

## Determination of activation energy of the pellets and sawdust using thermal analysis

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**Abstract.** The aim of this study is to describe the thermophysical properties of pellets and sawdust. Samples were chosen with regard to sustainability and environmental friendliness of materials. The main object of this paper was the investigation of thermal degradation of selected samples. Industrial pellets from Slovakia and sawdust from household source were compared. Materials suitable for pyrolysis are organic materials that degrade at increased temperature. Cellulose, hemicellulose and lignin are main components of biomass (wood) in varying proportions. Thermal processes were carried out from 25 °C to 850 °C using inert nitrogen atmosphere. Heating rate was linear from 5 °C min<sup>-1</sup>, 10 °C min<sup>-1</sup> to 20 °C min<sup>-1</sup>. Mass decrease to 150 °C corresponds to release of water and other lighter unbound hydrocarbons. Samples lose 6–8% of their mass due to the temperature. At main decrease the mass loss was between 62% and 69%. In some cases this decrease is in two drops that end at the temperature around 500 °C. Pyrolysis can be considered to consist of independent parallel reactions. In order to make theoretical groundwork for biomass pyrolysis available, activation energies were calculated with the help of two kinetic models (Kissinger-Akahira-Sunose and Flynn-Wall-Ozawa model). The residuals from pyrolysed samples are determined and temperature dependent profiles of the materials were obtained.

**Key words:** activation energy, biomass-waste, pyrolysis, thermogravimetric analysis.

### NOMENCLATURE:

DTG – Differential Thermogravimetric Analysis  
FWO – Flynn-Wall-Ozawa  
KAS – Kissinger-Akahira-Sunose  
TGA – Thermogravimetric Analysis  
 $A$  (s<sup>-1</sup>) – Pre-exponential factor  
 $E_a$  (kJ mol<sup>-1</sup>) – Activation energy  
 $R$  (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) – Universal gas constant  
 $T$  (K) – Temperature  
 $T_{wi}$  (K) – Temperature at conversion  $i$   
 $m$  (kg) – Mass

### *Subscripts*

$T$  – Instantaneous mass  
 $0$  – Initial mass  
 $k$  – Final mass

### *Greek symbols*

$\alpha$  (–) – Conversion  
 $\frac{d\alpha}{dt}$  (s<sup>-1</sup>) – Conversion rate  
 $\beta$  (K.min<sup>-1</sup>) – Heating rate.

## INTRODUCTION

The aim of this study is to describe thermophysical properties of pellets from wood and wood chips. Biomass is an organic product generated by a natural process. It is used and consumed in human activities. Biomass waste is currently adequately utilized in order to meet the energy demands of the population. Since the past decades, reserves of fossil fuels which are the major energy source in most countries are continuously being depleted (Blaschke et al., 2013; Jouhara et al., 2018). It is therefore favourable to seek replacement of these resources in more accessible commodities. Biomass can be this resource, for its availability and production amount. Natural biomass, special wood waste, is a renewable energy source, while biomass fuel is a sustainable energy resource (Suriapparao et al., 2014; Suzdalenko et al., 2014; Tomei & Helliwell, 2016). Since it is recognised that the biomass system and respective biofuels as sub-systems do not contribute to the greenhouse effect (due to the CO<sub>2</sub> neutral conversion), extensive investigations have been carried out worldwide to enhance the biomass use by substituting fossil fuels for energy conversion (Vassilev et al., 2010). Energy from the biomass can be obtained by thermal decomposition without access of air, reduced oxidant feed or simple burning. The thermal method of thermogravimetric analysis resembles the pyrolysis. Pyrolysis is the thermal degradation of substance at elevated temperature in the absence of oxygen or in a reduced oxygen atmosphere. Pyrolysis and gasification are the most commonly employed and the most appropriate processes for the generation of liquid biofuels, syngas, chemicals, or charcoal via pyrolysis and liquefaction processes (Soria-Verdugo et al., 2013; Chan et al., 2015). Most of the biomass has heterogeneous property attributes due to the fact that the biomass itself constitutes of numerous components, such as hemicellulose, cellulose, lignin, and minor amounts of extractives (Hu et al., 2017). These differences in biomass composition determine the nature of thermal decomposition and individual decomposition processes. Thermogravimetric analysis allows us to look at the thermal behaviour of biomass under various conditions of the oxidation environment (Nilova et al., 2017; Tamelová et al., 2019). We can also determine the shape of the thermogravimetric curve and thus the individual decomposition temperatures of the biomass components. According to the shape of the TGA curves, the pyrolysis of biomass materials determine the rate of the reaction and the temperature of the decomposition processes. From thermal degradation of materials we can identify thermal resistance, rate of processes, temperature of degradation and activation energy. The non-isothermal methods are the most commonly used for performing the kinetic analysis of solid state reactions (Fernandez et al., 2018). The kinetic analysis is conducted using an independent parallel reaction model to extract non-isothermal pyrolysis kinetic parameters including activation energy in the feedstocks. An independent parallel reaction model is adopted for modelling to ensure that the pseudo-components are degraded simultaneously and individually in a same temperature range (Bach et al., 2019). Interactions among the biomass pseudo-components are neglected. Individual pseudo-components can be described by the Eq. 1 (Ali et al., 2017; Bartocci et al., 2019). By using the TGA data, the kinetic parameters as well as pyrolysis mechanism can be determined according to different mathematical approaches (Hu et al., 2017). Pyrolysis has been employed to convert biomass feedstock into bio-fuels with high energy density, and biomass pyrolysis generates three product streams: liquid (bio-oil), gas, and solid product (biochar) (Liu & Han, 2015). The

