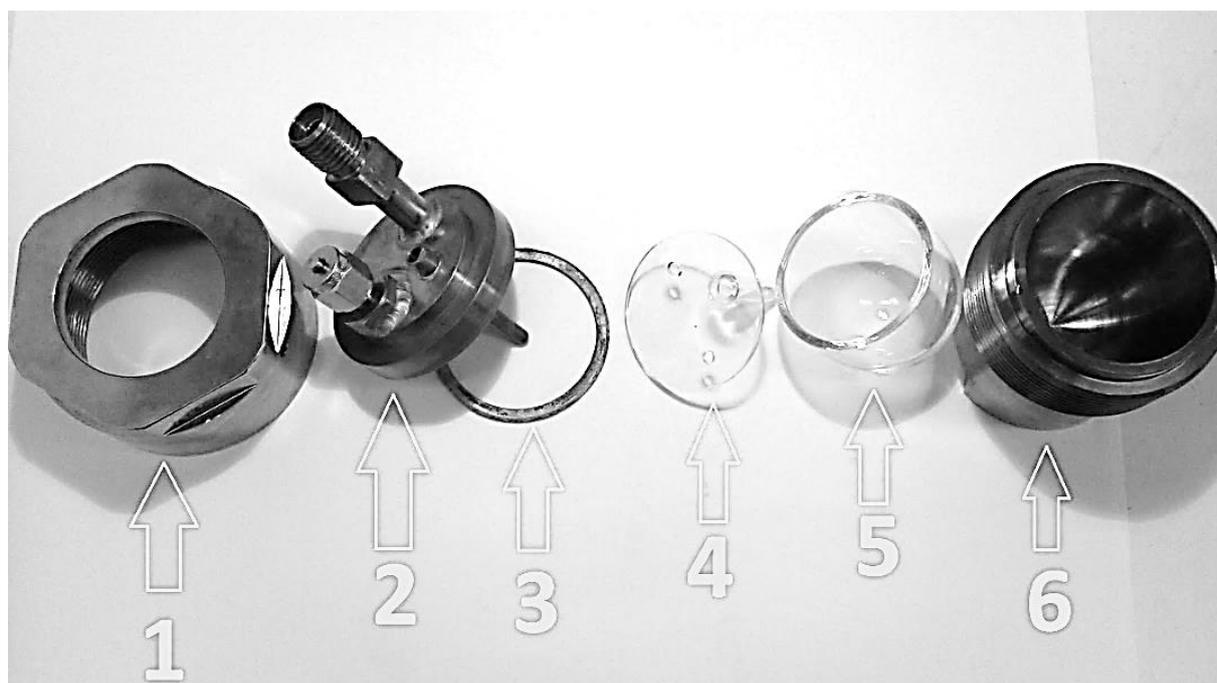

Fig. 2 SEDEX stainless steel vessel assembly 1 – Top part, 2 – Lid, 3 – Copper o-ring,
4 – Glass liner top, 5 – Glass liner bottom, 6 – Bottom part

The sample of spruce wood sawdust was conditioned for 24 hours at room temperature (21 °C) with the relative humidity of 45 %. Standard stainless steel sample vessel with glass liner for SEDEX was used (*Fig. 2*). The sample was investigated under dynamic heating conditions with three heating rates of 10, 25 and 45 °C/h in temperature range from 50 to 400 °C. The three different heating rates were chosen to obtain suitable amount of data for activation energy calculation based on the method according to Kissinger. The mass of the samples were recorded both before and after the experiment. The recorded masses are listed in table (Table 1).

Table 1 Sample masses before and after heating at different heating rates

Sample number	Heating rate [°C /h]	Sample mass before heating [g]	Sample mass after heating [g]
1	45	4.01	1.57
2	20	4.00	1.58
3	10	4.00	1.62

Suitable peaks of exothermic decomposition reaction were chosen from the measured data at all three heating rates and used for the calculation of activation energy according to the Kissinger method.

The SEDEX was calibrated with inert sample (quartz powder). The data acquired from the run with inert sample were stored in the memory and used as a reference data for later measurements under the same conditions in order to execute the sequential differential thermal analysis.

