Thermogravimetric and Kinetic Analysis of Raw and Torrefied Biomass Combustion

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The use of torrefied biomass as a substitute for untreated biomass may decrease some technological barriers that exist in biomass co-firing technologies e.g. low grindability, high moisture content, low energy density and hydrophilic nature of raw biomass. In this study the TG-MS-FTIR analysis and kinetic analysis of willow (*Salix viminalis L.*) and samples torrefied at 200, 220, 240, 260, 280 and 300 °C (TSWE 200, 220, 240, 260, 280 and 300), were performed. The TG-DTG curves show that in the case of willow and torrefied samples TSWE 200, 220, 240 and 260 there are pyrolysis and combustion stages, while in the case of TSWE 280 and 300 samples the peak associated with the pyrolysis process is negligible, in contrast to the peak associated with the combustion process. Analysis of the TG-MS results shows *m/z* signals of 18, 28, 29 and 44, which probably represent H_2O, CO and CO_2. The gaseous products were generated in two distinct ranges of temperature. H_2O, CO and CO_2 were produced in the 500 K to 650 K range with maximum yields at approximately 600 K. In the second range of temperature, 650 K to 800 K, only CO_2 was produced with maximum yields at approximately 710 K as a main product of combustion process. Analysis of the FTIR shows that the main gaseous products of the combustion process were H_2O, CO_2, CO and some organics including bonds: C=O (acids, aldehydes and ketones), C=C (alkenes, aromatics), C-O-C (ethers) and C-OH. Lignin mainly contributes hydrocarbons (3000–2800 cm^{-1}), while cellulose is the dominant origin of aldehydes (2860–2770 cm^{-1}) and carboxylic acids (1790–1650 cm^{-1}). Hydrocarbons, aldehydes, ketones and various acids were also generated from hemicellulose (1790–1650 cm^{-1}). In the kinetic analysis, the two-steps first order model (F1F1) was assumed. Activation energy (E_a) values for the first stage (pyrolysis) increased with increasing torrefaction temperature from 93 to 133 kJ/mol, while for the second stage (combustion) it decreased from 146 to 109 kJ/mol for raw willow, as well as torrefied willow at the temperature range of 200-260°C. In the case of samples torrefied at 280 and 300°C, the E_a values of the first and second stage were comparable to E_a of untreated willow and torrefied at 200°C. It was also found that samples torrefied at a higher temperature, had a higher ignition point and also a shorter burning time.

Keywords: torrefied biomass, torrefaction, combustion, TG-MS-FTIR investigation, kinetic model (F1F1)

1. INTRODUCTION

In 2007, the European Union established a clear framework to steer its energy and climate policies such that 20% of all energy will be supplied by renewable sources by 2020 (Green, 2013). Biomass is the most popular form of renewable energy, especially in developing countries and is a possible

replacement for fossil fuels in power generation. In Poland the most commonly used method for recovering energy from biomass is co-combustion with coal (50% of the total RES based electricity was coming from biomass co-firing in 2011(URE, 2013)). However, large scale biomass based electricity production faces several technological barriers which mainly result from different biomass properties as compared to those of coal.

When comparing the properties of coal used in power generation and biomass it should be noted that the basic qualitative elemental composition is the same. Differences occur resulting from the shares of individual elements and chemical compounds. The analysis of biomass composition reveals an average of approx. four times more oxygen, twice less carbon but also less sulphur and nitrogen. The consequence of these differences in properties is high volatiles content of biomass and high biomass reactivity (Ściążko et al., 2006). Biomass has much lower heating value (energy density) than that of coal, which results in a more expensive transportation and the necessity of different storage potential.

In Poland, co-combustion is carried out mostly in pulverised fuel boiler by a direct method using the existing fuel preparation system. Biomass has much worse grindability properties than coal. It is much more difficult to pulverise it into small sizes in mills designed for coal (Mroczek, 2009). As a result, the grinding of biomass-coal mixtures consumes more energy which is associated with an increase in the cost of energy production. Biomass has also much lower energy density than coal, giving rise to a more expensive transportation and the necessity of different storage potential (Kopczyński and Zuwała, 2013). Technological problems enhanced the development of not only new technologies in co-firing but also caused come-back to the implementation of biomass pre-treatment technologies, such as drying, compacting or torrefaction.

A promising pre-treatment method of biomass can be torrefaction, enabling to obtain more favorable physicochemical properties of bio-fuel to be used in coal-dedicated installations. The properties of torrefied biomass are more like those of coal than those of raw biomass. Torrefaction is a pre-treatment which serves to improve the properties of biomass in relation to thermochemical processing techniques for energy generation; for example, combustion, co-combustion with coal or gasification.

Torrefaction is a thermochemical treatment of biomass carried out in the temperature range from 200 to 300°C. It is accomplished under atmospheric pressure and in the absence of oxygen. In addition, the process is characterised by low particle heating rates (< 50°C/min) (Bergman, 2005).

Typical mass- and energy balance of torrefaction reveals that about 70% of the mass is retained as a solid product, containing 90% of the initial energy content. About 30% of the mass is converted into torrefaction gases, but contributes to only 10% of the energy content of biomass. Hence a considerable energy densification can be achieved, typically by a factor of 1.3 on mass basis (Bioenergy, 2000).

During torrefaction the biomass partly decomposes giving off various types of volatiles. The final solid product is often referred to as torrefied biomass. After torrefaction the characteristics of the original biomass are drastically changed and strongly depend on the process parameters (such as temperature, residence time, and others). Torrefied biomass has a homogenous structure, better milling performance compared to raw biomass, and has higher energy density (Bergman, 2005).

The material then changes from hydrophilic to hydrophobic type. With the removal of the light volatile fraction that contains most of the oxygen in the biomass, the heating value of the remaining material gradually increases from 19 MJ/kg to even 23 MJ/kg (for torrefied wood) (Koppejan et al., 2012).

