# Self-ignition potential assessment for different biomass feedstocks based on the dynamic thermal analysis

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| ARTICLE INFO | ABSTRACT |
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| | Despite many advantages of the utilization of biomass as a renewable energy source, certain bottlenecks during biomass plant operation can be identified. Transport and collection of biomass as well as non-uniform material characteristics are issues related to decreasing efficiency of logistics and fuel manipulation which can also cause economic problems with biomass collection, transport, and storage. Since biomass is an especially reactive fuel, this has raised concerns over its safe handling and utilization. Fires, and sometimes explosions, are a risk during all stages of fuel production as well as during handling and utilization of the product. This paper presents a novel method for assessing ignition risk and provides a ranking of relative risk of ignition of biomass fuels. Tests within this method include physical and chemical properties of biomass, thermal analysis measurements, and the calculation procedure steps which were made using characteristic temperatures from thermogravimetry recordings. The results of thermogravimetry analysis were used for determination of tangent slope of the mass loss rate curves in devolatilization zone at considered heating rates for all tested samples. Linear interpolation of the data obtained by tangent slope analysis and used heating rates may provide unique straight line for each sample in the ignition testing. Thermogravimetry index of spontaneous ignition ($TG_{spi}$) is obtained for all samples based on newly established formula. By varying gradient of linear dependence of self-heating coefficient against reference temperatures, mass and heat transfer limitations for various biomasses were discussed. The proposed method is accurate as well as relatively simple and quick, enabling determination of data necessary for design and application of appropriate measures to reduce fire and explosion hazard related to operation of biomass. |

## 1. Introduction

The energy accumulated in biomass is chemical in nature, and it could be transformed into heat and electricity on efficient and acceptable way (Khare et al., 2016). From this perspective, biomass has more characteristics of fossil fuels than other renewables, for a reasonable reason because fossil fuels are actually a fossil form of biomass. Historically, biomass has been the primary energy source for humankind, mainly in the form of wood used for heating and storing food, while the fossil fuels took over the primacy of the industrial revolution (van de Kaa et al., 2017). Nevertheless, biomass today accounts for 15% of total energy consumption, and it is significant that this share is meaningfully higher in developing countries than in industrialized countries (Demirbas and Demirbas, 2007). One of the most important factors determining the

potential role of biomass in the energy industry is the strong competition that exists between the value of biomass and the land necessary for its cultivation, which is not the case with other renewable sources. Biomass can be used as food, fertilizer, for the production of paper fibers and as a fuel. Biomass is nowadays increasingly referred to as a substitute for fossil fuels due to the much less harmful emissions from combustion (Cherubini, 2010). Emissions from the combustion of forest biomass or wood biomass have an important environmental impact, so a realistic picture of the situation is needed. Combustion of forest biomass and fossil fuels emit gases that are indistinguishable because in both cases large amounts of carbon dioxide and many other harmful substances are generated. However, the biomass is neutral with respect to the carbon dioxide produced by its combustion, since it is considered that the atmospheric load of $CO_2$ when using biomass as fuel is negligible because

the amount of $CO_2$ emitted during combustion is equal to the amount of $CO_2$ absorbed during plant growth. If logging and wood biomass increment is equal, biomass can be considered $CO_2$ neutral. So, it could be said that by using biomass instead of fossil fuels, carbon actually returns to the earth and does not go into the atmosphere whereas $CO_2$ it creates a greenhouse effect and causes climate change (Gustavsson et al., 2015).

In the Republic of Serbia, there is a significant potential for biomass use, but its utilization is still extremely modest due to logistical issues (Dodić et al., 2010). Those issues are related to collection, transport, storage and utilization of biomass as fuel in a relatively narrow radius from its origin. The complexity of these procedures is connected to low energy density of various biomass, high moisture content, and heterogeneity in shape and size. Therefore, in addition to a strong logistics infrastructure, appropriate biomass preparation is needed before exploitation. One way is to use biomass in the densified form (pellets and briquets), which are, based on the production process, is characterized by high energy density, low moisture content, and better homogeneity (Arranz et al., 2015). However, increasing the energy density of the fuel, together with lowering the moisture content, initiates problems with spontaneous (or self) ignition during storage and handling of those fuels, which requires additional safety measures (Sedlmayer et al., 2018). Standard experimental method for determination of this characteristic for solid biomass is not yet developed and auxiliary procedures which could be used for this purpose are highly demanding, which inspired the authors have developed the new approach for identification and assessment of spontaneous ignition potential for solid biomass by thermogravimetry (TG) – derivative thermogravimetry (DTG) analysis as one of modern techniques for fuels characterization (Torrent et al., 2015).

These techniques have been used to detect the temperatures at which the exothermic processes start for solid products of natural origin, such as fossil fuels, biomass or food products of different origin, and to estimate kinetic characteristics of the oxidation process (García-Torrent et al., 2012). Comparing these temperatures between different products is possible to establish a relative scale of the tendency to spontaneous combustion, since the lower the temperatures at which the exothermic processes are initiated, then the greater the tendency of the product to self-ignite (Chen et al., 2015). This procedure has been used for different types of coals (Yuan and Smith, 2012), for some food products (Ramírez et al., 2010) and sewage sludge (Fernandez-Anez et al., 2014), obtaining satisfactory results (Pejic et al., 2015). However, it has been detected a lack of detailed data on thermal analysis techniques applied to different biomasses from agriculture forestry to waste, subjected to different prerequisites to obtain the samples with different particle size treatments.

In order to apply a newly developed methodology, two biomass samples (forestry and agricultural waste biomass feedstock) were tested on simultaneous thermal analyzer and further analysis was performed in order to calculate the thermogravimetric index of spontaneous ignition ($TG_{spi}$) which could be used for comparison and classification of tested materials related to spontaneous ignition potential. In addition, the influence of particle size of tested samples on the degree of self-ignition risk was also analyzed.

The application of $TG_{spi}$ method is most commonly used in the case of thermal analysis (TA) testing in self-ignition assessment of fossil fuels (frequently for low-rank coals), but this method, to the authors best knowledge was not applied in the case lignocellulosic (biomass) materials. Therefore, the key turning point of this work would be the implications of $TG_{spi}$ method in self-ignition risk apprises in the biomass combustion process.

An inadequate storage and handling of the stored biomass material may result in fires and explosions, possibly causing injuries to employees, sometimes loss of lives and also considerable economic loss together with environmental damage. Immature plant materials freshly harvested, or grains with high moisture content are more easily attacked by bacteria, mites, molds. The biological activity of these microorganisms releases heat in the material. However, under certain conditions of temperature, pressure, and heat removal, this heat cannot be transferred to the

surroundings, and the temperature steadily rises. The increase in temperature initially occurs as a result of metabolic activity and therefore does not exceed 70–75 °C. Afterward a chemical oxidation starts up to at least 150 °C. Self-ignition not only leads to the decomposition of the material, with the release of flammable gas, but it also may be responsible for major fires and risk of explosion if the ignition point is reached. Spontaneous ignition is a complex process and many investigators may not fully understand the factors that promote it, and how to assess its likelihood. It occurs in solids, liquids, and gases. In the latter, it is more commonly known as "auto-ignition". Most common to flaming fires events is the involvement of solid configurations in spontaneous ignition. The heat transfer, or the inability to cool a hot material, initiates the process (Yang and Sheng, 2019). The process starts as a chemical reaction that is not yet deemed combustion, and the consequence of ignition can be smouldering or flaming. The key variables are the size of the material and nature of the heat transfer, and the particular chemical and physical properties of the material.