EXPERIMENTAL

The results of dynamic heating with all heating rates can be seen in following figures (Figure 3, Figure 4 and Figure 5).
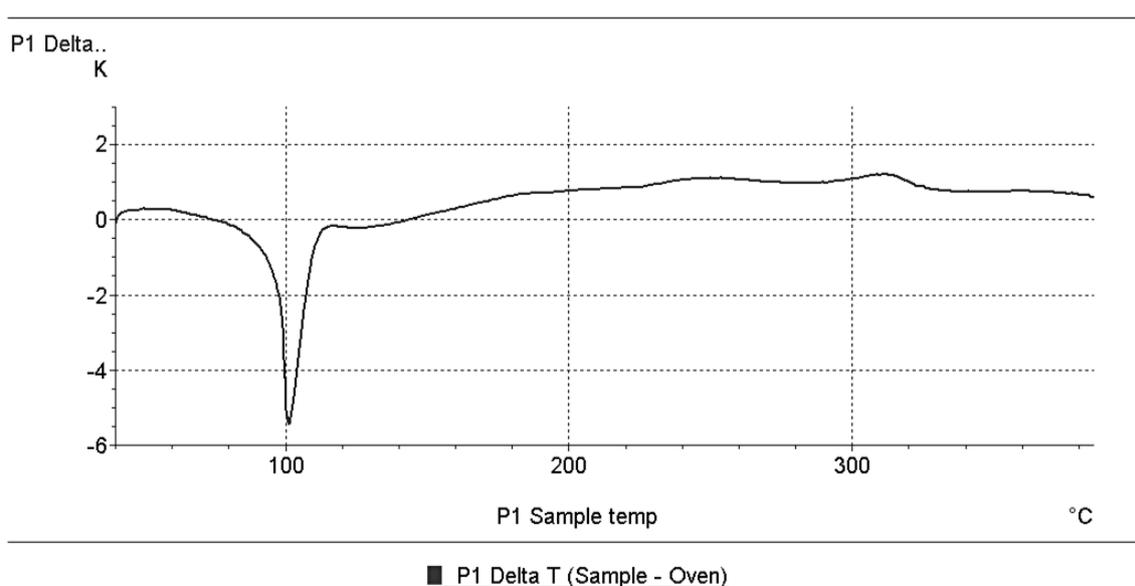

Fig. 3 DTA at heating rate of 45 °C/h

Two stages of decomposition were clearly observable, in the first case of heating with heating rate of 45 °C/h. The first decomposition reaction peak occurred at temperatures between

230 to 260 °C, and the second peak between 290-330 °C. There is possibility, that there was another decomposition reaction present at lower temperatures, but this peak is overlapping with the latent heat of water evaporation.

These peaks were observable also in the case of second heating with heating rate of 20 °C/h (Figure 4). However the first decomposition peak in not so clear, and therefore the temperatures of its occurrence cannot be determined. The second decomposition reaction occurred at temperatures between 280 – 310 °C.
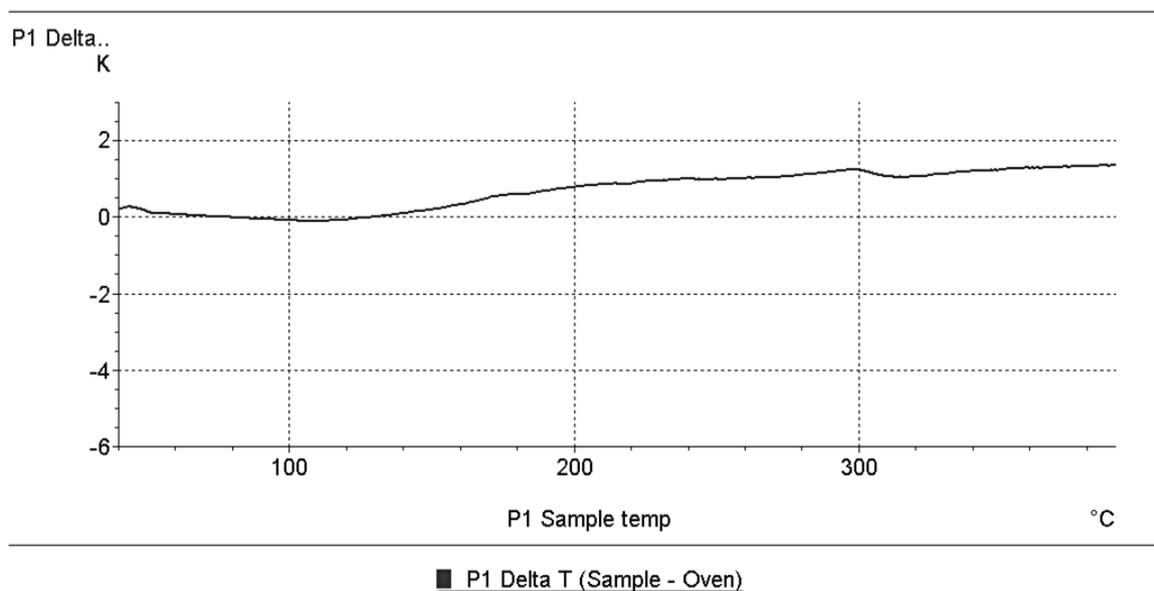

