

TGA-DSC-MS ANALYSIS OF PYROLYSIS PROCESS OF VARIOUS AGRICULTURAL RESIDUES

by

**Nebojša G. MANIĆ^{a*}, Bojan Ž. JANKOVIĆ^b, Dragoslava D. STOJILJKOVIĆ^a,
Vladimir V. JOVANOVIĆ^a, and Miloš B. RADOJEVIĆ^a**

^aFuel and Combustion Laboratory, Faculty of Mechanical Engineering,
University of Belgrade, Belgrade, Serbia

^bDepartment of General and Physical Chemistry, Faculty of Physical Chemistry,
University of Belgrade, Belgrade, Serbia

Original scientific paper
<https://doi.org/10.2298/TSCI180118182M>

Slow pyrolysis (gradual heating over a wide range of temperatures) characteristics of various biomasses (corn brakes, wheat straw, and hazelnut shell) were investigated by simultaneous thermal analysis (STA-TGA-DTG-DSC), coupled with mass spectrometry. Thermal decomposition of these samples was divided into three stages corresponding to removal of water, devolatilization, and formation of bio-char. It was found that differences in thermal behavior of the samples are due to differences in their composition. The mass spectrometry results showed that H₂, CH₄, H₂O, CO₂ (C₃H₈), CO, and C₂H₆ were main gaseous products released during pyrolysis. Within the pyrolysis processes, it was found that CO₂ can be used on the large scale for production of CO-rich syngas.

Key words: biomass, volatilization, syngas production, efficient bio-char yields

Introduction

The energy from the Sun is stored in biomass through the photosynthetic process. The photosynthesis starts with the capture of light by photosynthetic accessory pigments and conversion into electrical energy by the chlorophyll pigments of reaction centers. In a next stage, not photochemical, although light is required to activate certain enzymes, the stored chemical energy is used to reduce CO₂ and resulting synthesis of carbohydrates.

Biomass is a CO₂ neutral option for energy generation, and potential for the conversion of biomass into energy is rapidly increasing [1, 2]. According to Maniatis [3], the energy from biomass based on a short rotation forestry and other energy crops can contribute significantly toward the objectives of the Kyoto Agreement in reducing the GHG emissions and to the problems related to climate change. Nevertheless, a number of biomass technologies are available for converting the biomass to energy. These processes can change raw biomass into a variety of gaseous, liquid, or the solid materials that can then be used for energy generation. This conversion can be implemented in three ways: thermo-chemical (break down biomass under the high temperature), bio-chemical (break down biomass under microorganism or enzymatic processes), and chemical (oils from biomass can be chemically converted into a liquid fuel) [4, 5].

In recent years, there have been many developments in the science and technology related to thermo-chemical biomass conversions. So that, incineration, gasification and pyrolysis conversion are among established and best available thermo-chemical technologies [3]. These

*Corresponding author, e-mail: nmanic@mas.bg.ac.rs

thermal processes provide an efficient, environmentally acceptable, and the cost-effective method of providing a sustainable energy source.

Pyrolysis processes are conducted under an inert atmosphere for the production of solids (bio-char), liquids (bio-oils), or the high heating value gases. Their relative fractions depend on the operating conditions, the extreme situations are usually referred to slow pyrolysis, ~ 400 °C and using the slow heating rates characterized by high vapor residence time (5-30 min), and fast pyrolysis, which mainly maximize the production of bio-oil, where the biomass is quickly heated to a high temperature with use of a very high heating rates: $1000\text{-}10.000$ °C s⁻¹.

Bio-char represents the obtained solid product from pyrolysis. High values of carbon content and heating value in bio-char made it comparable to coal and coke used in a blast furnaces [6]. Process parameters in pyrolysis such as temperature, heating rate, residence time, pressure, and particle size are crucial in particular to achieve high quality of bio-char. Among the parameters, temperature is the most influenced parameter on bio-char quality and yield. Increasing of pyrolysis temperature leads to produce better quality of bio-char, *i.e.* higher carbon content, lower volatiles, lower ash content, and higher heating value (HHV). Whereas, bio-char yield is lower when pyrolysis temperature is high, which correspond to poor economic performance of pyrolysis processes [7].

Through pyrolysis process, it is possible to obtain a liquid fuel with higher value-added, *i.e.* bio-oil. This fuel is manageable in combustion processes [8] and generates lower toxic emissions compared to those of petroleum fuels. Bio-oil is a biofuel obtained by condensation of the vapors coming from biomass sources pyrolysis. However, bio-fuel is the liquid product of the fast pyrolysis of biomass. Many researchers have been engaged in its application and the further treatment.

One of the important products of the pyrolysis is production of gas fuels (hydrogen and syngas) [9] where other valuable gases, such as CO can also be generated by pyrolysis. These gases can be useful, among other applications, in chemical synthesis and high efficiency combustion systems such as fuel cells. Hydrogen, has been considered the most suitable alternative for future energy, aiming to reduce the dependence on fossil fuels and carbon based emissions. Largest consumption of hydrogen includes the synthesis of ammonia and methanol, upgrading the heavy hydrocarbons and (iron) ore reduction. In addition, CO₂ reforming of CH₄ can produce a syngas with a theoretical H₂/CO ratio of one, which is lower than H₂/CO ratio delivered by partial oxidation, steam reforming or autothermal reforming of CH₄ [10]. Such a syngas with a rich CO content offers possibility to produce syngas stoichiometries suitable for processes of the direct synthesis of aldehydes and alcohols or olefin/gasoline synthesis of Fischer-Tropsch synthesis [11].

The main goal of this work is the pyrolysis characterization of different types of biomass (lignocellulosic biomass as agricultural residues), using thermogravimetric analysis (TGA)/derivative thermogravimetry (DTG) – differential scanning calorimetry (DSC) coupled with mass spectrometry (MS) detection analysis, where latest generation device for thermal measurements is used. The used device allows simultaneous measurements of TG-DTG-DSC signals on the lab-scale grades.

Materials and methods

Used materials and sampling procedure

Various biomass samples were used for experiments by simultaneous thermal analysis (STA). Biomass samples included agricultural residues as follows: corn (*Zea mays*) brakes, wheat straw (*T. aestivum*), and hazelnut (*Corylus avellana*) shells. Corn was grown on domestic

fields in a central region of the Republic of Serbia. After peeling, corn brakes were left on a pile as industry leftovers for two months. Hazelnut shells came from suburban region of Serbia, near Capital city, Belgrade. After removing hazelnuts' inner part, shells were collected in bags and brought to the laboratory. Wheat straw was brought from mountains in Southern Serbia and it was already air dried before sample preparation started.