This research study is the first step of implementation of the proposed method to lignocellulosic (plant) materials to assess the tendency of these materials to self-ignition, where applied experimental conditions are adapted to the conditions that prevail in biomass stockpiles, where such materials are kept in very airy environments. Therefore, the main goal of this study is to provide a practical (laboratory) test to assess the propensity of the tested materials for self-ignition in the fire investigation for investigators with a scientific understanding of spontaneous ignition and its analysis. Since that this subject is complex, the presented method was explained from a scientific point of view in its simplest form.

## 2. Materials and methods

The internal laboratory method according to the previously established methodology was used for all experimental tests in order to assess the spontaneous ignition potential of the considered samples. The experimental procedure consists of thermogravimetric analysis (TGA) of the selected biomass samples in order to determine the thermogravimetric index ($TG_{spi}$) (Janković et al., 2020). According to the calculated $TG_{spi}$ index based on mathematical analysis of obtained experimental results, the assessment for spontaneous ignition potential for each sample was presented (Avila et al., 2014).

The biomass samples used for the experimental study were selected according to their origin. The assessment of spontaneous ignition potential was performed for the sawdust (SD) sample which represents the woody biomass and for wheat straw (WS) sample, which represents the agricultural biomass (ISO17225-1, 2014). The selected biomass samples were prepared for testing according to standard procedure and proximate and ultimate analysis was also determined according to relevant standards for biomass characterization (ISO14780, 2017).

To establish the correlation between the spontaneous ignition potential of raw biomass material and sample particle size dimensions, the detailed experimental tests of particle size distribution were performed. These experimental tests include determination of specific surface area and volume share as well as the distribution of particle size below 0.5 mm, 0.5–3 mm and over 3 mm, using Malvern Mastersizer laser diffraction apparatus 2000 (Malvern Instruments, Inc., UK).

TGA analysis was performed using Netzsch STA 449 F5 Jupiter system which includes the determination of the mass change curve and DTG curve, versus time and temperature. TGA tests were performed with the sample mass of $10 \pm 0.5$ mg and within temperature range from room temperature up to 650 °C. The applied heating rates ($\beta$) were 3, 5, 7, 10 and 20 °C·min$^{-1}$ with synthetic air (21% v/v $O_2$ + 79% v/v $N_2$) as a carrier gas with flow rate of 70 ml min$^{-1}$. Analysis of each sample was repeated twice and repeatability was checked. The repeatability of the tests was found to be more than 99%.

The characterization of ignition is complicated since the ignition temperature is not a fundamental parameter of the fuel; it depends on the sample mass, the heating rate of the particle, the surrounding gas, and the

indicator of ignition. For this reason, different experimental techniques may result in widely differing ignition temperatures for the same fuel (e.g. thermal analysis, single particle ignition measurements, dust layer ignition measurements, basket ignition measurements and pulse ignition measurements). The rate of self-heating which precedes the ignition is slow and will be significant only if insulation provided by the surrounding mass of material is sufficient. The larger the mass the lower is the temperature which will lead to spontaneous ignition. In our study, TGA was chosen for small fuel samples and slow heating (below 20 °C·min$^{-1}$), unlike for example, the pulse ignition, which is realized in isothermal reactor for larger sample sizes and more rapid heating. Therefore, this examination is closely related only to thermogravimetric ignition experimental setup. In addition, comparatively large sample size was used in order to ensure a larger number of biomass particles in the experiments. This results in a more well-defined average size of the particles and thus a better repeatability. The sample mass of 10 mg was used to prevent a significant effect of the mass and heat limitations phenomena, wherein the selected mass is acceptable for tests related to the fuel ignition behavior analysis (Mortari et al., 2010). Summarizing these conditions, it was assumed that with a given sample mass and as low as possible heating rates, will lead to an approximately uniform temperature distribution in the sample.

From the acquired TGA results for each sample at five different heating rates, the graphical evaluation was made in order to identify the three characteristic points (onset, inflection and peak temperatures) on the mass loss rate curve within the region, in which devolatilization process occurs. Those points are related to the sample characteristic temperature of the curve in which are produced, so it is possible to make a basic statistical analysis (in this case a linear interpolation), between the DTG values of these points and the sample temperature. This linear interpolation provides a linear equation defined by a slope and y–intercept. If the slopes of the five linear approximation are considered (one slope for each heating rate), it is possible to make a second basic statistical analysis between heating rates and slopes. A new linear approximation has been carried out, so a new linear equation can be acquired. The slope of this last line is designated as thermogravimetric index of spontaneous ignition (TG$_{spi}$). Based on the obtained values for TG$_{spi}$, the classification of spontaneous ignition potential for the tested samples was made according to the values given in Table 1.

## 3. Results and discussion

### 3.1. Proximate/ultimate results of solid fuels

The results of proximate and ultimate analysis for tested samples are presented in Table 2. The data for proximate analysis are given on air dried basis and while for ultimate analysis are given on dry basis. According to presented data, the SD sample has lower moisture content as well as higher content of volatile matter than WS. The heating value is also higher which indicate that SD sample could have different potential of spontaneous ignition, which could be related with higher energy density and lower moisture content. However, biomass offers important advantages as a combustion feedstock due to the high volatility of the fuel and high reactivity of both, the fuel and the resulting char. Comparing with solid fossil fuels, biomass contains much less carbon and more oxygen (Table 2) and has a low heating value (Jenkins et al., 1998).

**Table 1**
Classification of spontaneous ignition potential based on TG$_{spi}$ value.

| TG$_{spi}$ | Class |
| --- | --- |
| <0.02 | Non-reactive |
| 0.02–0.03 | Low reactive |
| 0.03–0.05 | Reactive |
| >0.05 | High reactive |

**Table 2**
Proximate and ultimate analysis of tested samples (SD – sawdust; WS – wheat straw).

| | | SD | WS |
| --- | --- | --- | --- |
| Proximate analysis (wt. %) | Moisture | 7.16 | 11.63 |
| | Volatile matter | 74.14 | 65.32 |
| | Fixed carbon | 17.02 | 15.17 |
| | Ash | 1.68 | 7.88 |
| Calorific value (MJ kg$^{-1}$) | HHV | 17.78 | 15.29 |
| | LHV[a] | 16.21 | 13.91 |
| Ultimate analysis[b] (wt. %) | C | 49.03 | 44.12 |
| | H | 6.61 | 6.34 |
| | O[c] | 40.52 | 39.99 |
| | N | 2.02 | 0.63 |
| | S | – | – |
| | H/C | 1.62 | 1.72 |
| | O/C | 0.62 | 0.68 |

[a] Calculated according to EN ISO 18125:2017.
[b] On dry basis.
[c] By the difference.