During the torrefaction process, the tenacious fibre structure of the original biomass material is largely destroyed through the breakdown of hemicellulose and to a smaller degree of cellulose molecules, so that the material becomes brittle and easy to grind (Ciolkosz, 2011). The torrefied products show significantly less smoking during combustion and a relatively faster rate of combustion (Pentananunt, 1990).

All these features make torrefied biomass better for energy generation application than untreated biomass. Torrefied biomass can be an attractive fuel as a substitute for raw biomass for applications in the industrial scale, where electricity is generated from biomass by co-firing with coal. The use of the torrefied biomass will increase the mass fraction of RES in the fuel mixture stream in co-firing technology by direct method since in the existing pulverised coal boilers the same steam parameters are maintained and ensure high boiler efficiency and a stable operating.

Thermogravimetric analysis (TG) coupled with mass spectrometry (MS) and Fourier transform infrared (FTIR) analysis is well-established methods for determining weight loss to study biomass thermal decomposition characteristics, reaction mechanisms and evolved products during pyrolysis and thermo-oxidative degradation. This method offers a potential for the non-destructive, simultaneous, real-time measurement of multiple gas phase compounds for complex mixtures. Pyrolysis and thermo-oxidative degradation thermo-gravimetric analysis involve the sample's thermal degradation in an inert and oxygen existing atmosphere, and the loss of sample weight can be simultaneously recorded at a uniform temperature ramping rate. Weight loss and calculated kinetic parameters are easily obtained from thermogravimetric analysis without considering complex chemical reactions taking place in thermal degradation. The evolved gases are detected in real-time, which is an important and often difficult task for many thermal applications (Ahamed and Alshehri, 2012; Gao et al., 2013; Lee and Fasina, 2009).

The present work concerns a study of the combustion process of raw material (willow) and samples torrefied at 200, 220, 240, 260, 280 and 300 ºC. The experiments were conducted using the thermogravimetric analysis (TGA) coupled with mass spectrometer (MS) and Fourier transformed infrared spectrometer (FTIR). This method presents a more detailed investigation and better understanding of the evolution of the reactions taking place during the combustion and the physical–chemical nature of the different stages of process with identification of gaseous products. Kinetic analysis of thermogravimetric curves of biomass samples, based on multi-step mechanism is also needed for the design of the combustion process and it was performed.

2. EXPERIMENTAL

2.1. Material

In this research, willow (*Salix viminalis L.*) was used as raw biomass. The torrefied biomass (TSWE) was prepared from raw biomass (ground to <5 mm) in a fixed bed reactor (Inconel retort) at different thermal conditions from 200 to 300 °C (with a temperature step of 20 °C)) in the absence of oxygen. Figure 1 shows a schematic of a biomass thermal conversion work station. In each test, a 70 g sample was placed in the retort and torrefied in a nitrogen atmosphere. When the final temperature had been reached with a stepwise increase of temperature 5°C/min, the sample was maintained at constant conditions for 30 min and then cooled down to room temperature. All samples of raw and torrefied biomass were subjected to proximate analyses, including the ash content (Ash), volatile matter content (VM) and ultimate analysis (C^a_t, H^a_t, N^a_t, S^a_t and O^a_t) and higher heating value. The results are shown in Table 1.

2.2. Proximate and ultimate analyses

According to our own laboratory procedures (based on Polish standards (PN-G-04516, 1998; PN-G-04512, 1980) the properties of raw biomass were determined. Standards for torrefied biomass have been not determined but the properties of samples of TSWE 200-TSWE 300 were tested, according to the procedure used for raw biomass.
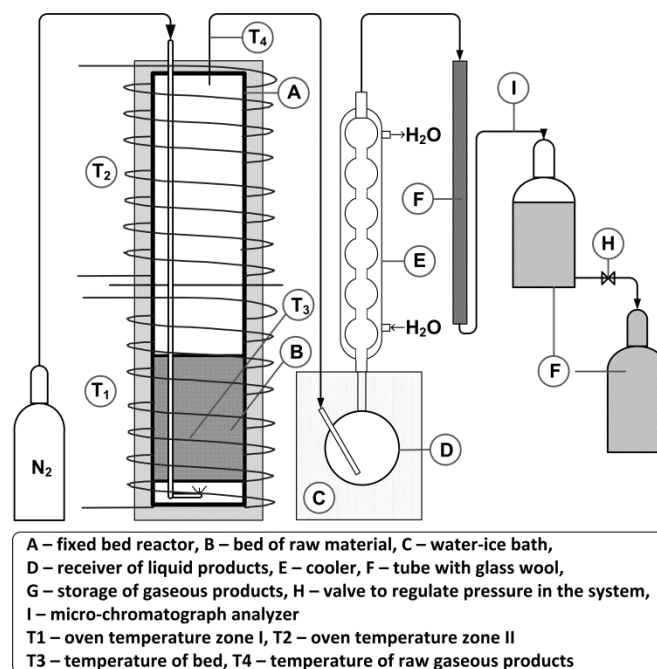
Fig. 1. Diagram of laboratory installation for thermal conversion of biomass

Volatile matter content in the raw and torrefied biomass was determined by a gravimetric method. The volatile matter content was measured by weighing a closed crucible before and after heating at 850 ± 15 °C for 7 min and calculating the difference between the total weight loss and the weight loss due to water evaporation.

The ash content of the samples was determined by incineration. This method involved placing a sample in a muffle furnace and heating it in air at a specific rate up to a temperature of 600 ± 10 °C and maintaining this temperature until reaching a constant weight.

The determination of the elementary composition of C^a_t, H^a_t, N^a_t, S^a_t and O^a_t was executed with a Vario Macro Cube automatic elemental analyser.