According to standard EN ISO 14780 [12] each biomass sample was prepared for experimental tests. Sample was removed from the transport packaging, and then placed inside the oven at 105 °C for 2 hours, in order to determine moisture left on the inner surfaces of the packing. This amount of moisture was included in the calculation of the total moisture content in the sample according to standard EN ISO 18134 [13]. Regarding the pre-drying process of the sample, which is necessary to remove residual moisture during preparation, sample was placed on a plate and left to reach moisture equilibrium with laboratory atmosphere conditions for 24 hours. After that period of time, sample was reduced in two steps using cutting mill, after which it was sieved through the 1 mm (18 Mesh sizes) sieve.

Finally, the obtained undersize was declared as a general analysis sample and divided into three test portions for further testing. First portion of prepared sample was used for determination of ultimate analysis (carbon, hydrogen, and nitrogen content), according to standard EN ISO 16948 [14]. The results of proximate analysis (total moisture, ash, volatile matter, and char content) were obtained from the second portion of prepared sample. Proximate analysis was performed in accordance with standard procedures defined in EN ISO 17225-1 [15]. The HHV and lower heating value (LHV) for tested samples were determined using bomb calorimeter (IKA C200, IKA® Works, Inc., Wilmington, USA), according to the standard EN ISO 18125 [16].

Simultaneous thermal analysis measurements

The STA (TGA-(DTG)-DSC) measurements were performed on third portion of prepared biomass sample. The NETZSCH STA 445 F5 Jupiter system (Erich NETZSCH GmbH & Co. Holding KG, Germany) was used for STA tests for all tested samples. Inert atmosphere was provided to maintain the pyrolysis process using high purity nitrogen (Class 4.6) as a carrier gas. At the same time, nitrogen was used as a protective gas in order to keep the high sensitive internal balance (0.1 µg). Both carrier and protective gas flow rates were set to the $\varphi = 50$ mL per minute. The weight measurements were carried out using internal balance which provided the following results: corn brakes 5.45 ± 0.10 mg, hazelnut shell 5.35 ± 0.10 mg and wheat straw 5.80 ± 0.50 mg, respectively. Alumina crucibles were used for tests, and during each measurement they were filled approximately up to the half. Crucible's lid was placed on the top, so the optimum heat transfer could be realized. Each sample was tested using three different heating rates ($\beta = 5, 10,$ and 20 °C per minute), one for each measurement. Using these heating rates, the samples were heated from room (ambient) temperature up to $T = 600$ °C. During all the measurements, the sample temperature controller (STC) was turned off, so the set temperature (600 °C) is referred to furnace temperature. Temperatures presented on diagrams are sample temperatures that, due to the construction of the furnace, never reached the set temperature. This heating mode resulted in better temperature curve linearity, than it would be possible if STC was turned on. The STA 445 F5 Jupiter runs under versatile Proteus® software and includes all operating tools to obtain a reliable measurements data and to evaluate them, or even carry out complicated analyses.

Mass spectrometry analysis

Determination of evolved gases from performed STA was carried out continuously using quadrupole mass spectrometer NETZSCH QMS 403 D Aëolos (QMS) (Erich NETZSCH GmbH & Co. Holding KG, Germany). The TGA/STA - QMS coupling was provided by transfer

line (quartz capillary tube) with diameter of 75 μm . Transfer line was heated and kept at constant temperature of 230 $^{\circ}\text{C}$ in order to avoid condensation of evolving volatile compounds. The QMS was operated under vacuum up to 10^{-7} bar, providing conditions necessary to detect gas components using their ions intensity according to their respective mass to charge ratios (m/z). Evolved gas composition was monitored and analysed graphically (on bar-graph cycles), with scanning mass units in the range from 1 to 80. Cycles were set to speed of 0.2 seconds per mass unit and carried out using stair mode. Excitation energy in the QMS was set up at 1200 eV with the resolution of 50 units.

From the selected range, the focus was on specific ions that correspond to gases evolved in pyrolysis process. Accordingly, the molecules with atomic mass units (amu) of 2, 16, 18, 28, 30, 44, 58, and 72 which correspond to H_2 , CH_4 , H_2O , CO , C_2H_6 , C_3H_8 (CO_2), C_4H_{10} and C_5H_{12} respectively, were analysed, and intensity peak areas obtained for each compound were compared.

Results and discussion

Results of proximate and ultimate analysis and bio-char yields

Table 1. present the results of proximate and ultimate analysis of tested biomass samples.

Table 1. Proximate and ultimate results for tested biomass samples

Proximate analysis [wt.%]	Corn brakes	Wheat straw	Hazelnut shell
Moisture	8.58	11.63	9.27
Volatile matter	73.94	65.32	68.08
Fixed carbon	16.00	15.17	20.97
Ash	1.48	7.88	1.67
HHV [MJkg^{-1}]	16.72	15.29	18.20
LHV [MJkg^{-1}]	15.10	13.91	16.68
Ultimate analysis ^a [wt.%]			
C	47.97	44.12	50.12
H	6.87	6.34	6.66
Ob	42.89	39.99	40.53
N	0.66	0.63	0.86
S	0.00	0.00	0.00

^a On a dry basis. ^b By the difference.

It can be seen from tab. 1 that all biomass samples are characterized by high volatile matter content, ranging from 65.32-73.94%, which makes them desirable for a good regulation of combustion or gasification processes. Among tested samples, wheat straw shows the highest ash content value (7.88%), because of the fact that among all agricultural residues, the high ash content of straw interfere with pulping process (apropos water must be spray onto the wheat straw when cutting it in pulp mill to prevent raising of the dust), the chemical recovery of pulping chemicals and the utilization of straw as a fuel. Raw materials have moisture content ranging 8.58-11.63% which can be attributed to open air conditions as well as to wet separation process. In addition, it can be observed from tab. 1 that corn brakes are characterized by highest value of volatile matter compared to other samples, which means it is characterized by highest conversion, in comparison to the sample with highest fixed carbon (hazelnut shell, tab. 1). From a theoretical point of view, corn brakes can be suitable for production of bio-oil, while hazelnut shell would be best raw material for production of bio-char, tab. 1. All tested samples have the

HHV values ranging from 15.29-18.20 MJ kg⁻¹, which corresponds to heating values of biomass derived bio-chars (11.83-44.20 MJ kg⁻¹) [17, 18]. Generally, the biomasses with high HHV values make them very attractive for the source-feeds for clean energy production instead of fossil-based solid fuels.