Fig. 4 *DTA at heating rate of 20 °C/h*

In the case of the last heating rate of 10 °C /h (Figure 5), the first decomposition reaction occurred somewhere in temperature range from 190 to 210 °C, and the second in temperature range from 270 to 290 °C.
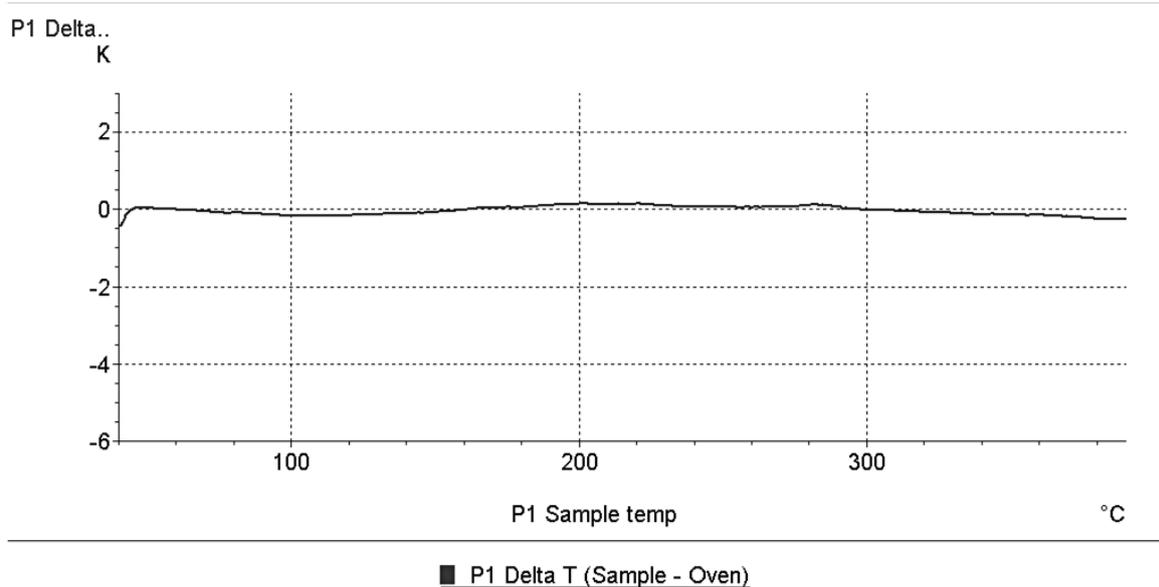

Fig. 5 *DTA at heating rate of 10 °C/h*

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Results from all three analysis contain area of water evaporation. This area could overlap other reaction. The smaller the heating rate, the wider the area.

RESULTS AND DISCUSSION

The summary of results from all three thermal analyses is listed in Table 2. In order to calculate the activation energy for decomposition reaction, it was necessary to identify temperature of this decomposition reaction for all three heating rates. Since the second decomposition reaction was the most significant in all three cases, the activation energy was calculated for this decomposition reaction.