distributions and properties of these product streams are strongly dependent on pyrolysis conditions (Zhengang & Guanghua, 2015). Wood is a composite material consisting of cellulose, hemicellulose and lignin as major cell wall constituent polymers with small amounts of minor components, including inorganic substances. Lignin is hydrophobic and is found to be covalently linked to the structures of hemicellulose (Hosoya et al., 2007; Rana et al., 2018). Furthermore, vapour phase carbonization of the volatile products from lignin was substantially inhibited in wood and demineralized wood. Any material containing major components of biomass, such as lignin, cellulose and hemicellulose, decomposes at 200 °C. This main decomposition proceeds to the temperature of 600 °C, where cellulose, lignin and hemicellulose are degraded. Despite this main decomposition, all mass changes during the course of degradation are important for the determination of kinetic parameters. By examining the kinetic parameters, we can determine the activation energy of the material in special conditions depending on the size of the conversion. The activation energy can be explained as energy that is required to activate atoms and molecules to a condition in which they can undergo chemical transformation or physical transport (Hlaváč et al., 2016).

## MATERIALS AND METHODS

Thermogravimetric analysis was performed on two samples from different sources using the Mettler Toledo TGA/DSC 1 instrument. Samples were chosen with regard to sustainability and environmental friendliness of materials. Industrial pellets from Slovakia and waste wood from household source were compared. Pellets and waste wood were not specifically modified. Samples were provided by Slovak company for pellets production. High quality pellets from mix of soft woods like spruce with low ash content, around 0.80%. Waste wood was sawdust and it arose by treatment of wood in household, predominantly spruce. Samples were weighted on KERN 220-5M scales with an accuracy of 0.01 mg to 0.1 mg. Graphs were created in STAR<sup>®</sup> SW 12.10 software and kinetic parameters were calculated by using Excel.

TGA was performed at three different heating rates: 5 °C min<sup>-1</sup>, 10 °C min<sup>-1</sup> and 20 °C min<sup>-1</sup>. Masses of samples were in the range 92–101 mg for pellets and 23–30 mg for sawdust and were placed in a closed alumina container. The temperature program was set from 25 °C (room temperature) to 850 °C, at a nitrogen atmosphere with a flow rate of 50 mL min<sup>-1</sup>. Measurements were executed in an inert environment without access of air.

Kinetic parameters of biomass thermal degradation can be calculated by Arrhenius law

$$\frac{d\alpha}{dt} = Ae^{\left(\frac{-E_a}{RT}\right)} f(\alpha) \quad (1)$$

where  $\alpha$  – conversion;  $R$  – universal gas constant;  $A$  – pre-exponential factor;  $T$  – thermodynamic temperature;  $E_a$  – activation energy and  $f(\alpha)$  – reaction model, J mol<sup>-1</sup> K<sup>-1</sup>; K; kJ mol<sup>-1</sup>. Value of the conversion or extent of the conversion during pyrolysis can be expressed as

$$\alpha = \frac{m_0 - m_t}{m_0 - m_k} \quad (2)$$

where  $m_0$  – initial mass, mg;  $m_i$  – immediate mass (mg) and  $m_k$  – final mass, mg; (Vyazovkin et al., 2011; Ondro et al., 2017). At a constant heating rate ( $\beta$ ) the temperature changes are linear with time, and the iso-conversional methods can be used for the determination of kinetics parameters. The iso-conversional methods require performing a series of experiments at different temperature programs and yield the values of effective activation energy as a function of conversion. More often the activation energy is found to vary with the extent of conversion. Iso-conversional methods are widely used in literature for evaluation of the activation energy.