In addition, the concentration of C and H is the lowest for wheat straw, while their highest concentration was identified for hazelnut shell, tab. 1. The wheat straw has a something lower content of O compared to other samples, which may indicate creation of smaller amount of inorganic vapors during combustion. Agricultural biomass has a low heating value due to its high ash content, where it was reported [19] that biomass with a high ash content is not an ideal fuel source, because the ash content is one of the main factors that directly influence the heating value of biomass. High carbon and low oxygen in biomass as compared to coal (73.1% of carbon and 8.7% of oxygen) are favorable for combustion applications, while the higher proportion of carbon (relative to hydrogen and oxygen content) (for example, wheat straw and hazelnut shells, tab. 1. increases the energy content of a fuel because energy contained in carbon-carbon bonds is greater than that of carbon-oxygen and carbon-hydrogen bonds [20].

Bio-char yield for considered samples was calculated from STA experiments using a relation: bio-char yield (%) = $[(m_t^*) / (m_i)] \times 100$, where m_t^* is the mass at desired temperature and time, while m_i is the mass at time $t = 0$ (min). Table 2 lists values of bio-char yields of biomass samples in pyrolysis process obtained at different operating temperatures and residence times at 10 °C per minute.

Table 2. Bio-char yields of tested biomass samples at different operating temperatures and residence times for the heating rate of $\beta = 10$ °C per minute

	Corn brakes				Wheat straw				Hazelnut shell			
T [°C]	250	350	450	550	250	350	450	550	250	350	450	550
t [minute]	24.50	33.76	43.50	53.31	24.50	34.00	43.83	53.58	24.47	33.75	43.55	53.26
Yield [%]	89.21	43.42	30.38	26.65	90.87	46.15	34.21	30.60	88.00	52.98	36.24	31.66

It can be seen from tab. 2 that for all biomass samples, the bio-char yields are negatively correlated with increasing pyrolysis severity (increased operating temperature and longer residence times). Among tested samples, corn brakes have the lowest bio-char yield for $T \geq 450$ °C along residence time $t > 43.50$ minute. At high operating temperatures, probably, there is a significant distinction in composition of cell wall components and extractives in this type of biomass sample in comparison with wheat straw and hazelnut shell. From presented results it can be seen that hazelnut shell has the highest bio-char yield (except at the lowest operating temperature). From these results, it follows that high initial moisture for wheat straw, tab. 1, produces high bio-char yield at the lowest operating temperature, and then visibly decreases with increase of residence time, tab. 2. Obtained results for bio-char yields are in the range for bio-char yield under slow pyrolysis of biomass feedstock 2 -60 % [21]. Fairly high bio-char yields in this study can be attributed to lower value of nitrogen flow rate, where carrier gas can regulate vapor residence time and has an impact on char forming reactions.

The TGA-DTG-DSC curves of pyrolysis processes

Experimental TG-DTG-DSC curves for thermal decomposition of corn brakes (a), wheat straw (b), and hazelnut shell (c) under an atmosphere of nitrogen are shown on figs. 1-3.

All TGA curves, fig. 1, show three main stages which are typical for biomass pyrolysis process. The first stage corresponds to moisture release (water evaporation) (pre-pyrolysis stage), which occurs approximately in the temperature range 25-175 °C. The remaining two stages are

attributed to active and passive pyrolysis, respectively. The active pyrolysis stage is characterized by largest mass loss where various vapors and gases are released as a result of decomposition processes of hemicelluloses and cellulose which takes place in this stage, within temperature ranges 175-380 °C and 250-380 °C, respectively.

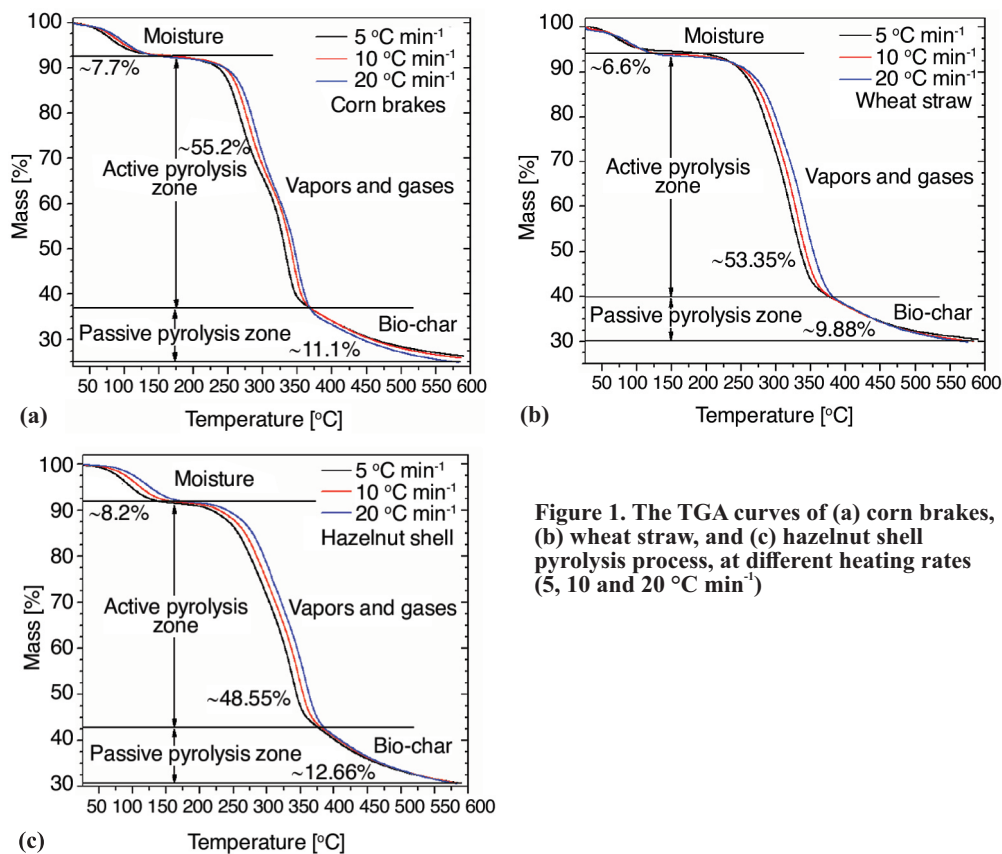


Figure 1. The TGA curves of (a) corn brakes, (b) wheat straw, and (c) hazelnut shell pyrolysis process, at different heating rates (5, 10 and 20 °C min⁻¹)

On the other hand, the lignin is decomposed in both stages: active and passive pyrolysis stages in the temperature range 175-600 °C, without characteristic peaks, fig. 2. However, various biomasses show different heat effects in respect to the number of endothermic and exothermic peaks at fixed heating rate, fig. 3. The depth of endothermic peak related to pre-pyrolysis stage varies from sample to sample, which is in correlation with moisture content in samples tab. 1. One of the processes is certainly *masked* given that probably there is an advantage of overlapping decomposition reactions, related to one of the pseudo-components in biomass samples [22].