Carbon, hydrogen, nitrogen and sulphur content was determined according to our own laboratory procedure (Q/LG/15A) (Muzyka et al., 2011) while oxygen content was determined according to own laboratory procedure (Q/LG/16A) (Muzyka et al., 2011). A higher heating value of HHV (or Gross Calorific Value) was determined according to our own laboratory procedure (Q/LP/12/A:2011) with a LECO AC500 apparatus.

2.3. Thermogravimetric and kinetic analysis

Analysis of biomass combustion process was performed with coupled TG-MS-FTIR analysis techniques. Thermogravimetric analysis (TGA) was carried out using STA 409PG Luxx (NETZSCH-Gerätebau, Germany), coupled to a quadrupole mass spectrometer (QMS Aeolos) produced by NETZSCH-Gerätebau GmbH, Germany and Tensor 27 infrared spectrometer (FTIR) produced by Bruker Optics GmbH, Germany. Samples were placed in a crucible made of Al_2O_3. The process of raw (*Salix viminalis L*.) and torrefied (TSWE 200, TSWE 220, TSWE 240, TSWE 260, TSWE 280, TSWE 300) biomass combustion was performed at the temperatures between 313 and 1273 K using three heating rates 5, 10 and 20 K/min, under the flow of argon (25 ml/min) used as a purge gas and synthetic air (50 ml/min). The samples weighed 5.0±0.1 mg.

The obtained results allowed to assess the mass loss during the reaction as well as the initial and final temperatures of each stage of the combustion processes. The gaseous products were identified based on MS and FTIR techniques.

3. RESULTS AND DISCUSSION

The proximate and ultimate analysis results of the investigated raw and torrefied biomass samples are reported in Table 1.

Table 1. Proximate and ultimate analysis of biomass samples (analytical state)

Sample	Torrefaction temperature [K]	Ash [%]	Volatiles [%]	Carbon [%]	Hydrogen [%]	Nitrogen [%]	Oxygen [%]	HHV [kJ/kg]
Raw willow	-	1.90	74.93	48.2	5.57	0.73	38.87	17 467
TSWE 200	473	1.94	70.00	48.5	6.20	0.85	37.46	19 330
TSWE 220	493	2.62	68.64	51.1	6.14	0.90	34.50	20 468
TSWE 240	513	3.03	65.94	54.0	6.05	1.03	31.98	21 202
TSWE 260	533	3.84	59.63	56.8	5.80	1.10	31.34	22 572
TSWE 280	553	4.34	47.40	64.5	5.39	1.35	22.20	25 916
TSWE 300	573	5.00	42.80	66.0	5.19	1.44	19.11	26 506

A reduction in volatile matter and oxygen content with an increasing temperature of the torrefaction process could be seen while the ash and C, H, N content increased with increasing torrefaction temperature. The same tendencies were observed by other researchers (Kopczyński and Zuwała, 2013; Phanphanich and Mani, 2011; Wannapeera et al., 2011). For example, the reduction in volatile matter for the product of torrefaction at 573 K was almost doubled, from 74.9 % (willow) to 42.8 % (TSWE300). Higher heating value (HHV) also increased with increasing temperature.

Thermogravimetric analysis of the combustion process is presented for an exemplary heating rate of 10 K/min and is shown in the Fig. 2 as a mass loss (TG) and rate of mass loss (DTG). For other heating rates (5 and 20 K/min) the evolution of TG curves are similar.
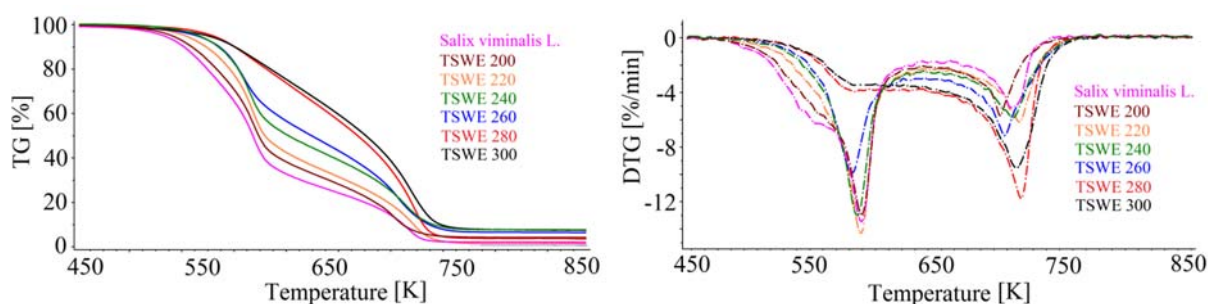

Fig. 2. TG-DTG curves of biomass sample combustion

Biomass consists of three components: xylan (hemicellulose), cellulose and lignin, which occur in different proportions and decompose at different temperatures and rates. On the basis of the data obtained by Yang et al. (2004, 2007) most of the weight loss happens from 493 K to 573 K, due to hemicellulose degradation and the decomposition of cellulose occurs at 573-613 K and the breakdown of lignin starts above 613 K.

The combustion of biomass samples can be divided into three stages, proceeding in the following temperature ranges. The first stage occurs between 313 K and 423 K and results in moisture evolution with a mass loss from 0.1 to 1.1%. The second stage takes place between 423 K and 637 K and it is characterised by volatilisation (pyrolysis) process of cellulosic and hemicellulosic fractions (holocellulosic component). The third stage, for which the temperature varies between 637 K and 1273 K, is characterised by char combustion, producing volatiles and solid residues (Caballero et al., 1997; Conesa et al., 1997; Gao et al., 2013).

The maximum mass loss and their temperatures for different biomass samples are reported in Table 2. On the basis of these data (Table 2, Fig. 2), it can be seen that the mass loss in the pyrolysis stage decreases with the temperature of torrefaction, while in the combustion stage it increases. Based on the DTG curves (Fig. 2) there are two peaks in the case of willow and torrefied samples TSWE 200, 220, 240 and 260 (pyrolysis and combustion stages), and for two other cases, the peak associated with the pyrolysis process is negligible, in contrast to the peak associated with the combustion process.