On the other hand, it should be emphasized that various biomass samples may have highly variable composition and properties, especially with respect to moisture, structural properties (related to the content of hemicelluloses, cellulose and lignin components) and inorganic constituents (including elements Si, K, Na, Cl, P, Ca, Mg and Fe which can be involved in reactions leading to ash fouling and slagging during combustion process). Considering results presented in Table 2, the wood or woody (forestry) biomass samples (such as SD) have a greater content of volatile matter than agricultural biomass samples (such as WS), and, also, a much more lowered content of moisture. So, if we consider the actual biomass samples, every sample has its own advantages and disadvantages, but according to their composition, biomasses may be classified in respect to specific compounds, which they are enriched or depleted in them (Jenkins et al., 1998). As an important issue, it should be noted that moisture content affects on the self-heating process (Tian et al., 2017). It was found that in the case of agricultural residues (Tian et al., 2017), the elevated moisture content significantly affects on the self-heating properties, leading to a shorter induction time for the onset of self-ignition, where the temperature rises more rapidly depending on the maximum (peak) temperature magnitude. Namely, the relatively high-moisture content might delay the ignition of biomass particles. If the delay is significant, the flame could move further and further away from the burner extinguishing itself. This is countered to some extent by the fact that ignition temperature of dry biomass is much lower than that of coal.

In addition, based on the data of ultimate analysis (Table 2), both samples are sulphur free, and the SD sample has higher content of carbon and nitrogen. The contents of oxygen and hydrogen are almost the same, which also could be related to spontaneous ignition potential due to improved oxidation process. Fig. 1 shows the Van-Krevelen diagram for the considered biomass samples compared to other solid fossil fuels. It can be observed on presented diagram, that position of wheat straw (full circle symbol) belongs to the position of cellulose riched biomass feedstock (Jenkins et al., 1998). On the other hand, the position of sawdust sample on the Van-Krevelen diagram corresponds to the region where the wood biomasses are situated (Jenkins et al., 1998). Our tested samples are characteristic biomass feedstocks, where WS and SD are on the top right corner with very high H/C and O/C ratio, while the coal is near the lower left with low H/C and O/C ratio (Fig. 1); unlike coal, the properties of biomass are highly variable and heterogeneous. This properties diversity is obviously reflected through Van-Krevelen diagram, where, unlike the coal, when stored for an extended period, biomass absorbs moisture and decay.

Besides the adverse effect on thermal efficiency, moisture could also lead to the development of harmful fungus. High moisture content is an important factor driver for the development of fungal and bacterial
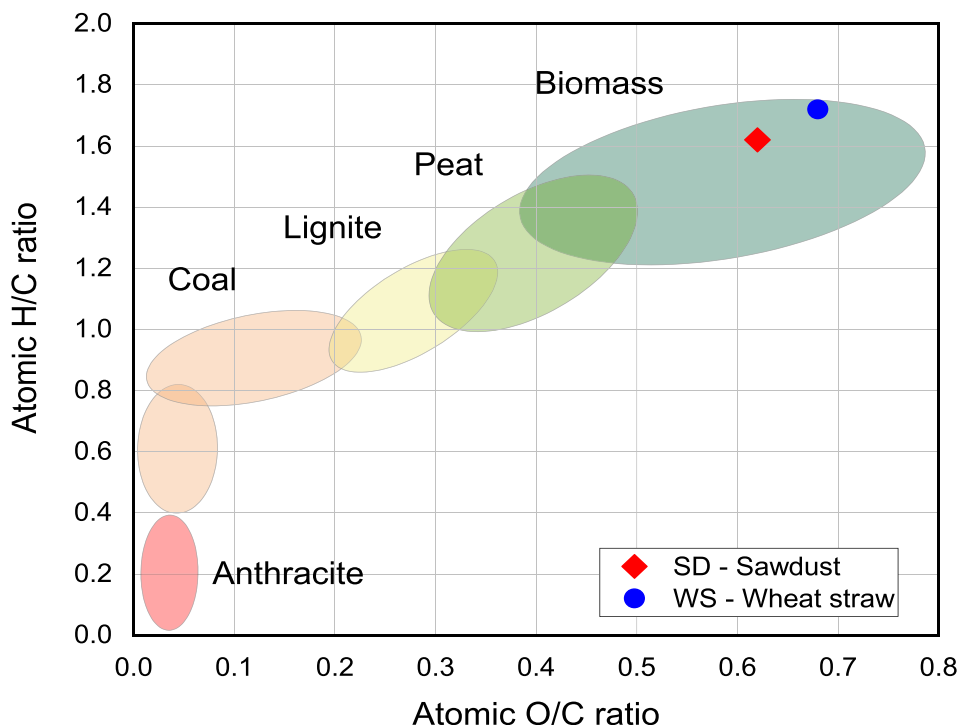
**Fig. 1.** Van-Krevelen diagram for considered biomass samples.

communities which play a key role in reducing the fuel quality and catalyzing the process of self-ignition.

The high moisture content in biomass feedstock can increase the transportation cost and affect the combustion behavior in terms of system efficiency and emissions when used in the thermo-chemical conversion processes. Moisture in biomass may reduce the net calorific value (LHV) (this can be seen for WS sample as typical example, from results shown in Table 2), because a fraction of the heat is used to vaporize the water.

### 3.2. Particle size distribution analysis

Tables 3 and 4 show the results of particle size distribution properties related to sawdust (SD) and wheat straw (WS) samples. The software within Mastersizer 2000 provides a granulometric curve as volume (%) against particle size (Figs. 2 and 3). Six main parameters were obtained through this software: 1) the grain diameter where 10% of distribution has a smaller particle size - d(0.1), 2) the grain diameter where 50% of distribution has a smaller particle size - d(0.5), 3) the grain diameter where 90% of distribution has a smaller particle size - d(0.9), 4) total area of lignocellulosic material per unit of mass - specific surface area, 5) the diameter of the sphere that has the same volume/surface area ratio as the particle of interest - D [3,2] (surface weighted mean), and 6) the diameter of the sphere of equal volume to the particle - D [4,3] (volume weighted mean).

**Table 3**
Particle size distribution for SD – sawdust.

| Concentration (% vol.) | Span | Uniformity | Specific area (m$^2$ g$^{-1}$) | Surface weighted mean D [3,2] (μm) | Volume weighted mean D [4,3] (μm) |
|---|---|---|---|---|---|
| 0.0032 d(0.1) (μm) | 1.636 d(0.5) (μm) | 0.494 d(0.9) (μm) | 0.0192 Size 0.010–500 μm | 313.04 Size 500–3000 μm | 688.16 Size >3000 μm |
| 203.29 | 635.83 | 1243.2 | 35.51 | 64.49 | 0 |

**Table 4**
Particle size distribution for WS – wheat straw.

| Concentration (% vol.) | Span | Uniformity | Specific area (m$^2$ g$^{-1}$) | Surface weighted mean D [3,2] (μm) | Volume weighted mean D [4,3] (μm) |
|---|---|---|---|---|---|
| 0.0022 d(0.1) (μm) | 2.142 d(0.5) (μm) | 0.662 d(0.9) (μm) | 0.0379 Size 0.010–500 μm | 158.20 Size 500–3000 μm | 535.13 Size >3000 μm |
| 120.80 | 449.56 | 1083.68 | 55.08 | 44.92 | 0 |

Particle shape and particle size distribution are both important factors which could influence the physical properties of granular materials. Due to the high content of cellulose, hemicelluloses and lignin, biomass material is anisotropic in spatial structure, which induces the evident difference in mechanical property in different directions. Consequently, these properties also can impact on the self-heating characteristics of studied biomass samples. Considering our tested samples, both SD and WS (Tables 3 and 4) are characterized by similar uniformity of particles, reflecting that different kinds of biomass particles are coincident well in size distributions (Figs. 2 and 3). WS has almost twice as large specific surface area than SD, as flake-like geometry particles and with a smaller d(0.1) value, which can result in the use of higher heating rates and faster heat and mass transfer to the particle (Lu et al., 2010). This is important property, since those samples with particle sizes in the range of 710–840 μm (within particle sizes of 500–3000 μm, showed in Tables 3 and 4) (Bharadwaj et al., 2004), both intra-particle heat and mass transfer are important when considering biomass particle devolatilization of particle sizes relevant for suspension firing.