The DSC curve for hazelnut shell, fig. 3(c), is only distinguished from other DSC curves. Certain variations in the heat effects can be significantly stimulated by concentration of three important pseudo-components (hemicellulose, cellulose, and lignin) present in samples, which also affects the development of decomposition paths. For wheat straw, the slight exothermic effect in the passive pyrolysis which is attributed to bio-char forming was designated by “3”, while for other samples this is indicated by “4”, fig. 3. It should be mentioned that strength of endothermic peak caused by volatilization of moisture can be enhanced by higher gas flow,

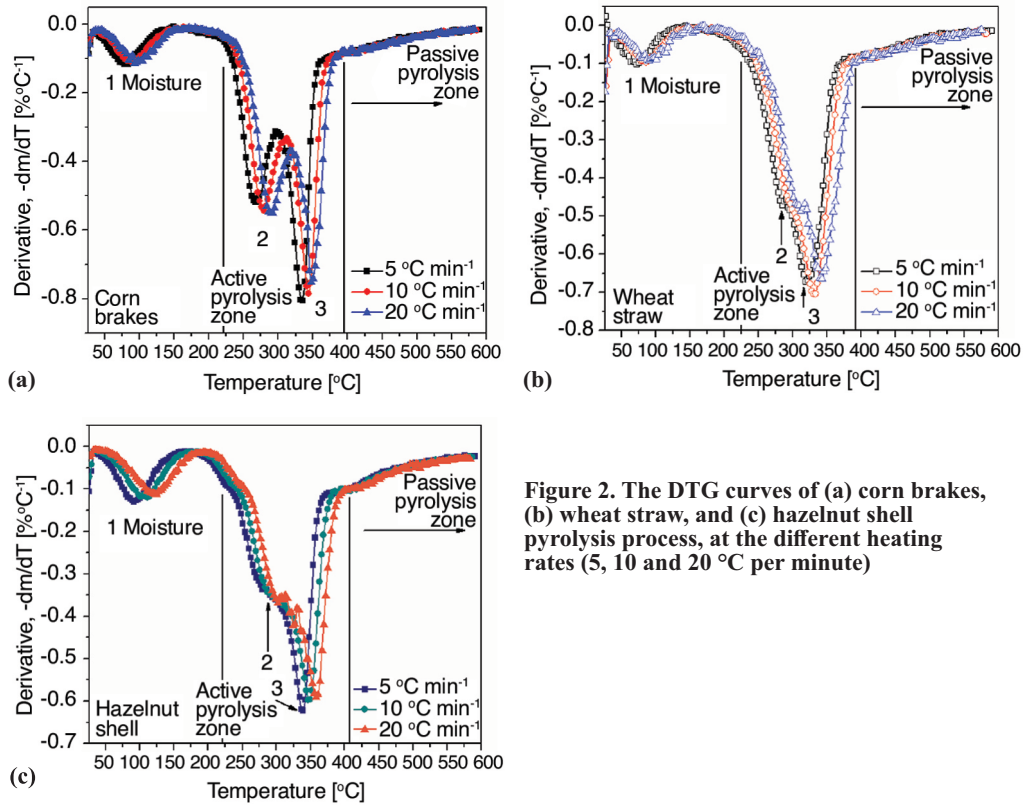


Figure 2. The DTG curves of (a) corn brakes, (b) wheat straw, and (c) hazelnut shell pyrolysis process, at the different heating rates (5, 10 and 20 °C per minute)

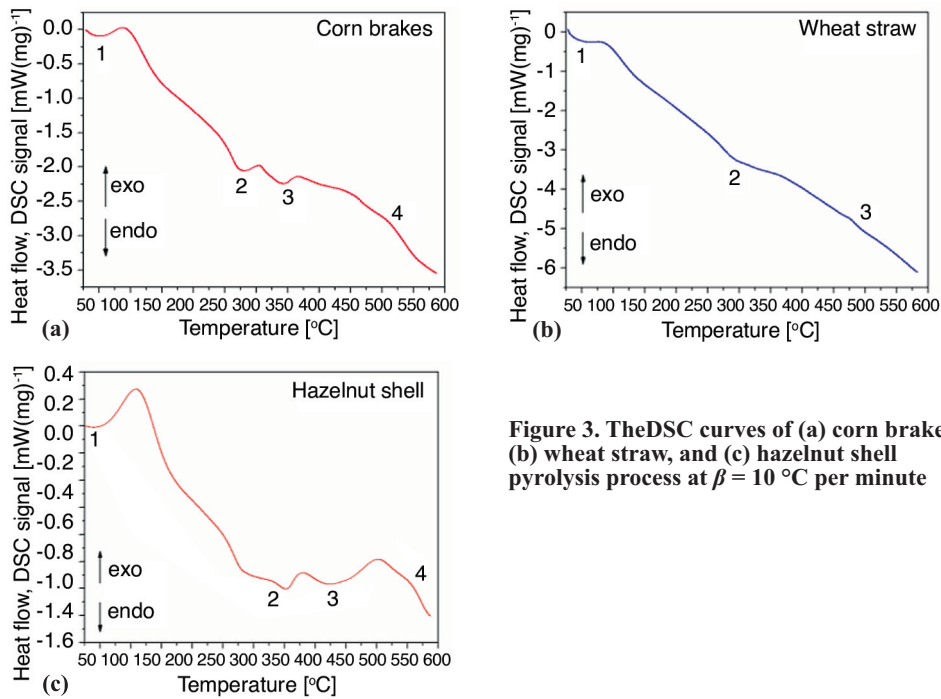


Figure 3. The DSC curves of (a) corn brakes, (b) wheat straw, and (c) hazelnut shell pyrolysis process at $\beta = 10$ °C per minute

while with an increase of pyrolysis temperature, the heat of exothermic reaction during pyrolysis can increase gradually.

Regardless of pyrolytic behavior, only DTG curve related to corn brakes pyrolysis, fig. 2(a) show two distinctive peaks attributed to decomposition reactions of hemicellulose and cellulose in an active pyrolysis stage (designated by “2” and “3”).

For other two samples figs. 2(b) and 2(c), the well-defined peak which was present in corn brakes pyrolysis is transformed into the *shoulder*. Considering all DTG curves, long tails in a passive pyrolysis stage can be attributed to decomposition of lignin at temperatures above 400 °C, where pyrolysis proceeds with a slower mass loss rate.