Table 2. Maximum mass loss and its temperature for different biomass samples for the heating rate of 10 K/min

Sample	Maximum mass loss [%](temperature [K])			Residual mass [%]
	Temperature range 313-423 K	Temperature range 423-637 K	Temperature range 637-1273 K	
Salix viminalis L.	1.1	75.1 (588 K)	21.8 (707 K)	2.0
TSWE 200	0.6	67.0 (588 K)	28.2 (698 K)	4.2
TSWE 220	0.4	66.5 (587 K)	31.8 (713 K)	1.3
TSWE 240	0.1	56.1 (584 K)	36.3 (708 K)	7.5
TSWE 260	0.7	51.0 (580 K)	42.2 (701 K)	6.1
TSWE 280	0.3	34.3 (582 K)	62.2 (714 K)	3.2
TSWE 300	0.8	26.7 (609 K)	65.8 (711 K)	6.7

The decomposition of torrefied biomass is shifted to a higher temperature and the degree of the shift increases with the severity of torrefaction. This may be due to the hemicellulose removal in torrefaction process. For the torrefied biomass pyrolysis, the shoulder in DTG curve is eliminated, especially for samples subjected to the high temperature torrefaction. The peak of DTG along with the maximum weight loss is mainly contributed by cellulose. The DTG peak of torrefied biomass TSWE 200, 220, 240 and 260 shows a slight reduction compared to that of raw biomass, suggesting insignificant effects on cellulose in torrefaction. However, the DTG peaks of torrefied biomass are reduced significantly when the torrefaction temperature increases up to 553 K due to the depletion of the majority of hemicellulosic and cellulosic fractions in the torrefaction process (Ren et al., 2013).

In the range of 423-637 K the mass loss decreases from 75.1 % in the case of willow combustion to 26.7 % in the case of TSWE 300 combustion. In the range of 637-1273 K the trend is reversed and the mass loss increases from 21.8 % for a willow sample to 65.7 % for TSWE 300 sample. The temperatures of maximum DTG for volatilisation process are similar (584 ± 4 K) for the all investigated samples except TSWE 300 (609 K). In the case of combustion process temperature of maximum DTG for all samples is equal 706 ± 8K.

Several combustion characteristic parameters are defined, i.e. ignition temperature (T_i), peak temperature (T_{max}), burn-out temperature (T_b) and burning time (BT). The ignition temperature is the temperature at which a sudden decrease is seen in the DTG curve. The peak temperature represents the place where the rate of weight loss reaches its maximum due to a rapid volatilisation accompanied by the formation of carbonaceous residue. The burnout temperature is the temperature on the DTG curve where oxidation is completed. The burning time is the time interval in which the dried fuel starts to lose

weight until the end of combustion where the weight stabilises. Results are shown in Table 3. The inclusion of several important parameters such as ignition temperature, burnout temperature, or mean burning rate in the index gives a comparatively comprehensive evaluation and can be regarded as a reference for practical operation (López-González et al., 2014; Wang et al., 2009). The characteristic parameters are reported in Table 3.

Table 3. Characteristic temperature of raw and torrefied biomass combustion process

Sample	Ignition temp. (T_i) [K]	Temp. max DTG [K]	Combustion temp. (T_c) [K]	Burning time (T_b) [min]
Salix viminalis L.	547	588	765	22
TSWE 200	550	588	765	21
TSWE 220	559	587	770	21
TSWE 240	560	584	765	20
TSWE 260	557	580	770	21
TSWE 280	639	714	765	12
TSWE 300	631	711	765	13

The ignition temperatures of the combustion process in the case of willow and torrefied samples TSWE 200, TSWE 220, TSWE 240 and TSWE 260 are in the range from 547 to 560 K, whereas for samples TSWE 280 and TSWE 300 are significantly higher (greater than 630 K). All samples are completely burnt at the temperature of 765-770 K, after 20-22 minutes for willow and torrefied samples TSWE 200, TSWE 220, TSWE 240 and TSWE 260, and 12-13 minutes for TSWE 280 and TSWE 300. On this basis it can be concluded that biomass combustion process is easy. This is due to the high volatile and low ash content in the samples. Therefore samples with higher torrefaction temperatures have a higher ignition temperature and a shorter time of combustion. These results are in agreement with research conducted by Wang et al. (2012).

A qualitative analysis of gases produced in the combustion of biomass samples was carried out using mass spectrometry (MS) and infrared spectroscopy (FTIR).

The evolution of gaseous products as a MS analysis (for the heating rate of 10 K/min) for combustion of exemplary samples TSWE 200 and TSWE 300 is shown in Fig. 3. For other heating rates (5 and 20 K/min) and samples the evolution of gaseous products is the same.

The MS results show m/z signals of 18, 28, 29 and 44, which probably represent H_2O ($m/z = 18$), CO ($m/z = 28$ and 29) and CO_2 ($m/z = 28$ and 44). Based on Fig. 3, it can be clearly seen that the gaseous products are generated in two distinct ranges of temperature. H_2O, CO and CO_2 are produced in the 500 K to 650 K range and reach their maximum yields at approximately 600 K. In the second range of temperature, 650 K to 800 K, only CO_2 is produced with its maximum yields at approximately 710 K as a main product of combustion process. The highest rate of gas evolution is consistent with the DTG peaks presented in Fig. 3. Additionally it can be seen that gaseous products are evolved in two ranges of ion current. Products with *m/z* signal of 28 are produced in higher values of ion current (10^{-9} A) and products with *m/z* of 18, 29 and 44 are produced in the values equal 10^{-11} A of ion current. The effects of combustion process for two exemplary samples, which were torrefied at 473 and 573 K, are presented in Fig. 3. The evolution of the same gaseous products can be observed in case of other investigated samples.