Considering results presented in Tables 3 and 4, it should be noted that all biomass samples are characterized with larger particle sizes (fourth and fifth columns in Tables 3 and 4) which is disadvantageous if samples are saved for testing in fired boilers or in high-temperature furnace-balance systems.

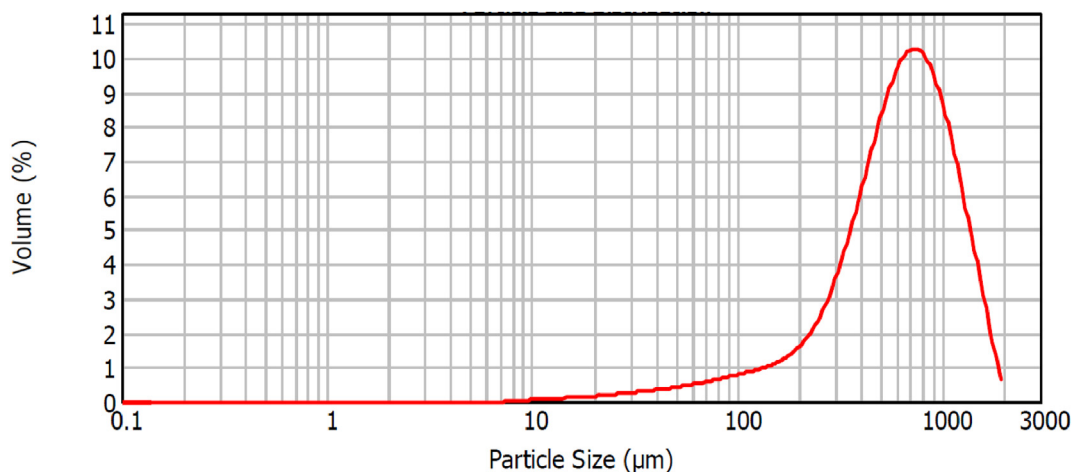In this study, it was found that the breakup of biomass particles was

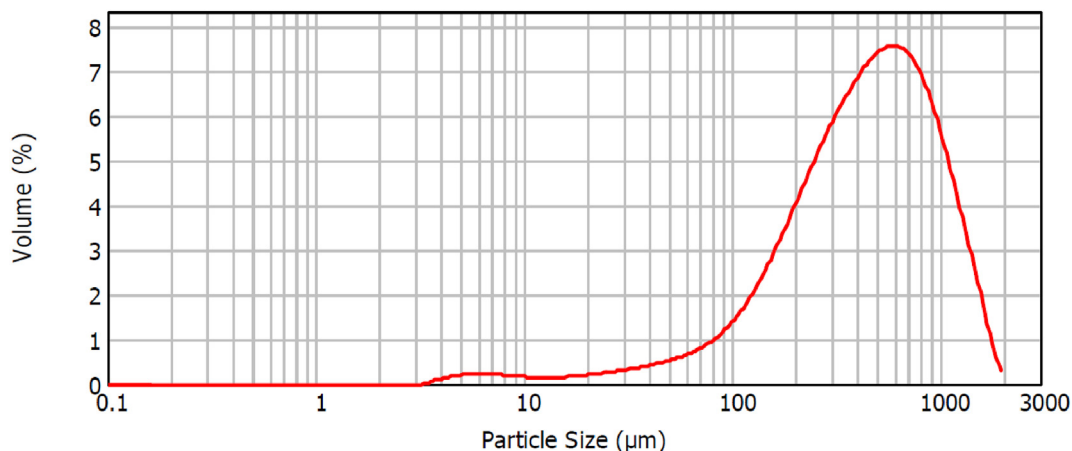**Fig. 2.** Particle size distribution for SD – sawdust.



**Fig. 3.** Particle size distribution for WS – wheat straw.

directional obviously, which would conduce to forming larger aspect ratio. Such directional breakup would be related with the anisotropic structure of biomass materials, and this can be seen from Figs. 2 and 3 where distributions are more asymmetrical with shift behavior to the right, on the side with a large particle size. The anisotropy is more pronounced in the case of WS sample (agricultural biomass) that characterizes by the wider distribution (Fig. 3). In the case of coal, the fracture process of coal particle would be determined by the inner cracks, and the breakup of coal particle would not present the anisotropy. In addition, the coincidence of size distributions between different kinds of biomass particles would also be dependent on the similarity of biomass materials in their microstructure (Guo et al., 2012). One of the main drawbacks related to using TG technique for studying the self-ignition potential of biomass was described by (Grotkjær et al., 2003). They reported that ignition temperature of the solid fuel is highly dependent on the particle size, while the sample studied in TGA apparatus is normally at fine sizes and the testable quantity is small, which is difficult to study the impact of particle size on the ignition behavior. These observations have also been reported by (Li et al., 2016). Using TGA-DTG techniques allow the theoretical considerations about "relative" self-ignition risk assessment for biomass samples.

### 3.3. TGA-DTG tests

The thermal characteristics of different particle sizes of SD and WS samples under synthetic air conditions are examined using TGA-DTG

technique at heating rate of 20 °Cmin$^{-1}$. Since that difference between particle sizes is not large (SD: Size 0.010–500 μm with mean 35.51 μm, and WS: Size 0.010–500 μm with mean 55.08 μm), this difference has almost no effect on the shape of the TG curves (Figs. 4 and 5), but shape difference of DTG curves arises from variable lignocellulosic composition among samples. The unique thermal characteristics of both samples are reflected through the first DTG peak at lower temperatures with a peak around 90 °C which can be attributed to moisture removal. It is also worthwhile to point out that the respective thresholds for dehydration are reached at lower temperatures for oxidative conditions than under pure nitrogen (inert) atmosphere. Under oxidation atmosphere, for both samples, a second sharp drop in mass loss (%) occurs at temperatures higher than 350 °C (Figs. 4 and 5), due to the combustion of char which occurs after release of volatile matters.