KAS model (Kissinger-Akahira-Sunose) is one of the best methods, used for the relation between heating rate and inverse temperature, by relationship

$$\ln\left(\frac{\beta_i}{T_{ai}^2}\right) = const - \frac{E_\alpha}{RT_{ai}} \quad (3)$$

The activation energy is given as the slope of linear fit of function of natural logarithm  $\frac{\beta_i}{T_{ai}^2}$  and inverted value of the temperature (Starkin et al., 2003; Vyazovkin & Sbirrazzuoli, 2006; Damartizs et al., 2011; Ali et al., 2017).

FWO model (Flynn-Wall-Ozawa) is one of the most commonly accepted methods for the computation of kinetics parameters. The method uses data from thermogravimetric analysis for the determination of the activation energy. The activation energy is obtained from the slope of the linear fit of the plot between  $\ln(\beta_i)$  and inverted value of the temperature. The integral solution after integration with respect to temperature is shown by Eq. (4)

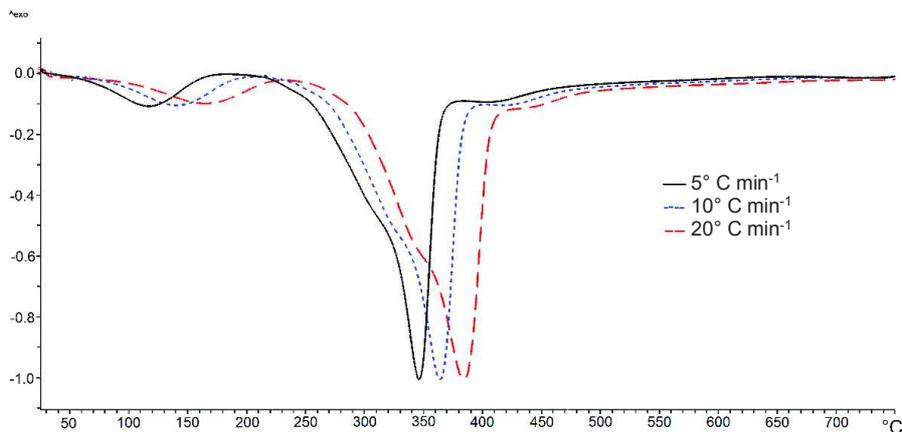
$$\ln \beta_i = const - 1.052 \left( \frac{E_\alpha}{RT_\alpha} \right) \quad (4)$$

(Flynn & Wall, 1966; Vyazovkin & Sbirrazzuoli., 2006; Damartizs et al., 2011; Ali et al., 2017).

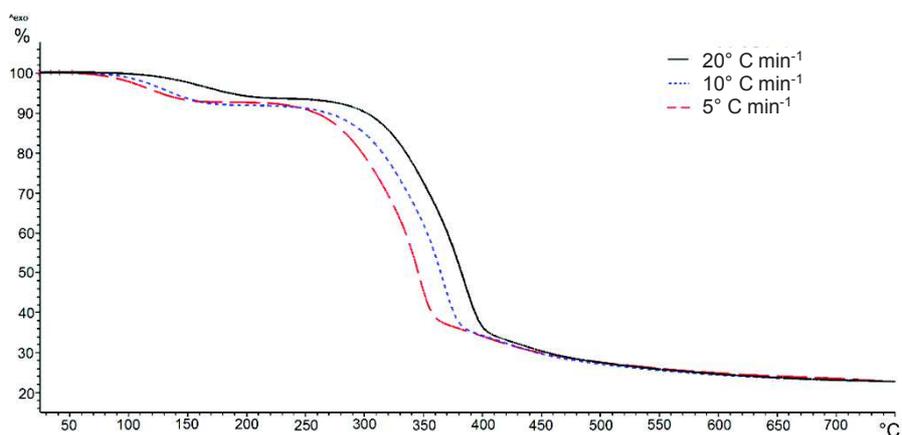
## RESULTS AND DISCUSSION

When comparing individual measurements, only the expected change in the same sample and different heating rates was evident. As the heating rate increases, the TGA curve shifts to higher temperatures. Data for individual graphs are obtained from the TG data shown in Figs 2, 3. TG were performed with reduced oxygen access in a nitrogen stream as carrier gas with the rate of flow 50 mL min<sup>-1</sup>.