Fig. 4 presents three-dimensional FTIR spectrum with absorbance displayed as a function of the wavenumber and temperature for combustion of TSWE 200 and 300 samples.
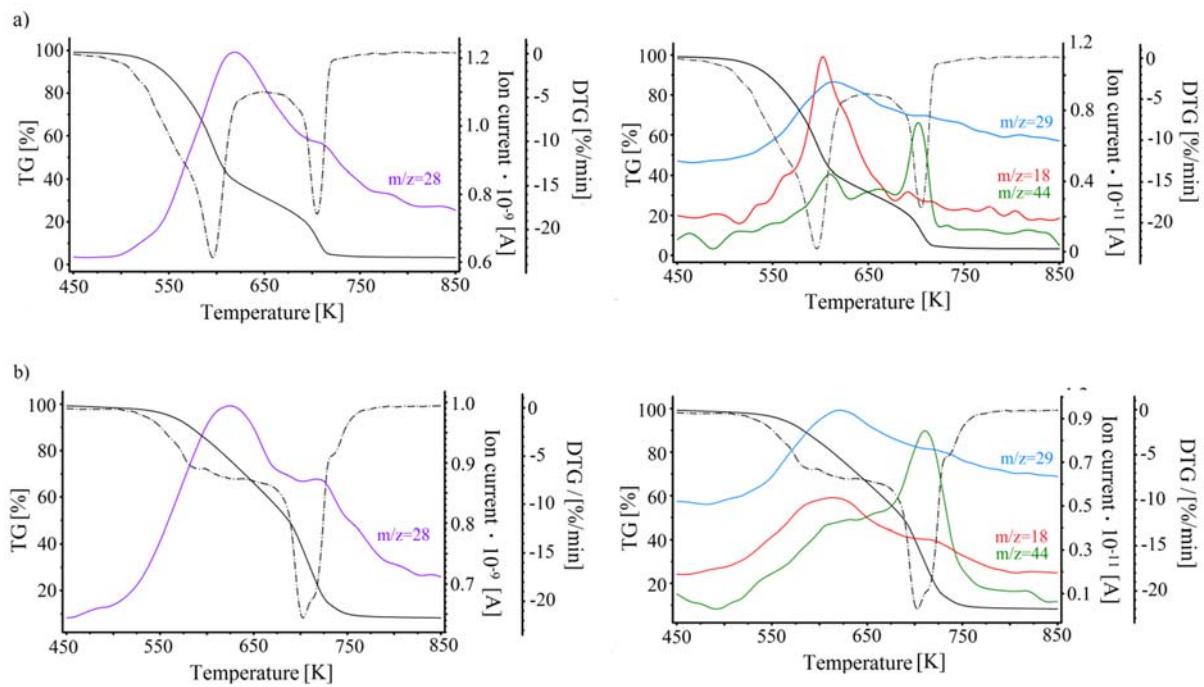
Fig. 3. Gaseous products evolution during combustion process of samples: a) TSWE 200 b) TSWE 300
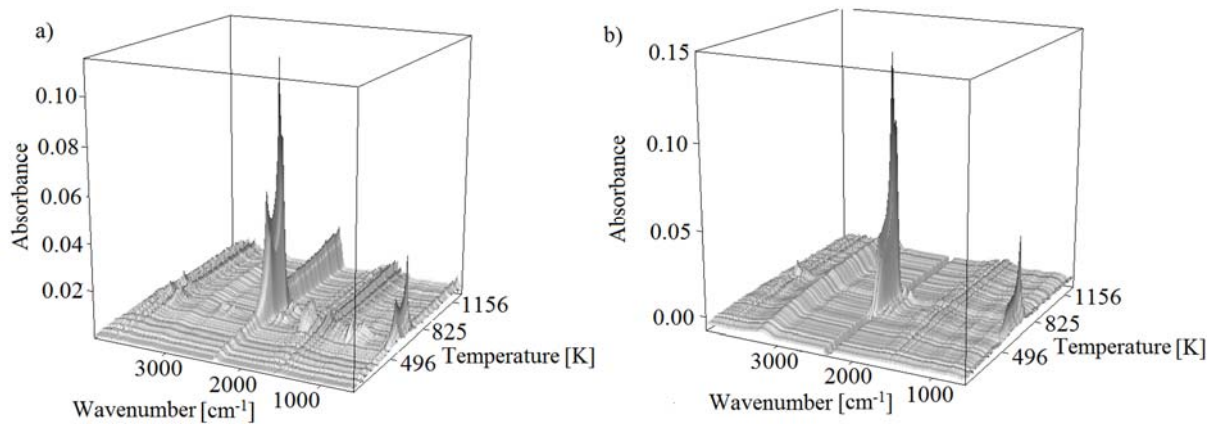(for 10 K/min)

Fig. 4. 3D-FTIR contour map of combustion process of samples a) TSWE 200 b) TSWE 300

From the 3D contour map, the FTIR spectra of two stages (pyrolysis and combustion) for combustion of TSWE 200 TSWE 260 and TSWE 300 samples were extracted and are shown in Fig. 5.
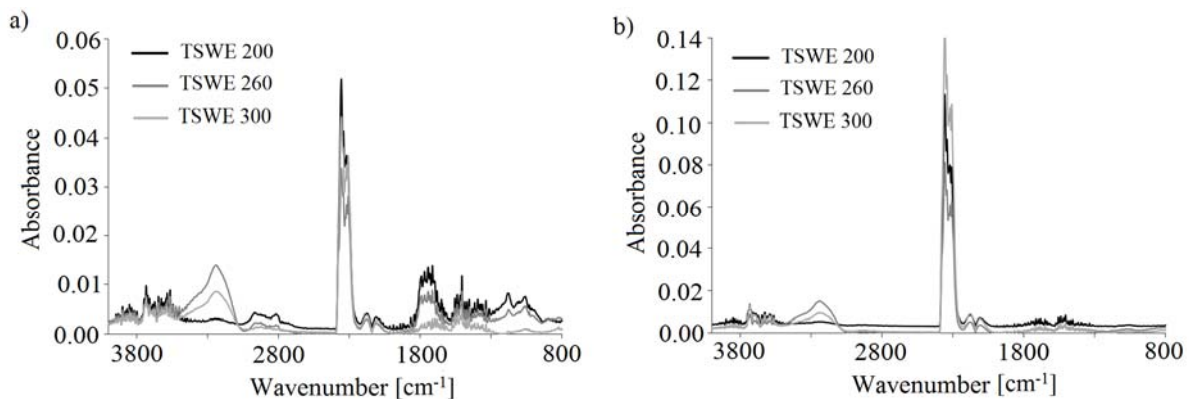