The influence of particle size could not really be observed for the samples under air environment. The curves are nearly overlapped for temperatures below 350 °C. This is the stage of volatile matters release and dominated by the temperature. For temperatures higher than 350 °C, the slight differences among the curves may be caused by the different content of mineral matters and distribution of fixed carbon (Table 2). This might also be indicated in DTG curves, but the particle size has caused little difference among samples through the external shapes in respect to the occurrence of one sharp DTG peak for SD sample near 350 °C, and wider peak prolonged with "shoulder" for WS sample at temperature little lower than 350 °C (Figs. 4 and 5). On the other hand, the second DTG peak appears at 500 and 450 °C for SD and WS sample,
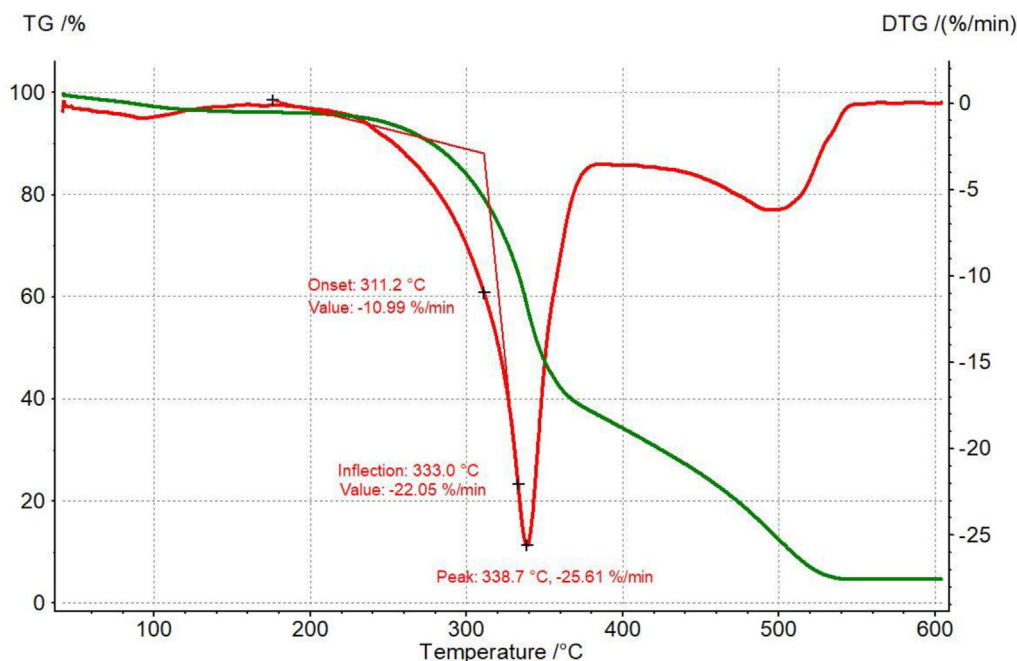
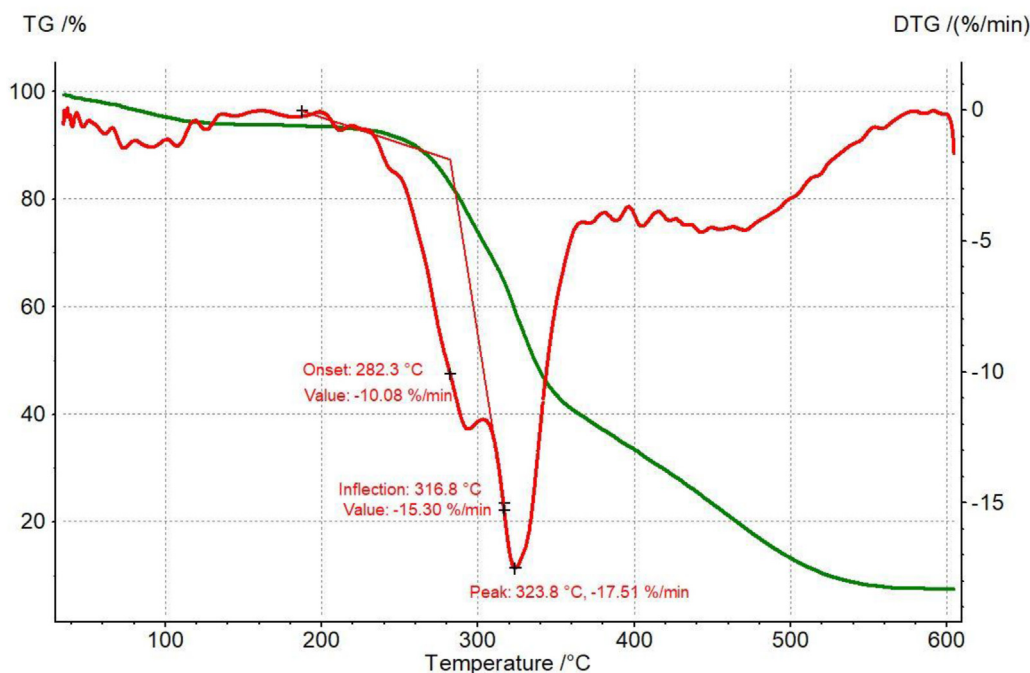**Fig. 4.** TG and DTG curve for SD sample at heating rate 20 °Cmin⁻¹.



**Fig. 5.** TG and DTG curve for WS sample at heating rate 20 °Cmin⁻¹.

respectively.

The maximum (peak) mass loss temperature (Peak temperature) obtained by TG analysis is an indicator of the reactivity of the product represents the yield of volatiles due to the observed process. The higher this temperature, the lower the reactivity of the biomass sample. In conventional TGA measurements, the loss of mass experienced by the sample occurs slowly, and it is therefore difficult to assign a single oxidation temperature. In the case of the samples studied and due to their structural composition, two main points of maximum mass loss, the resultant from the devolatilization of cellulose (SD sample), and/or

devolatilization of cellulose + hemicelluloses (overlapping decomposition reactions) (WS sample) and other that corresponding to devolatilization of lignin (higher temperatures beyond 400 °C) are obtained, as can be seen from Figs. 4 and 5.

As a general rule, when an oxygen stream is used instead of air stream, the reaction takes place quicker, and the sample has a sudden mass loss and that particular or characteristic temperature can be easily determined for each tested sample. In the case of air atmosphere, this is a much more complicated determination, and therefore the analysis is reduced on the second stage of the process where volatile matter is

consumed.

The characteristic temperature values (the onset ($T_{onset}$), the inflection ($T_{inf}$) and the peak temperature ($T_{peak}$) points) during thermal decomposition of tested biomass samples in an air atmosphere (for heating rates of 3, 5, 7, 10 and 20 °C min$^{-1}$), together with determined slopes (estimated by the procedure described in section 2) are listed in Tables 5 and 6. In both tables, for every considered heating rate, the two repeated measurements are performed which were designated by "Test no. 1" and "Test no. 2" (replicates). The best correlated measurements (analyzed replicates at various heating rates) (the higher $R^2$ – Adj. R-square value) were chosen for further self-heating analysis.

It can be observed from Tables 5 and 6 that compared with the peak temperatures, at other characteristic temperatures (the onset and the inflection), the rate of combustion of tested lignocellulosic materials becomes rapid and in fact, these temperatures are close to the peak value in TGA measurements. The onset temperature belongs to combustion induction temperature (IT) when the combustion starts, and it is within the first sharp drop in the mass loss (%) (below 350 °C) (Figs. 4 and 5).

Based on the obtained $T_{peak}$ (maximum) values, the self-ignition risk assessment can be estimated for tested biomass samples. Table 7 lists the average values of $T_{peak}$ for all tested samples, and their classification to self-ignition risk according to literature reports (Fernandez-Anez et al., 2014).

From results presented in Table 7, it can be identified that both samples exhibit medium risk for self-heating process. However, straw is not a uniform fuel. Different types/sorts of straw have the different combustion properties. Handling of straw can cause dust but that is more a work environment problem than a risk for dust explosions. The risk for self-ignition is not large either, but the risk of fire spreading in the dry straw is high, if the fuel is ignited by an external source.