The mass loss on the main section was shifted by 10 °C when changing the heating rate by 5 °C min<sup>-1</sup> and by 20 °C at a speed increase of 10 °C min<sup>-1</sup>. The main peak of the DTG curve was at the temperature of 340 °C at 5 °C min<sup>-1</sup>, at the temperature of 360 °C and 390 °C at the heating rate of 10 °C min<sup>-1</sup> and 20 °C min<sup>-1</sup>, respectively (Fig. 1). Temperatures of peak DTG correspond to 30–80% conversion, according to heating rate. For sawdust they are at conversion from 50% to 70%, at temperature of 350 °C to 400 °C. The changes in the mass of samples are shown in Fig. 2. Vaporization was carried out till the temperature of 170 °C at the heating rate 5 °C min<sup>-1</sup>.



**Figure 1.** DTG curves for the pellets of degradation  $5\text{ °C min}^{-1}$  (solid line),  $10\text{ °C min}^{-1}$  (spotted),  $20\text{ °C min}^{-1}$  (dashed).

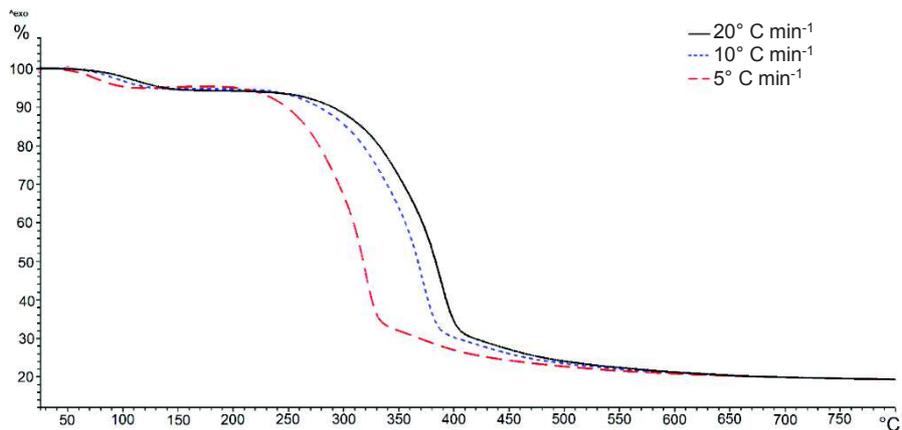


**Figure 2.** Dependency of mass loss (%) for pellets to temperature, TGA curves of degradation  $5\text{ °C min}^{-1}$  (long-dashed lines),  $10\text{ °C min}^{-1}$  (short-dashed lines),  $20\text{ °C min}^{-1}$  (solid line).

The evaporation process is finished at approximately  $210\text{ °C}$  at the heating rate  $20\text{ °C min}^{-1}$ . The main decomposition of the hemicellulose material occurs at temperature of  $250\text{ °C}$  to  $400\text{ °C}$ , a decrease from above  $500\text{ °C}$  is attributed to the decomposition process of the secondary pyrolysis products.