Table 2 Summary of TDA results for heating rates of 10, 20 and 45 °C/h

Heating rate	45 °C/h	20 °C/h	10 °C/h
Sample mass before heating	4.05 g	4.00 g	4.00 g
Sample mass before after heating	1.57 g	1.58 g	1.62 g
Mass loss	61.4 %	60.6 %	59.6 %
Minimum delta T	- 5.50 °C	-0.11 °C	0.45 °C
Sample temperature at min delta T	100 °C	110 °C	40 °C
Maximum delta T	1.22 °C	1.38 °C	0.16 °C
Sample temperature at max delta T	312 °C	390 °C	201 °C
First decomposition reaction	230 – 260 °C	N/A	190 – 210 °C
Second decomposition reaction	290 – 330 °C	280 – 310 °C	270 – 290 °C

The activation energy for the second decomposition reaction was calculated according the Kissinger method. The proportion $1000/T$ was chosen for the dependence to make the calculation in kJ/mol. Heating rate of the sample was fitted into the formula in K/min and the temperature in K. Values listed in Table 3 were used for the calculation.

Table 3 Values used for the calculation of activation energy

Heating rate	45 °C/h	20 °C/h	10 °C/h
Sample temperature at max delta T in the case of second decomposition reaction	311 ºC	299.5 ºC	281 ºC

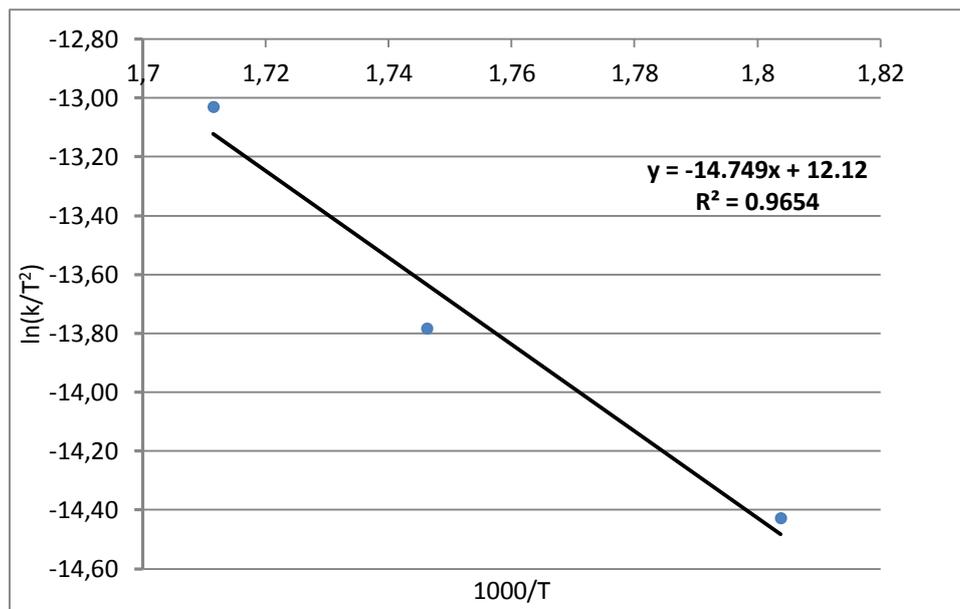The dependence based on data from Table 3 according to Kissinger is presented in *Fig. 6*.

Fig. 6 *Dependence described by Kissinger*

The slope of the regression equation (Fig. *6*) was used to calculate the activation energy. The calculated activation energy was 122.63 KJ/mol.

J. V. Rissanen, et. al. (8) states in his paper that the activation energy he calculated for hemicelluloses obtained from spruce wood was approximately 120 kJ / mol. This value is comparable to the value obtained through the Kissinger method from the measured data.

CONCLUSION

The measured and calculated data show, that the safety calorimeter SEDEX can be utilized for the calculation of activation energy. One of the advantages of evaluation by SEDEX is the possibility of analyzing samples of larger volumes. The standard steel vessel for SEDEX allows samples up to 20 ml in volume to be analyzed. However, the limitation lies in the limited heating rate for larger volumes. In this case the device was limited to the maximal heating rate of 45 °C/h in the case of use of the standard steel vessel for SEDEX.

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