Fig. 5. FTIR spectra for combustion of investigated samples in the stage: a) pyrolysis b) combustion

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The specific wavenumbers of the IR peaks of the main gas species from biomass combustion are listed in Table 4.

Table 4. Attribution of the IR bands of the gases evolved during TSWE 200 combustion process

Wavenumber [cm^{-1}]	Functional group
4000-3500	O-H stretching
3000-2800	C-H aliphatic stretching
2400-2310	CO_2
2182, 2114	CO
1790-1650	C=O stretching (acids, aldehydes, ketones)
1680-1600	C=C stretching (alkenes)
1600-1500	C=C stretching (aromatics)
1300	C-O-C stretching (ethers)
1200-1000	C-OH

Analysis of the FTIR spectrum shows that the main gaseous products of the combustion process in the temperature of first stage are H_2O, CO_2, CO and some organics including bonds: C=O (acids, aldehydes and ketones), C=C (alkenes, aromatics), C-O-C (ethers) and C-OH. (Gao et al., 2013). The spectral regions of 3000–2800 cm^{-1} represent C–H stretching, and show the formation of hydrocarbons, formaldehyde, acetaldehyde and others (Li et al., 2001). Lignin mainly contributes to hydrocarbon formation (3000–2800 cm^{-1}), while cellulose is the dominant origin of the aldehydes (2860–2770 cm^{-1}). Hydrocarbons and aldehydes are also generated from hemicellulose. The strong absorption bands appearing at 1790–1650 cm^{-1} represent the flexible vibration of C=O bond, corresponding to various acids, aldehydes and ketones, which are mainly obtained from pyrolysis of cellulose and hemicellulose (Yang et al., 2006). The distinct band of 1790–1650 cm^{-1} indicates that carboxylic acids are largely generated from cellulose.

The gas products are generated in two separate ranges of temperature, in agreement with the results from the MS analysis. H_2O, CO, organic compounds (light hydrocarbons and oxygenated compounds) and CO_2 are produced in the 500 K to 650 K range and reach their maximum yields at approximately 600 K (Fig. 5a). In the second range of temperatures, from 650 K to 800 K, CO_2 is produced, with its maximum yields at approximately 710 K (Fig. 5b). The main products of combustion process at the temperature of this stage are CO and CO_2, other gases are burnt to CO and CO_2. The highest gas evolution rate is consistent with the DTG peaks presented in Fig. 3. Comparing peaks corresponding to gaseous products in the first stage of combustion process (Fig. 5a), it can be concluded that the peaks of organic compounds decrease with the temperature of torrefaction. For TSWE 280 and TSWE 300 the first stage is negligible and up to 553 and 573 K most gases were evolved during the decomposition of biomass components in the torrefaction process. For other heating rates (5 and 20 K/min) and samples the evolution of gaseous products was the same.

3.1. Kinetic analysis

Kinetic analysis was performed for combustion of all investigated samples, which was carried out using three heating rates: 5, 10 and 20 K/min. As was mentioned earlier, during this process three regions of mass loss can be distinguished. The first region – moisture evolution – was excluded from the calculation of kinetic parameters. In the literature (Branca et al., 2007; Chen et al., 2008; Fang et al., 2006; Font et al., 2009; Jauhiainen et al., 2004; Senneca et al., 2002; Senneca et al., 2007) there are a lot of different models used for modelling combustion and pyrolysis processes of biomass. In our work,

the two-steps first order model (F1F1) was assumed due to its simplicity and good fitting to experimental data (Shoujie et al., 2013).

The reaction rate is a function of the temperature and the conversion and can be expressed as

$$\frac{d\alpha}{dt} = f(\alpha)f(T) \tag{1}$$

and $f(T)$ is determined from the Arrhenius equation:

$$f(T) = A\exp\left(\frac{E_a}{RT}\right) \tag{2}$$

Under dynamic conditions, the kinetic equation becomes a thermokinetic equation. If

$$\beta = \frac{dT}{dt} = \text{const} > 0, \text{ then } \frac{d\alpha}{dT} = \frac{f(T)}{\beta}f(\alpha) \tag{3}$$

The combustion process proceeds according to a two-step reaction. Each step is the first order reaction, so the kinetic equation is:

$$\frac{d\alpha}{dT} = \frac{1}{\beta}\left[f(\alpha_1)f(T_1) + \beta f(\alpha_2)f(T_2)\right] \tag{4}$$

$$\frac{d\alpha}{dT} = \frac{1}{\beta}f(\alpha_1)A_1\exp\left(\frac{E_{a1}}{RT_1}\right) + f(\alpha_2)A_2\exp\left(\frac{E_{a2}}{RT_2}\right) \tag{5}$$

where $f(\alpha_1)f(T_1)$ is good approximation in the range (α_0-α_1) and (T_0-T_1) while $f(\alpha_2)f(T_2)$ is good approximation in the range (α_1- α) and (T_1-T), α_0 and α are the initial (at the initial temperature T_0) and final (at the final temperature T) conversion stage, α_1 is the conversion stage at the temperature T_1, where the DTG curve reaches its minimum (the peak between two maximum DTG peaks).