### 3.4. Generic discussion and closing remarks

If we consider above-presented results with results related with particle size distributions, it can be concluded that exist very good agreement between self-ignition risk assessments and influence of particle size. Namely, both samples are characterized with particles larger than 400 µm (d(0.5) (µm) values in Tables 3 and 4), where these sizes correspond to the particles in pellets beyond the particle size spectrum of explosible dust (Koppejan et al., 2013). In actual cases, the self-ignition risk was significantly reduced (Table 7). Compared particle sizes of tested samples, generally, WS sample has smaller particles than ones for SD sample (Tables 3 and 4), and therefore, we can assume that WS has a higher bulk density. It prevents heat dissipation outward through convection, the dominant process of heat transfer within investigated biomass, and favors heat accumulation, therefore also contributing to the intensity of the self-heating. However, the faster reactions of the smaller particles lead to the faster exhaust of oxygen and consumption of nutrients within sample; the higher resistance to gas transport limits oxygen supply. These imply that the oxidation reactions are unable to be sustained at higher heating rates for longer time, resulting in the decreases of the temperatures (Table 6) and the shorter period of significant self-heating. However, since that specific temperature values attached to SD sample are higher than those related to WS sample (for $T_{peak}$ values) (Tables 5 and 6), it can be noted that, especially, the maximum (peak) temperatures increase as the sample become finer. This may be a consequence of liberated mineral constituents (which they are more present in the wood biomass than in herbaceous and agricultural biomass). Therefore, the less developed biomass sample (wheat straw – WS with coarse particles) has lower values of $T_{peak}$ which consist more hemicelluloses than SD biomass which is mainly formed by cellulose. So, the WS sample exhibits a higher reactivity under oxidizing atmosphere compared to SD sample. This is also reflected through lowering the average $T_{peak}$ value, presented in Table 7. Since that coals as well as wheat straw (WS) have low amounts of volatiles (Table 2), the low values of diffusivities and specific heat, but higher bulk density, the WS similar to coal, will shows an increased risk

**Table 5**

The characteristic temperatures and DTG values for SD sample at different heating rates.

| Heating rate [°C min$^{-1}$] | | Unit | SD – sawdust sample | | | | |
|---|---|---|---|---|---|---|---|
| | | | Onset | Inflection | Peak | Slope | $R^2$ |
| 3 | Test no.1 | T [°C] | 286.6 | 301 | 305.8 | 0.1304 | 0.9970 |
| | | DTG [%/min] | 1.72 | 3.51 | 4.26 | | |
| | Test no.2 | T [°C] | 287.2 | 301.4 | 305.9 | 0.1387 | 0.9977 |
| | | DTG [%/min] | 1.8 | 3.68 | 4.43 | | |
| 5 | Test no.1 | T [°C] | 294.4 | 309.4 | 314.7 | 0.1974 | 0.9985 |
| | | DTG [%/min] | 2.96 | 5.81 | 7.01 | | |
| | Test no.2 | T [°C] | 293 | 308.3 | 313.6 | 0.2923 | 0.9979 |
| | | DTG [%/min] | 4.25 | 8.52 | 10.35 | | |
| 7 | Test no.1 | T [°C] | 299 | 315.2 | 320.6 | 0.2499 | 0.9979 |
| | | DTG [%/min] | 4.01 | 7.88 | 9.48 | | |
| | Test no.2 | T [°C] | 299.8 | 315 | 320.6 | 0.2730 | 0.9917 |
| | | DTG [%/min] | 4.15 | 8.1 | 9.9 | | |
| 10 | Test no.1 | T [°C] | 299 | 320 | 327.3 | 0.2567 | 0.9991 |
| | | DTG [%/min] | 4.83 | 10.05 | 12.16 | | |
| | Test no.2 | T [°C] | 297.6 | 318.9 | 325.9 | 0.2678 | 0.9879 |
| | | DTG [%/min] | 5.45 | 10.95 | 13.11 | | |
| 20 | Test no.1 | T [°C] | 295.4 | 328 | 337.9 | 0.3356 | 0.9196 |
| | | DTG [%/min] | 7.88 | 18.62 | 22.23 | | |
| | Test no.2 | T [°C] | 311.2 | 333 | 338.7 | 0.5249 | 0.9986 |
| | | DTG [%/min] | 10.99 | 22.05 | 25.61 | | |

to spontaneous ignition. Coke and coals present only one peak on the DTG curve, but biomasses with lower content of volatiles (such as WS sample) present $T_{peak}$ value with "distorted" DTG peak (with formation of "shoulder" feature) which means that this biomass feedstock has a more amount hemicelluloses than cellulose. So, the volatiles liberated from hemicelluloses richer biomass decomposition may have significant role in the total amount of determined volatile matter, and also can the significant influence on the final granulometry of tested sample (fine or coarse particles). Consequently, the granulometric property of tested biomass sample is conditioned by the structural composition of lignocellulosic material, which is also reflected in its self-ignition properties. In addition, when the particle size is bigger (such in the case of WS sample), the gaps between the particles full of oxygen are larger, so the ignition easiness is higher. This is in agreement with previous observations related to the wheat straw (WS) sample. However, on the other hand, the ignition is more difficult because the air is less conductive than the own substance. In this case, the second effect may be stronger than the first and by enlarging the particle size, it is possible to increase $T_{peak}$ value, and ignition of a dust layer is more difficult. The same effect occurs with the onset temperature, the higher the particle size, the higher the onset temperature, so the combustion of the biomass sample starts at the higher temperatures. So that, increasing the particle size and preventing the production of dust of extremely small particle size is also in the case a possibility to prevent the ignition risk in this kind of agricultural (cereal) plants.

It should be emphasized as very important fact, that in the case of biomasses, it is still not clear whether these materials can undergo spontaneous combustion in the same way as with coals cases. In our study, for example, the influence of biological activity on the self-heating processes was totally ignored. Therefore, this study needs to be further expanded. Future works must include an investigation into the interaction between lignin, hemicelluloses and cellulose components to link the

**Table 6**

The characteristic temperatures and DTG values for WS sample at different heating rates.

| Heating rate [K/min] | | Unit | WS- wheat straw sample | | | | |
|---|---|---|---|---|---|---|---|
| | | | Onset | Inflection | Peak | Slope | $R^2$ |
| 3 | Test no.1 | T [°C] | 278.9 | 294.7 | 299.7 | 0.0769 | 0.9931 |
| | | DTG [%/min] | 1.78 | 2.9 | 3.42 | | |
| | Test no.2 | T [°C] | 277.8 | 295.3 | 300 | 0.0634 | 0.9918 |
| | | DTG [%/min] | 1.76 | 2.78 | 3.21 | | |
| 5 | Test no.1 | T [°C] | 284.6 | 302 | 307.6 | 0.1075 | 0.9938 |
| | | DTG [%/min] | 2.94 | 4.67 | 5.47 | | |
| | Test no.2 | T [°C] | 282.1 | 302.3 | 307.8 | 0.0868 | 0.9916 |
| | | DTG [%/min] | 2.84 | 4.45 | 5.14 | | |
| 7 | Test no.1 | T [°C] | 288.7 | 307.2 | 313 | 0.1326 | 0.9899 |
| | | DTG [%/min] | 4.06 | 6.28 | 7.38 | | |
| | Test no.2 | T [°C] | 284.5 | 302.1 | 307.7 | 0.1032 | 0.9917 |
| | | DTG [%/min] | 2.87 | 4.53 | 5.33 | | |
| 10 | Test no.1 | T [°C] | 287.3 | 310.3 | 317.5 | 0.1216 | 0.9979 |
| | | DTG [%/min] | 5.87 | 8.29 | 9.7 | | |
| | Test no.2 | T [°C] | 277.1 | 309.5 | 316.9 | 0.0992 | 0.9822 |
| | | DTG [%/min] | 5.23 | 8.08 | 9.37 | | |
| 20 | Test no.1 | T [°C] | 308.6 | 318 | 326.5 | 0.2418 | 0.9962 |
| | | DTG [%/min] | 13.01 | 15.51 | 17.33 | | |
| | Test no.2 | T [°C] | 282.3 | 316.8 | 323.8 | 0.1702 | 0.9817 |
| | | DTG [%/min] | 10.08 | 15.30 | 17.51 | | |