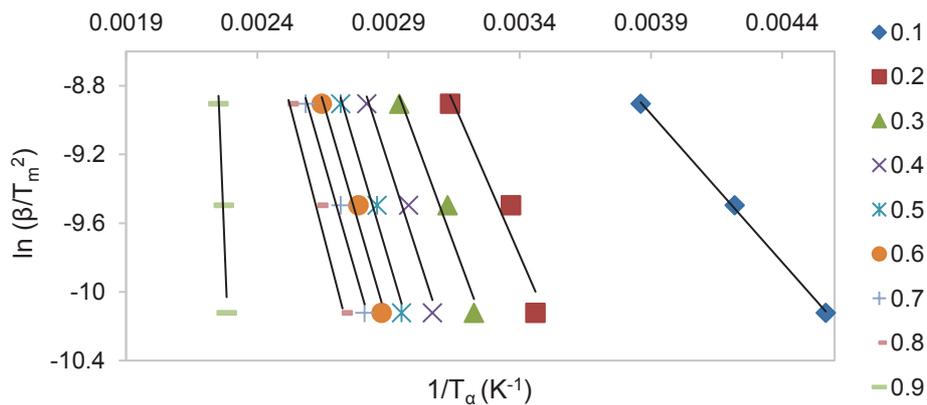
The DTG curve shows two main mass changes at heating rate  $20\text{ °C min}^{-1}$  at temperatures around  $150\text{ °C}$  and  $370\text{ °C}$ . For the heating rate of  $5\text{ °C min}^{-1}$ , these temperatures are  $120\text{ °C}$  and  $350\text{ °C}$  where evaporation and major biomass decomposition occur. The decomposition peak of approximately  $350\text{ °C}$  is little shifted to the right side, which corresponds to another decomposition process change in mass. This decrease covers a temperature range from  $250\text{ °C}$  to  $350\text{ °C}$ , with a peak at  $300\text{ °C}$ . For higher heating speeds, these speeds move to higher temperatures (Damartizs et al., 2011; Ali et al., 2017). This overlapping process corresponds to the breakdown of cellulose.

The major decomposition peak in the temperature range from 300 °C to 450 °C has a peak at 345 °C and corresponds to the breakdown of hemicellulose bonds. As expected, when the heating rate is increased, these peaks are shifted to higher temperatures. Decomposition peaks correspond to temperatures of 365 °C and 385 °C for the heating rate of 10 °C min<sup>-1</sup> and 20 °C min<sup>-1</sup>, respectively. For sawdust, the temperature range is approximately same for the pellets at the heating rate of 10 °C min<sup>-1</sup> and 20 °C min<sup>-1</sup>. Small difference was found in heating rate of 5 °C min<sup>-1</sup>, this decomposition is shifted to lower temperatures with a peak at 325 °C (Fig. 3).

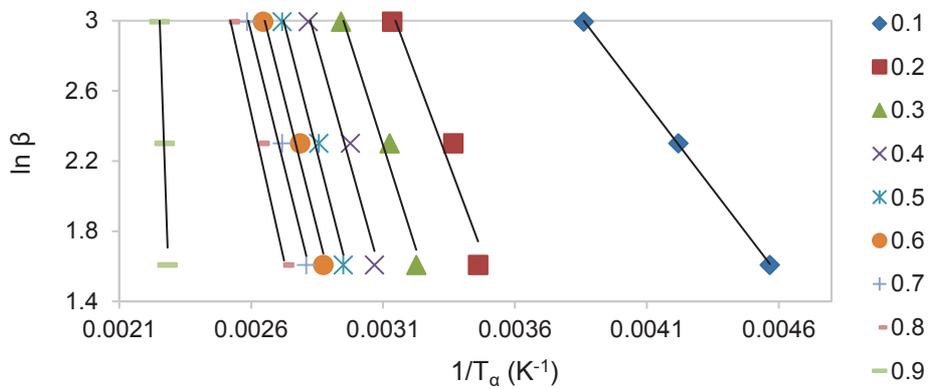


**Figure 3.** Dependency of mass loss (%) for sawdust to temperature, TGA curves of degradation at 5 °C min<sup>-1</sup> (solid line), 10 °C min<sup>-1</sup> (dashed), 20 °C min<sup>-1</sup> (spotted).

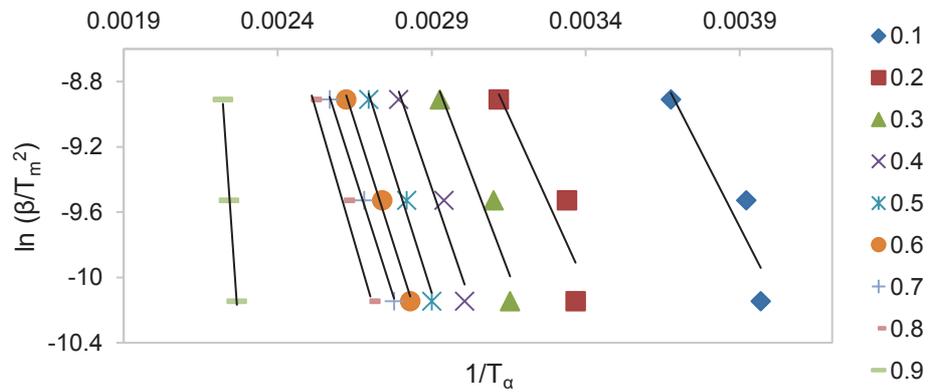
Conversion rate temperature was determined from TG curves. Individual activation energies for a conversion range from 0.1 to 0.9 were determined from the slope of the trend line and Eqs 3, 4 were used to create Figs 4–7.