Based on these results, it can be concluded that at high heating rates, separate DTG peaks did not arise because some of them were decomposed simultaneously and several adjacent peaks were united to form overlapped wider and higher peaks. This is consequence of heat and mass transfer limitations. In this respect, with an increase in heating rate, the temperature in furnace space can be a little higher as the temperature of a particle and the rate of decomposition are higher than release of volatiles. Differences in molecular structures and chemical nature of three pseudo-components account for observed dissimilar behaviors. Namely, it is obvious that variations in appearance in DTG curves are primary related to variation in percentage of hemicelluloses presented in biomass samples. Namely, the higher lignin content may lead to a slower decomposition with a more energy needed, whereas a higher cellulose and hemicelluloses content decomposes faster and produces a larger fraction of gaseous products [23]. Detected exothermic effects within the passive pyrolysis stage can be attributed to decomposition patterns of hemicelluloses and lignin that are related to their high charring nature, and which is in contrast with decomposition of cellulose taking place by the full volatilization [24, 25]. Bio-char consists of the residue of lignin [26-28], where lignin continues to further exothermic polymerization stage of bio-char. At higher temperatures, the polymerization of biomass bio-char continuously occurred and polymerization reaction is dependent on the unique properties of bio-char of tested sample. At low heating rates, the bio-char yield from lignin exceeds 50 % by weight.

Analysis of the gases produced during pyrolysis

The TGA-MS profiles of the evolved gases during pyrolysis, H₂, CH₄, C₂H₆, C₄H₁₀, C₅H₁₂ and profiles of the changes in the ion current as a function of temperature (the mass spectra) for pyrolytic water (H₂O), CO₂ (C₃H₈), and CO for various types of biomass (CB - corn brakes, WS - wheat straw, and HS-hazelnut shell) at the different heating rates of 5, 10, and 20 °C per minute are shown in figs. 4(a) - 6(f), respectively.

The present study was focused on the main volatile products of biomass pyrolysis on the basis of changes in ion currents across the temperature range of 40-600 °C, and on their relevancy, assigned to the ion/mass intensities (*m/z*) with corresponded screening analysis performed in the selected-ion monitoring (SIM) mode (the ions characteristic of each molecules, such as: 2, 16, 18, 28, 44,... for H₂, CH₄, H₂O, CO, CO₂, ... were monitored) and which is in accordance with database of National Institute of Standards and Technology (NIST).

For tested samples, at all observed heating rates, the primary devolatilization stage was identified with major mass loss and the release of organic compounds which leads to formation of bio-char, where this stage releases H₂, CH₄, H₂O, CO₂ (also C₃H₈), CO, including light hydrocarbons figs. 4-6. The maximas in DTG curves, fig. 2, correspond to the maximum of gas release, as shown in figs. 4-6. It can be observed that with an increase of the heating rate, the *intensity* of ion current also increases, so that rate of the gas products release is higher. For CB and WS, the light gases, H₂, CH₄ (C₂-C₃), and CO₂ figs. 4(a)-5(f) evolve at a wide temperature range and their evolu-

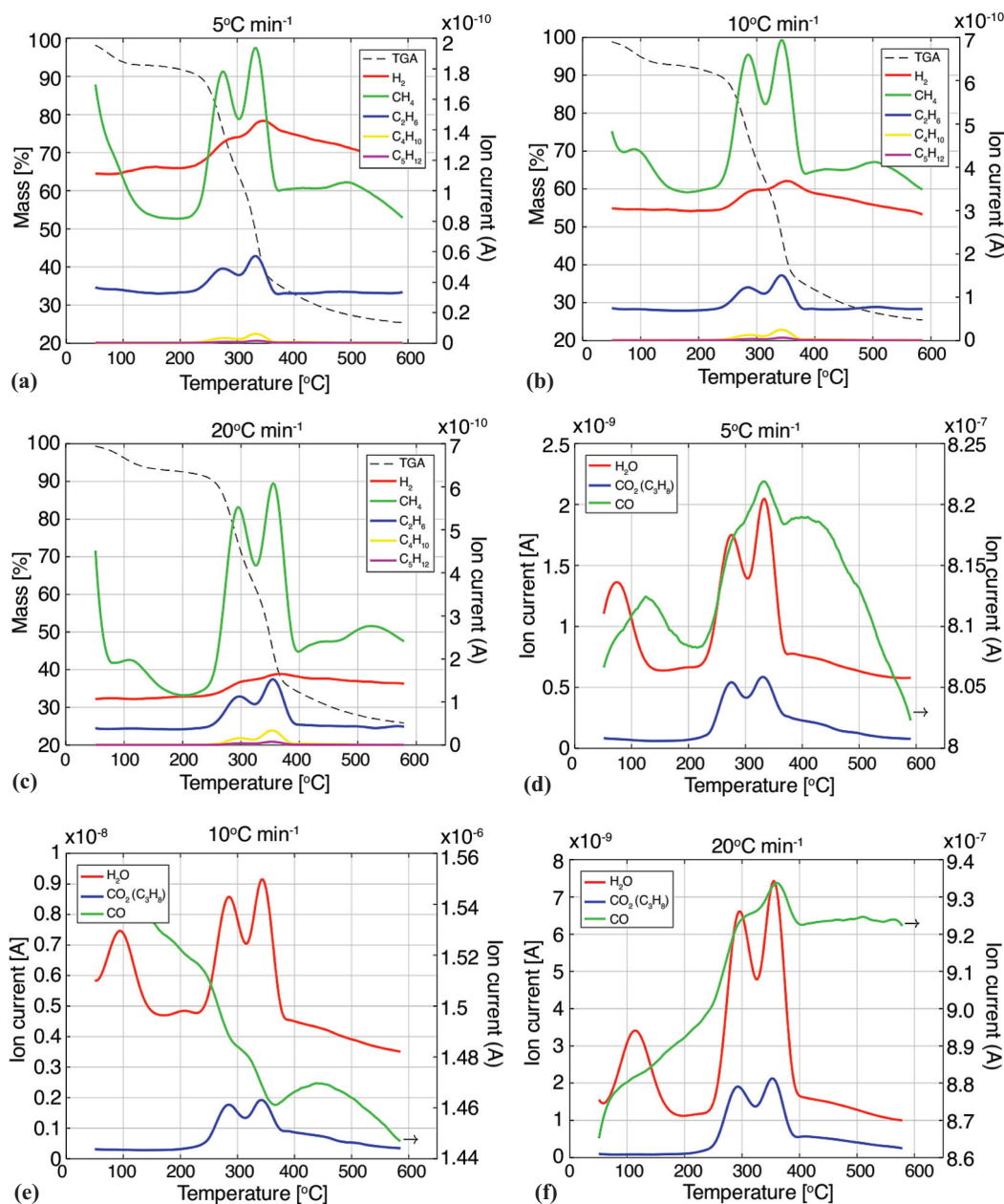


Figure 4. Simultaneous TGA-MS profiles of evolved gases during pyrolysis of corn brakes (CB)

tion profiles are similar to DTG maximum rates. In addition, for both cases, some deviations are observed for CO evolution profile and this profile varies with heating rate change. Largest deviation shows CO evolution profile of HS pyrolysis in respect to DTG maxima features, and this deviation is particularly pronounced, when changing heating rate from lowest to highest rate of heating. This is consequence of non-profiled DTG peak, but a clear appearance of *shoulder*, which in many cases depends on hemicelluloses' concentration (if the concentration is low).