**Table 7**

Self-ignition potential assessment for tested biomasses based on the $T_{peak}$ values.

| Tested samples | | SD – sawdust | | WS- wheat straw | |
|---|---|---|---|---|---|
| Self-ignition risk | $T_{peak}$ (°C) | Self-ignition risk | $T_{peak}$ (°C) | Self-ignition risk | $T_{peak}$ (°C) |
| Very high | ≤250 | Medium | 321.4 | Medium [a] | 311.8 [a] |
| High | 250–299 | | | | |
| Medium | 300–349 | | | | |
| Low | ≥350 | | | | |

[a] Established $T_{peak}$ value is very close to the maximum (peak) temperatures with high self-ignition potential property.

reactivity of the raw biomass materials and their classification in respect to self-ignition risks.

In the further analysis, the careful classification of observed peaks in DTG curves represents one of the important tools in determination of reactivity, especially for biomass samples which tend (or have the potential) to show an increased risk of self-ignition. The advantage of this test is that it provides an analytic tool to compare between different biomass types. Within this testing, it can be analyzed the second (II) and third (III) peaks in DTG curves (Tables 5 and 6). Their lowest values correspond to the highest reactive biomass sample. In accordance with this test, it was showed that WS (wheat straw) sample (in Tables 5 and 6, the values of the rate DTG [%/min]) shows a higher reactivity in an air atmosphere than the SD (sawdust) sample, and therefore a higher probability to self-ignition.

Table 8 lists the values of the index of spontaneous ignition ($TG_{spi}$) for tested biomass samples. Fig. 6 shows the dependence of established slopes versus heating rates (the procedure was described earlier in this study), with marked linear correlations between these two quantities, which makes it possible to obtain $TG_{spi}$ values.

**Table 8**

Calculated values for $TG_{spi}$ for tested biomass samples.

| Heating rate (°C min$^{-1}$) | SD-Sawdust | WS-Wheat straw |
|---|---|---|
| 3 | 0.1387 | 0.0769 |
| 5 | 0.1974 | 0.0868 |
| 7 | 0.2499 | 0.1032 |
| 10 | 0.2567 | 0.1216 |
| 20 | 0.5249 | 0.2418 |
| $TG_{spi}$ | **0.0220** | **0.0099** |
| $R^2$ | 0.9755 | 0.9795 |

It can be observed from obtained values of $TG_{spi}$ index (Table 8), that SD sample exhibits the low reactivity in an air stream (Table 7), which is in good agreement with results obtained by other reactivity tests, such as the behavior of $T_{peak}$ values. On the other hand, the $TG_{spi}$ index value for WS sample shows that this biomass is non-reactive, which is in complete disagreement with the other results. This result also shows unrealistic features, as can be seen from the extremely large slope difference from Fig. 6. These results show that $TG_{spi}$ index testing cannot be applied to all types of biomass. This test shows significantly opposite results, with the implication that it is non-sensitive to the biological reactivity of the samples, which also depends on their chemical structure (namely, the different types of biomass may have different structural units from which molecules of hemicelluloses and lignin are made (this can vary from one biomass sample to another – as example, the WS is much richer with arabinose and galactose units than SD, but the WS has much less mannose units and it is poorer with galacturonic acid than SD; non-glucose carbohydrates are higher in WS sample than in SD sample, considering compositional analysis on dry base (Chen, 2014)).

Therefore, the different approaches created (and/or their combinations) represent the better idea about the potential of biomass to undergo the spontaneous combustion.

## 4. Conclusions

In this study, the new developed methodology for determination of spontaneous combustion potential of biomass samples was applied. The actual methodology includes TGA-DTG technique measurements on two selected biomass feedstocks as sawdust (SD) (woody biomass) and wheat straw (WS) (agricultural biomass). The self-ignition potential and reactivity of the samples in an air atmosphere were tested on the basis of thermal characteristic of the samples during combustion. The influence of particle size of samples on the degree of self-ignition risk was also analyzed. Based on the specific temperature value (such as onset and peak (maximum) temperature, $T_{peak}$) test results, the WS sample exhibits a higher reactivity under oxidizing atmosphere compared to SD sample. It was found that less developed biomass sample (wheat straw – WS with coarse particles) has lower values of $T_{peak}$ which consist more hemicelluloses than SD sample, which is mainly formed by cellulose. It was concluded that lignocellulosic content and its chemical structure strongly affect on the $T_{peak}$ values as well as on the combustion induction temperature.

It was identified that volatiles liberated from hemicelluloses richer biomass decomposition (wheat straw – WS) may have significant role in the total amount of determined volatile matter, as well as significant influence on the final granulometry of tested sample. The results from thermogravimetric index ($TG_{spi}$) testing show good agreement with the results obtained from the analysis of the $T_{peak}$ values and characteristics of the DTG curves for SD (sawdust) sample, but completely opposite results related to WS (wheat straw) sample. It was concluded that $TG_{spi}$ testing is insensitive to the biological activity of different types of biomass, which is conditioned by the structural composition of lignocellulosic material.

A comprehensive analysis of our obtained results indicates that the same testing procedure applied for coals is inadequate for various types
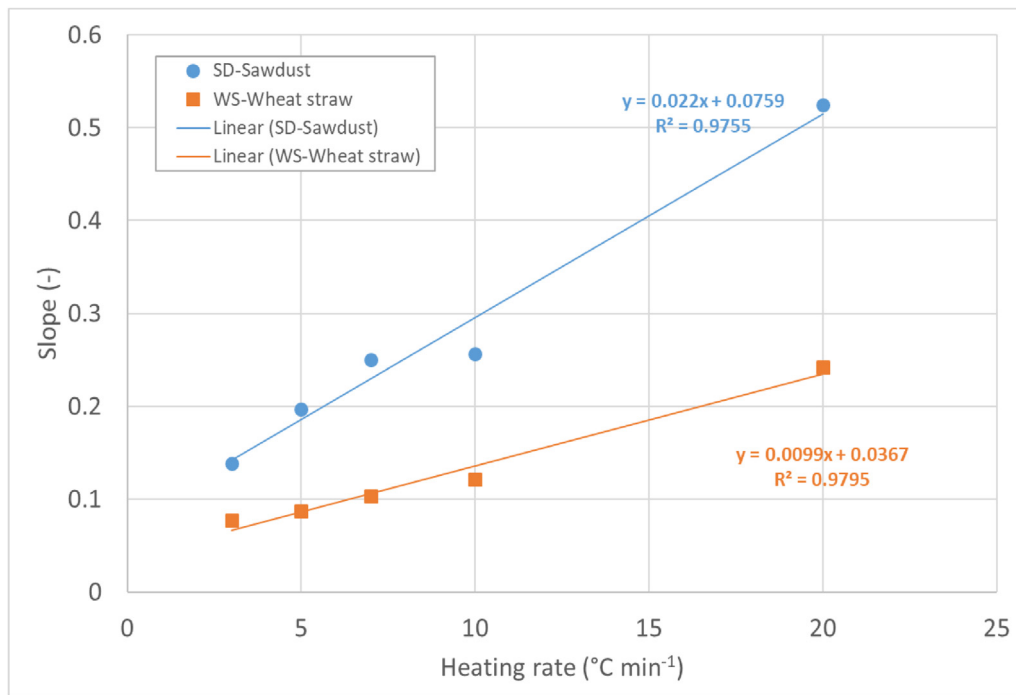
**Fig. 6.** Linear interpolation of calculated slopes at different heating rates.