For solving equations and calculation kinetic parameters, the numerical Levenberg-Marquardt method was used (Marquardt, 1963). This method minimises the dependence defined by the Eq. (5):

$$\text{Min}(\delta(A_i, E_{ai})) = \alpha_i - \overrightarrow{F_i(A_i, E_{ai})} \text{ for } i = 1, 2, 3 \tag{6}$$

where $\overrightarrow{F_i(A_i, E_{ai})} = \dfrac{d\alpha_i}{dT}$ for $i = 1, 2, 3$.

The objective function (*OF*) was used as the sum of the square difference between experimental and calculated data (Conesa and Domene, 2011):

$$OF = \sum_j \sum_i (TG_{\exp ij} - TG_{calcij})^2 \tag{7}$$

where i represents the experimental data at time t in the experiment with a heating rate j. The value of TG_{exp} or TG_{calc} represents the mass loss in the experimental and calculated data, respectively.

The deviation between experimental and calculated curves is defined as:

$$SSE = \frac{\sqrt{OF/n}}{\max(TG_{\exp j})} \cdot 100\% \tag{8}$$

The correlation coefficient between experimental and calculated curves is defined as:

$$R = \sqrt{1 - \frac{OF}{\sum_j (\sum_i TG_{\exp ij}^2 - (\sum_i TG_{\exp ij})^2/N_j)}} \tag{9}$$

Figure 6 shows TG-DTG curves of combustion process of TSWE 200 and 300 samples for three heating rates. For other samples the evolution of TG curves in three heating rates is similar.
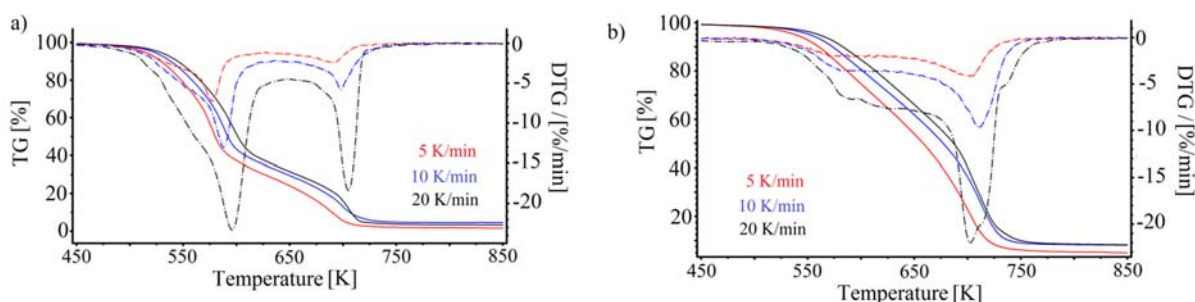

Fig. 6. TG-DTG curves of combustion process of samples: a) TSWE 200 b) TSWE 300

Table 5 presents kinetic parameters (activation energy E_a and pre-exponential factor A) of the combustion process calculated based on TG curves and F1F1 model.

Table 5. The values od activation energy and pre-exponential factor of combustion process

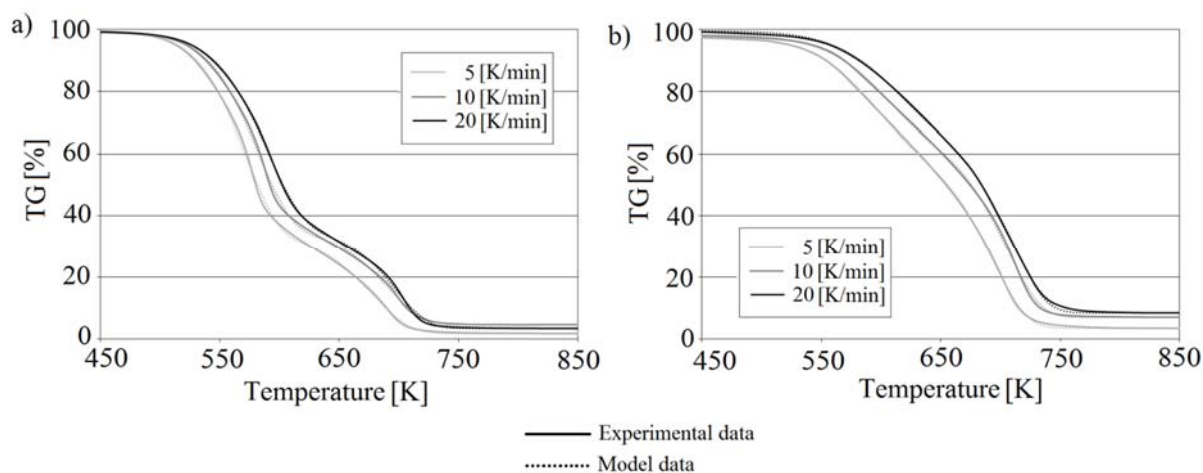| Sample	E_{a1} [kJ/mol]	A_1 [1/s]	E_{a2} [kJ/mol]	A_2 [1/s]
Salix viminalis L.	93	$1.7 \cdot 10^6$	146	$1.5 \cdot 10^9$
TSWE 200	98	$2.1 \cdot 10^6$	141	$2.3 \cdot 10^8$
TSWE 220	121	$4.2 \cdot 10^8$	116	$4.5 \cdot 10^6$
TSWE 240	131	$2.9 \cdot 10^9$	113	$1.9 \cdot 10^6$
TSWE 260	133	$7.4 \cdot 10^9$	109	$8.8 \cdot 10^5$
TSWE 280	86	$2.3 \cdot 10^5$	138	$1.7 \cdot 10^8$
TSWE 300	82	$5.8 \cdot 10^4$	136	$8.6 \cdot 10^7$

Fig. 7. Fit of TG measurements, simulated with the two-step first order reaction model for the heating rates of 5, 10 and 20 K/min for the combustion of samples a) TSWE 200 b) TSWE 300

Figure 7 shows a satisfactory fit of model data to experimental data using the two-step first order model for TSWE 200 and 300 sample combustion as exemplary results.