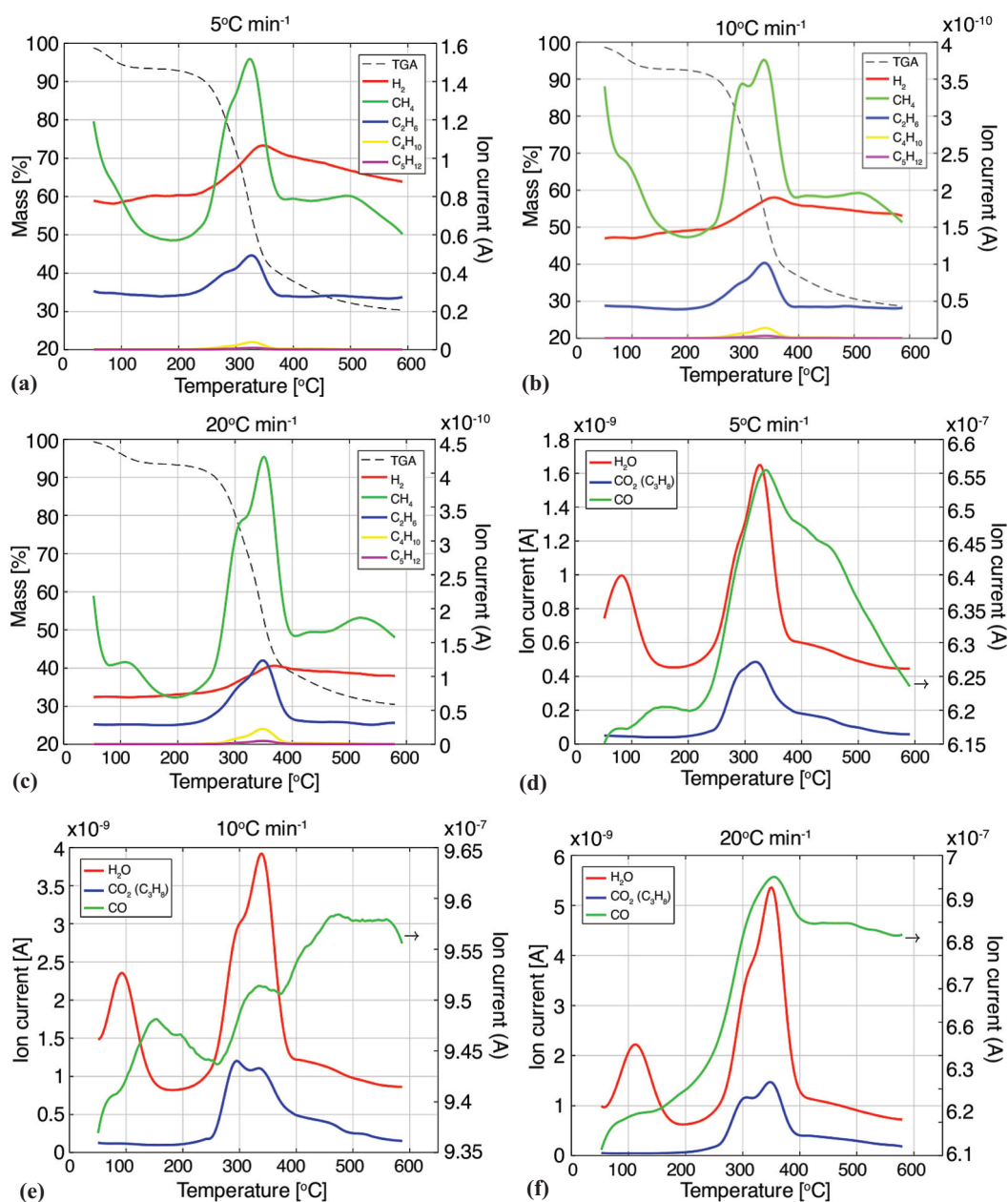


Figure 5. Simultaneous TGA-MS profiles of evolved gases during pyrolysis of wheat straw (WS)

Having in mind these results and comparing the CO gas profiles (including CO₂ profile), it can be concluded that contribution of lignin plays a significant role and its contribution largely depends on the heating rate. Since the lignin is decomposed continuously in a wide temperature range, with undefined mass loss rate, such behavior is manifested through a series of *unsteady* profiles of CO evolution. It should be noted that CH₄ and H₂ peaks are detected in passive pyrolysis zone for $T > 450$ °C. This secondary pyrolysis is the result of decomposition of heavy

molecules in bio-char. The H_2 evolved is, in fact, only a part of present hydrogen due to higher volatile matter content in samples.

It should also be noted that regarding to H_2 , the charring and restructuring processes, which include dehydrogenation reactions, are responsible for its production, starting at temperature above 450 °C, depending on the sample. The CH_4 , as well as other C_2 and C_3 hydrocarbons, present local maxima at temperatures different than ones of the DTG rate maxima (for HS) figs. 6 (a)-6(f). For HS, two local maxima at 10 and 20 °C per minute in temperature