of biomass (wood and agricultural biomasses). In parallel to this, it was found that the rate of the process also depends on the main chemical components found in the samples such as cellulose, hemicelluloses and lignin, on which the characteristic temperatures (the combustion induction temperature and peak temperature) depends. Therefore, to examine more closely reactive characteristics of biomass samples observed by using TGA technique (related to the intrinsic material properties), the adequate the experimental reactor system must be implemented. In that manner, the thermal and mass evolution of the large system will shows an enhanced dependency on particle morphology and in original physical properties of tested samples. The actual methodology makes it faster and easier to categorize the different types of biomass which allows testing on self-ignition by this approach, and those types of biomass for which the testing for coals can be applied.

For this reason, some particular tests for estimating biomass propensity to self-heating need to be developed, including the potential effects produced by biological activity in these materials.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### References

Arranz, J., Miranda, M., Montero, I., Sepúlveda, F., Rojas, C., 2015. Characterization and combustion behaviour of commercial and experimental wood pellets in South West Europe. Fuel 142, 199–207.

Avila, C., Wu, T., Lester, E., 2014. Estimating the spontaneous combustion potential of coals using thermogravimetric analysis. Energy Fuels 28 (3), 1765–1773.

Bharadwaj, A., Baxter, L.L., Robinson, A.L., 2004. Effects of intraparticle heat and mass transfer on biomass devolatilization: experimental results and model predictions. Energy Fuels 18 (4), 1021–1031.

Chen, G., Ma, X., Lin, M., Lin, Y., Yu, Z., 2015. Study on thermochemical kinetic characteristics and interaction during low temperature oxidation of blended coals. J. Energy Inst. 88 (3), 221–228.

Chen, H., 2014. Biotechnology of Lignocellulose: Theory and Practice. Spinger & Chemical Industry Press, Beijing, China.

Cherubini, F., 2010. The biorefinery concept: using biomass instead of oil for producing energy and chemicals. Energy Convers. Manag. 51 (7), 1412–1421.

Demirbas, A.H., Demirbas, I., 2007. Importance of rural bioenergy for developing countries. Energy Convers. Manag. 48 (8), 2386–2398.

Dodić, S.N., Popov, S.D., Dodić, J.M., Ranković, J.A., Zavargo, Z.Z., Golušin, M.T., 2010. An overview of biomass energy utilization in Vojvodina. Renew. Sustain. Energy Rev. 14 (1), 550–553.

Fernandez-Anez, N., Garcia-Torrent, J., Medic-Pejic, L., 2014. Flammability properties of thermally dried sewage sludge. Fuel 134, 636–643.

García-Torrent, J., Ramírez-Gómez, Á., Querol-Aragón, E., Grima-Olmedo, C., Medic-Pejic, L., 2012. Determination of the risk of self-ignition of coals and biomass materials. J. Hazard Mater. 213, 230–235.

Grotkjær, T., Dam-Johansen, K., Jensen, A.D., Glarborg, P., 2003. An experimental study of biomass ignition. Fuel 82 (7), 825–833.

Guo, Q., Chen, X., Liu, H., 2012. Experimental research on shape and size distribution of biomass particle. Fuel 94, 551–555.

Gustavsson, L., Haus, S., Ortiz, C.A., Sathre, R., Le Truong, N., 2015. Climate effects of bioenergy from forest residues in comparison to fossil energy. Appl. Energy 138, 36–50.

ISO14780, 2017. ISO 14780:2017 - Solid Biofuels - Sample Preparation. International Standard Organization.

ISO17225-1, 2014. ISO 17225-1:2014 - Solid Biofuels - Fuel Specifications and Classes - Part 1: General Requirements. International Standard Organization.

Janković, B., Manić, N., Stojiljković, D., Jovanović, V., 2020. The assessment of spontaneous ignition potential of coals using TGA–DTG technique. Combust. Flame 211, 32–43.

Jenkins, B., Baxter, L., Miles Jr., T., Miles, T., 1998. Combustion properties of biomass. Fuel Process. Technol. 54 (1–3), 17–46.

Khare, V., Nema, S., Baredar, P., 2016. Solar–wind hybrid renewable energy system: a review. Renew. Sustain. Energy Rev. 58, 23–33.

Koppejan, J., Lönnermark, A., Persson, H., Larsson, I., Blomqvist, P., Arshadi, M., Valencia-Reyes, E., Melin, S., Howes, P., Wheeler, P., 2013. Health and safety aspects of solid biomass storage, transportation and feeding. IEA Bioenergy 1, 3–23.

Li, J., Paul, M.C., Czajka, K.M., 2016. Studies of ignition behavior of biomass particles in a down-fire reactor for improving co-firing performance. Energy Fuels 30 (7), 5870–5877.

Lu, H., Ip, E., Scott, J., Foster, P., Vickers, M., Baxter, L.L., 2010. Effects of particle shape and size on devolatilization of biomass particle. Fuel 89 (5), 1156–1168.

Mortari, D.A., Ávila, I., Dos Santos, A., Crnkovic, P., 2010. Study of thermal decomposition and ignition temperature of bagasse, coal and their blends. Revista de Engenharia Térmica 9 (1–2), 81–88.

Pejic, L.M., Anez, N.F., Torrent, J.G., Ramírez-Gómez, Á., 2015. Determination of spontaneous combustion of thermally dried sewage sludge. J. Loss Prev. Process. Ind. 36, 352–357.

Ramírez, Á., García-Torrent, J., Tascón, A., 2010. Experimental determination of self-heating and self-ignition risks associated with the dusts of agricultural materials commonly stored in silos. J. Hazard Mater. 175 (1–3), 920–927.

Sedlmayer, I., Arshadi, M., Haslinger, W., Hofbauer, H., Larsson, I., Lönnermark, A., Nilsson, C., Pollex, A., Schmidl, C., Stelte, W., 2018. Determination of off-gassing and self-heating potential of wood pellets–Method comparison and correlation analysis. Fuel 234, 894–903.

Tian, X., Zhang, H., Sheng, C., 2017. Self-heating of agricultural residues during storage and its impact on fuel properties. Energy Fuels 32 (4), 4227–4236.

Torrent, J.G., Anez, N.F., Pejic, L.M., Mateos, L.M., 2015. Assessment of self-ignition risks of solid biofuels by thermal analysis. Fuel 143, 484–491.

van de Kaa, G., Kamp, L., Rezaei, J., 2017. Selection of biomass thermochemical conversion technology in The Netherlands: a best worst method approach. J. Clean. Prod. 166, 32–39.

Yang, L., Sheng, J.J., 2019. Feasibility of using the frank–kamenetskii theory to predict the spontaneous ignition of the crude oil–sand mixture. Energy Fuels 33 (6), 4816–4825.

Yuan, L., Smith, A.C., 2012. The effect of ventilation on spontaneous heating of coal. J. Loss Prev. Process. Ind. 25 (1), 131–137.