Activation energy values for the first stage (pyrolysis) increased with the increasing temperature of torrefaction from 93 to 133 kJ/mol, while the second stage (combustion) decrease from 146 to 109 kJ/mol for all samples, except TSWE 280 and 300. A similar correlation can be seen in the case of

a pre-exponential value A. In the case of samples torrefied at high temperatures the activation energy values of the first stage are the smallest (86 and 82 kJ/mol for TSWE 280 and 300 samples, respectively) and the activation energy values of the second stage are similar:138 and 136 kJ/mol for TSWE 280 and 300 samples, respectively. In the case of combustion of TSWE 280 and 300 the pyrolysis stage has a negligible impact for the overall combustion process.

Moreover, the values of activation energy and pre-exponential factor can be divided into three groups. The first group includes samples of *Salix viminalis L.* and TSWE 200 and is characterised by smaller values of activation energy (<100 kJ/mol) and pre-exponential factor in the pyrolysis stage than in the combustion stage, where the values of energy activation are higher than 140 kJ/mol. The kinetic parameters of the second stage are the highest of all. Combustion process of these two samples consists of two stages: volatilisation and combustion. The second group includes samples of TSWE 220, 240 and 260 and is characterised by higher values of activation energy and pre-exponential factor in the pyrolysis stage than in the combustion stage. In this case activation energy is higher than 110 kJ/mol. Pyrolysis has a smaller impact on overall process, because same biomass components are decomposed in torrefaction.

The last group includes samples of TSWE 280 and 300 and is characterised by the smallest values of kinetic parameters in the pyrolysis stage. The pyrolysis stage has a negligible impact on the overall process and mainly combustion stage takes place. The second stage proceeds with quite high values of kinetic parameters.

These trends may be attributed to the modified structure of cellulose and lignin in torrefied biomass. Hemicellulosic fraction is decomposed up to 673 K and in higher temperatures there are only cellulosic and ligninic fractions in the biomass structure, which are slowly decomposed and burnt.

The R value is very high ($R > 0.999$) and the deviations between experimental and calculated curves are below 10 % which can prove that the calculated data is fitted to the experimental data very well.

4. CONCLUSION

In this research, the thermo-chemical properties of Salix viminalis L. and its torrefied samples in the combustion process have been studied using TGA, FTIR and MS techniques. Based on the results presented here, particular conclusions can be drawn:

- Torrefied biomass properties strongly depend on torrefaction temperatures. The decrease in moisture, volatile matter and oxygen content with the rise of the temperature of the torrefaction process could be observed. Oppositely the ash, C, H, N content and higher heating value (HHV), increased with the torrefaction process temperature increase.
- Combustion of biomass samples can be divided into three stages with the following temperature ranges: 313-423 K (moisture evolution), 423-637 K (volatilisation) and 637-1273 K (char combustion). In the case of willow and torrefied samples TSWE 200, 220, 240 and 260 there are pyrolysis and combustion stages, and in the case of TSWE 280 and 300 samples the peak associated with the pyrolysis process is negligible, in contrast to the peak associated with the combustion process.
- Several combustion characteristic parameters such as ignition temperature (Ti), peak temperature (Tmax), burn-out temperature (Tb) and burning time (BT) were determined. On this basis it can be concluded that samples with higher torrefaction temperatures have a higher ignition temperature and a shorter time of combustion.
- Analysis of the MS and FTIR results show that the main gaseous products of the combustion process at the temperature of first stage are H_2O, CO_2, CO and some organic compounds and in the second stage those are CO_2, CO. Comparing peaks corresponding to gaseous products in the

first stage of combustion process, it can be concluded that the peaks of organic compounds decrease with the temperature of torrefaction.

- In the kinetic analysis, the two-steps first order model (F1F1) was assumed. Activation energy values for the first stage (pyrolysis) increased with the increased the temperature of torrefaction from 93 to 133 kJ/mol, while at the second stage (combustion) decreased from 146 to 109 kJ/mol for all samples, except TSWE 280 and 300. A similar correlation can be seen in the case of a pre-exponential value A. In the case of samples torrefied at high temperatures the activation energy values of the first stage are the smallest (86 and 82 kJ/mol for TSWE 280 and 300 samples, respectively) and the activation energy values of the second stage are similar 138 and 136 kJ/mol for TSWE 280 and 300 samples, respectively.
- The R value is very high (R> 0.999) and the deviations between experimental and calculated curves are below 10 % which can prove that the calculated data is fitted to the experimental data very well.

SYMBOLS

A	exponential coefficient, 1/s
C_t^a	total carbon in sample on an air-dry basis
E_a	activation energy, kJ/mol
$f(\alpha)$	structural factor or a model of the reaction
$f(T)$	Arrhenius equation,
H_t^a	total hydrogen in sample on an air-dry basis,
i	experimental data point at time t,
j	experimental data point at heating rate β,
N_t^a	total nitrogen in sample on an air-dry basis
O_t^a	total oxygen in sample on an air-dry basis
R	ideal gas constant, kJ/(mol·K)
S_t^a	sulphur in sample on an air-dry basis,
t	time, s
T	temperature, K
TG_{exp}	the mass loss in the experimental data, %
TG_{calc}	the mass loss in the calculated data, %

Greek symbols

α	conversion, %
α_0	initial conversion (at the initial temperature T_0), %
α	final conversion (at the final temperature T), %
α_1	conversion in the temperature T_1, where the DTG curve reaches minimum (the peak between two maximum DTG peaks), %
β	heating rate, K/s

Abbreviations

DTG	derivative thermogravimetry

HHV	higher heating value,
OF	objective function, Eq. (6)
RES	renewable energy sources
VM	volatile matter

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