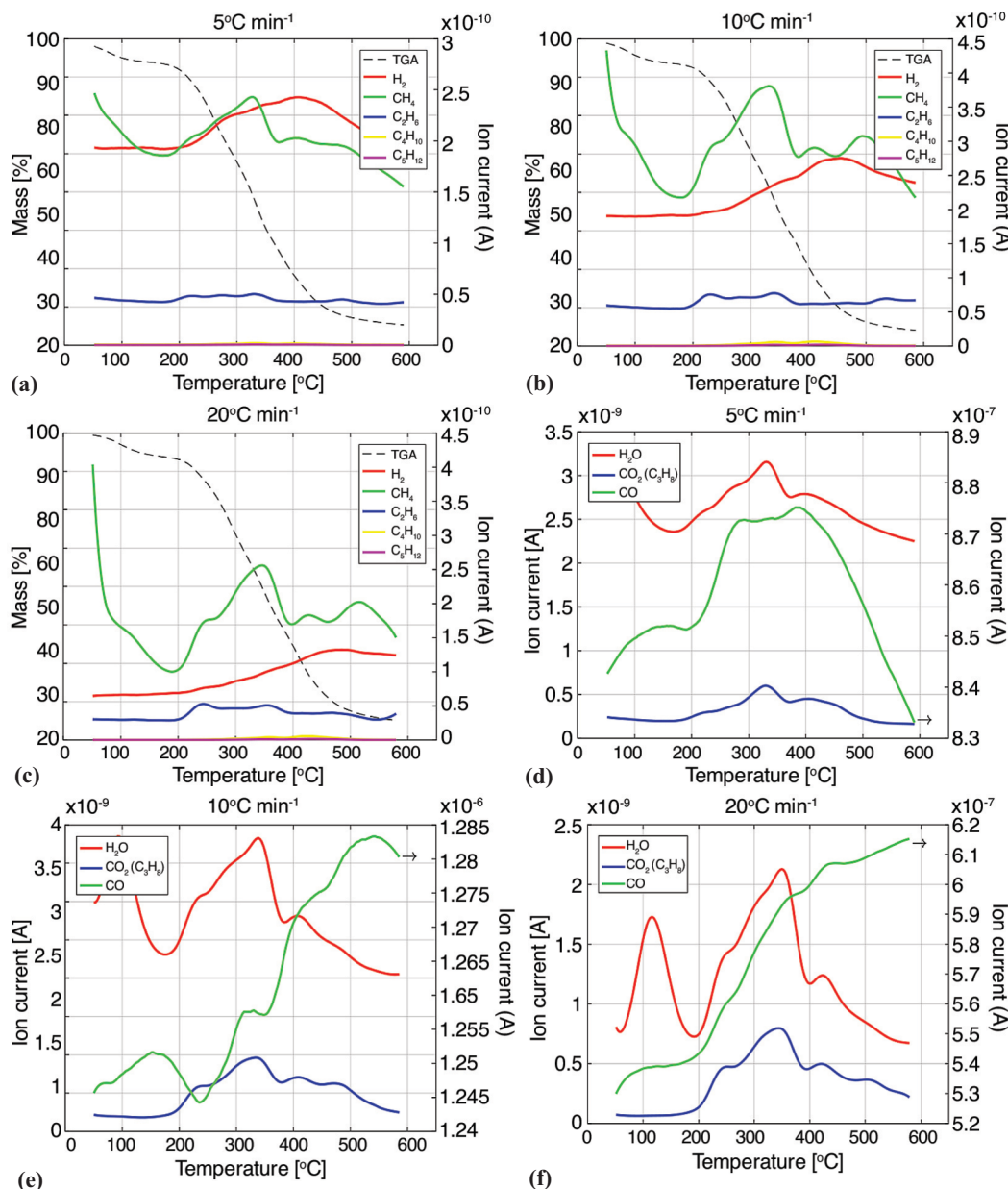


Figure 6. Simultaneous TGA-MS profiles of evolved gases during pyrolysis of hazelnut shell (HS)

ranges 400-450 °C / 450-550 °C correspond to methane evolution peaks. The lower temperature peak can be attributed to -OCH₃ functional group cracking, while the higher temperature peak is due to charring processes [29].

A relatively significant amounts of CO and H₂O were detected because of large number of hydroxyl groups and oxygen atoms present in the samples (cellulose, hemicelluloses, and lignin). However, we can note that majority of gases is generated in temperature range of 200-500 °C, where differences occur in respect to change of the heating rate and in peak *intensity*.

At temperatures below 200 °C, there is just release of H₂O figs. 4(d)-6(f); its peaks coincide with those of DTG curves, during evaporation step. The release of H₂O and CO₂ (C₃) occurs between 200 and 500 °C. These two gases are characterized mainly by two peaks, where H₂O was produced on all the interval of decomposition of biomass, indicating their provenance from different origins. The peak obtained at approximately 105 °C is due to release of absorbed water, while peaks beyond 200 °C correspond to water formed during decomposition of hemicelluloses, cellulose and lignin. Productions of C₂H₆ results from decomposition of cellulose while release of CH₄ at low temperatures, comes from decompositions of cellulose and hemicelluloses [30]. At high temperatures, CH₄ is mainly produced by cracking of the methoxyl groups [31].

Figure 7(a)-7(h) shows simultaneous comparison of individual gaseous products for each sample at a fixed value of the heating rate (10 °C per minute).

Usually (for water and carbon dioxide), the shape of the mass spectrometric curves resembles DTG curve. The shape similarities of the mass spectra of these compounds with shapes of DTG curves for all biomasses are obvious. On the other hand, however, the hydrogen signal has a different behavior. At a fixed rate of heating, for WS, the ion current of hydrogen increases from low temperature to approximately 350 °C, and then decreases to higher temperatures fig. 7(a). However, for CS, the ion current of hydrogen increases also from low temperature and maintains at a constant value in a very narrow temperature range and then increases up to 340 °C, and then decreases to higher temperatures fig. 7(a). Considering DTG curve at 10 °C per minute, it can be observed that there are some differences with behavior of the mass signal. The largest differences can be seen in the case of HS, where maximum ion current is reached at approximately 460 °C, which is completely opposite to maximum mass loss rate identified on DTG curves related to this system fig. 2(c), and fig. 7(a). It can be assumed that the mass spectrometric signal is strongly overlapping with DTG peak. For CS, the mass spectrometric signal for hydrogen is overlap only partially with DTG curve. It can be concluded that main source for hydrogen production arises from thermal volatilization of biomass pseudo-components. The CH₄ mass spectrometric signal (except for HS) is similar to the shape of DTG curves. However, for CB and HS, the CH₄ signals show wide peaks in temperature ranges 450-580 °C and 460-580 °C, respectively.

This means that in considered cases, the most pronounced sources for CH₄ production are from two origins: volatilization at lower temperatures and charring process at high temperature. For volatilization, the cleavage of methoxyl groups present in lignin is more important here. At high temperatures, the CH₄ production is attributed to charring processes which involve aliphatic and aromatic chars. Broad peaks in high temperature zone can be explained by the fact that the methane could be obtained from bio-char in current temperature ranges.