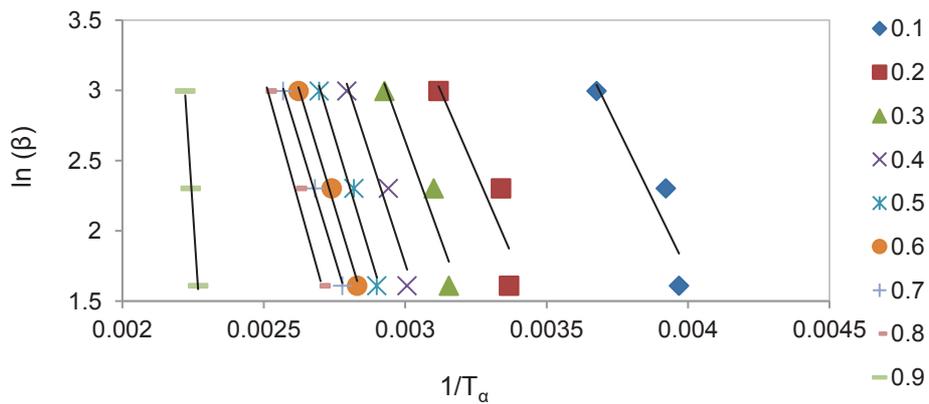
**Figure 4.** Typical linear regression lines of iso-conversional methods at individual conversions for pellets by KAS method.



**Figure 5.** Typical linear regression lines of iso-conversional methods at individual conversions for pellets by FWO method.



**Figure 6.** Typical linear regression lines of iso-conversional methods at individual conversions for sawdust by KAS method.



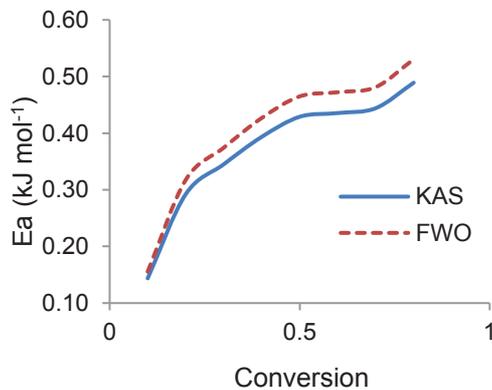
**Figure 7.** Typical linear regression lines of iso-conversional methods at individual conversions for sawdust by FWO method.

Conversion rate 0.9 was not used in comparison because big increase of activation energy occurred. The activation energy of the pellet for the individual conversion values ranges from 14.36 kJ mol<sup>-1</sup> to 48.91 kJ mol<sup>-1</sup> for the KAS model. For the FWO model, these values are not very different and range from 15.54 kJ mol<sup>-1</sup> to 53.05 kJ mol<sup>-1</sup>, with a conversion from 10% to 80%. Specific values for each model and conversion value are shown in Table 1. For sawdust, the activation energy ranges from 30.56 kJ mol<sup>-1</sup> to 53.82 kJ mol<sup>-1</sup> for the KAS model. The lowest activation energy is for 10% conversion and the highest value at 80% conversion. For the FWO model, the activation energy was from 32.54 kJ mol<sup>-1</sup> to 57.30 kJ mol<sup>-1</sup>, for the conversion of 10% to 80%. All values of activation energy for individual models and samples are shown in Table 1, where  $\alpha$  is taken as conversion from 10% to 90%.

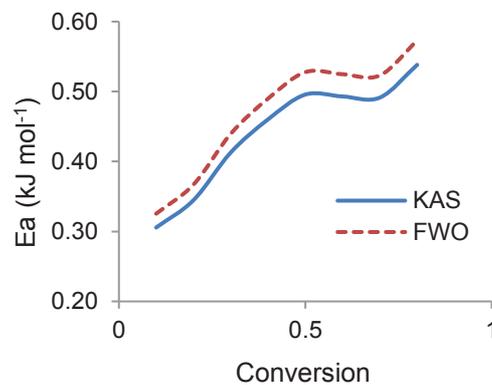
**Table 1.** Overview of the obtained activation energies

$\alpha$	Pellets		Sawdust	
	$E_a$ KAS (kJ mol <sup>-1</sup> )	$E_a$ FWO (kJ mol <sup>-1</sup> )	$E_a$ KAS (kJ mol <sup>-1</sup> )	$E_a$ FWO (kJ mol <sup>-1</sup> )
0.1	14.36	15.54	30.56	32.54
0.2	29.21	31.73	34.47	36.70
0.3	34.50	37.43	41.29	43.96
0.4	39.34	42.67	46.02	48.99
0.5	42.89	46.49	49.57	52.77
0.6	43.55	47.22	49.30	52.48
0.7	44.41	48.13	49.14	52.31
0.8	48.91	53.05	53.82	57.29
0.9	315.93	342.89	225.84	217.91

Activation energy increases with the degree of conversion increase (Table 1). The final value for conversion of pellets resp. sawdust for 90% is higher about 267.02 kJ mol<sup>-1</sup> resp. 172.02 kJ mol<sup>-1</sup> for the KAS model and about 289.84 kJ mol<sup>-1</sup> resp. 160.62 kJ mol<sup>-1</sup> for FWO model. The energy value for conversion 0.9 is different for both models and both are not included in the overall activation energy evaluation due to the inaccurate character of the process description.



**Figure 8.** Activation energies of pyrolytic process for pellets.



**Figure 9.** Activation energies of pyrolytic process for sawdust.

Conversion dependencies of activation energy for both wood samples are shown in Figs 8 and 9. It is possible to observe from Fig. 8 and Fig. 9 that activation energy of pellets and sawdust increases with increasing conversion. Activation energy increases with conversion degree for both sawdust and pellets (Table 1). In the conversion zone

from 0.55 to 0.8 a less large increase is observed. It can be ascribed to the fact that there existed composed samples (Bartocci et al., 2019). The activation energy of the pellets is in every case between 1.5% and 18.1% for the KAS model and 1.6% to 17% for the FWO model, for the same conversions of material. The highest difference between the models 4.67% was obtained in the case of pellets for the conversion of 0.2.

Authors Wu et al. (2019) explored activation energy of pellets at the gasification. Their values of activation energy ranged from 8.77 kJ mol<sup>-1</sup> to 59.57 kJ mol<sup>-1</sup> for individual gaseous products. Activation energy values of pellets and wood powder varied from 92.33 kJ mol<sup>-1</sup> to 71.20 kJ mol<sup>-1</sup> (Haobin et al., 2018). Authors Guo et al. (2014) determined the activation energy for fresh wood pellets in ranges from 50 kJ mol<sup>-1</sup> to 60 kJ mol<sup>-1</sup>. We obtained similar activation energy by TGA experiments for sawdust and pellets. It can be seen from Figs 8 and 9 that the activation energy of the KAS model is lower than for the FWO. The progress of activation energy is the same for both methods. The same character of the activation energy with increasing conversion is reported in literature from authors Ali et al (2017). The energy value for conversion 0.9 is different for both models and both are not included in the overall activation energy evaluation due to the inaccurate character of the process description.

## CONCLUSION

The behaviour of ligninocellulosic material in the form of sawdust and pellets was studied during thermal degradation without access of air by using TGA. The design of the TGA curve corresponds to the shape of the curve for biomass with different contents of cellulose, hemicellulose and lignin. Cellulose decomposed in a narrow range of temperatures, covered by the decomposition of other components corresponding to the wood biomass composition. The biggest mass loss corresponding to the thermal degradation is evident at temperatures from 250 °C to 400 °C, depending on the heating rate. At these temperatures, the decomposition of cellulose, hemicellulose and lignin occurs in two parts. Temperature shifts to higher temperatures at higher heating rates are expected and may be due to heat transfer in the sample. The determination of the activation energy was based on iso-conversional methods that are most suitable to determine the activation energy for samples of biomass. We also found out that values of activation energy of pellets and sawdust are different. This can be caused by different composition of materials. For heat treatment of wood materials, it is necessary to know their kinetics parameters and the results can be used for further understanding of pyrolysis process. Due to the structural changes in sawdust during pelleting, we assume change of the activation energy. Links created due to the compaction could result in a decrease of the activation energy.

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