At lower temperatures, the mass signals of H₂O, CO, and CO₂ (C₃) evolutions fig. 7(d)-7(f) are due to volatilization of hemicelluloses and partially of cellulose (CO was most likely generated from cellulose pyrolysis). The distinct emission of CO₂ appeared from 200 °C, and it reached a high mass spectrometric peaks within 300 to 400 °C fig. 7(d), which is major pyrolysis

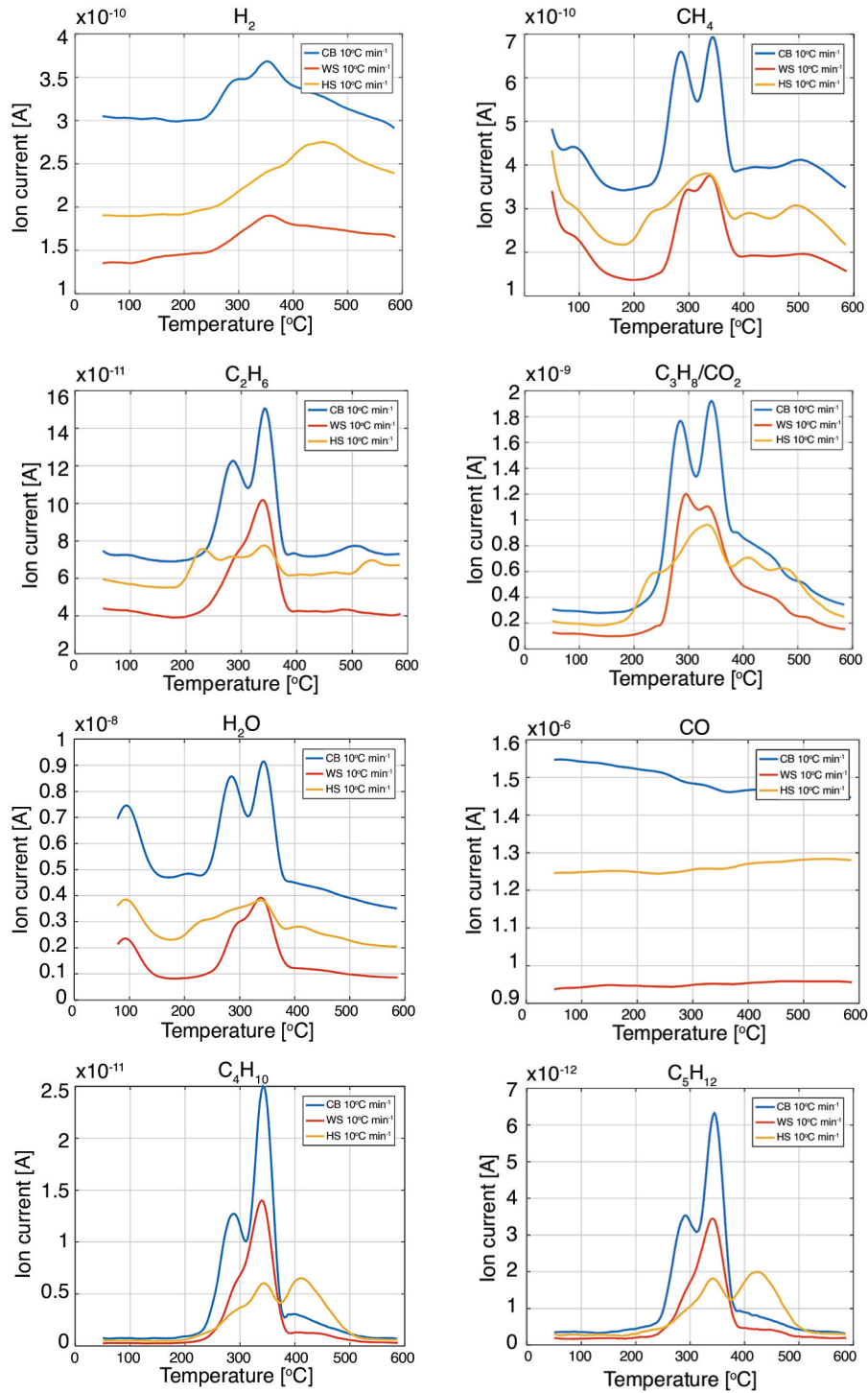


Figure 7. Comparison of individual gaseous products for each tested biomass sample (CB, WS and HS) at a fixed value of the heating rate (10 °C per minute)

zone of celluloses. Peak around 350 °C, was ascribed to decomposition of aromatic and aliphatic carboxyl groups in celluloses. It can be assumed that below 500 °C, the abundant presence of C = O groups in hemicelluloses can be favorable for CO₂ emission. As temperature increased, more stable ether structures and oxygen-bearing heterocycles in lignin were also decomposed into the CO₂ [32].

Compared to hemicelluloses and lignin, cellulose released most of gaseous products in a narrow temperature range (300-400 °C). On the other hand, hemicelluloses and lignin, released the methane and -CH₃ groups at about 500 °C. Consequently, the methane was generated at about 420 °C from hemicelluloses, and at about 500 °C from lignin. However, the highest concentration emission of methane occur about 380 °C. The methane emission at relatively lower temperatures was most likely released from C-C bond cleavage in aliphatic chains whereas the methane emission at higher temperatures was mainly produced from cracking of a weakly bonded methoxyl-O-CH₃ group as well as the break of having higher bond energy of methylene group -CH₂ [33]. Considering biomass pseudo-components pyrolysis, the methane was mainly released from pyrolysis of lignin, because it contains more methoxyl-O-CH₃ chemical groups than hemicelluloses and celluloses.

In addition to above considerations, the hydrogen formation which arises at high temperatures (> 450 °C) can be attributed to secondary reactions as steam reforming and/or tar cracking [34]. At lower temperatures, the hydrogen emission was mainly generated from thermal decomposition of cellulose and hemicelluloses. At $T > 450$ °C, the decreasing trends in hydrogen mass signal may reveals that lignin pyrolysis could also generate the hydrogen.

Conclusions

This work presents the characterization analysis of pyrolysis process of various biomasses (corn brakes, wheat straw, and hazelnut shell) using simultaneous thermal analysis - mass spectrometry techniques, in an inert atmosphere. The ultimate and proximate analysis of tested biomass samples indicated the differences related to the same types of biomasses. The following conclusions can be drawn from this study:

- The TGA and DTG results showed that pyrolysis was represented by three successive steps: the first step corresponded to evaporation of moisture, while the second and third steps can be attributed to active and passive pyrolysis, respectively. The active pyrolysis stage is characterized by the largest mass loss where various vapors and gases are released as a result of decomposition processes of hemicelluloses and cellulose. The third pseudo-component of biomass (lignin) is decomposed in both stages: active and passive pyrolysis stages, without characteristic thermo-analytical peaks. It was found that certain variations in the heat effects can be significantly stimulated by concentration of the three pseudo-components present in tested biomasses, which also affects the development of their decomposition paths. It was established that differences in molecular structures and chemical nature of three pseudo-components in biomasses should be accounted for dissimilarities observed in DTG curves. It was concluded that identified variations in appearance in DTG curves are primary related to the variation in percentage of hemicelluloses presented in biomass samples.
- The mass spectrometry results showed that H₂, CH₄, H₂O, CO₂ (C₃H₈), CO, and C₂H₆ were the main gaseous products released during the pyrolysis. It was found that majority of gases is generated in temperature range 200-500 °C for all tested samples, where differences occur in respect to changes of the heating rate and in mass spectrometry peak *intensity*. It was found that H₂O, CO and CO₂ evolutions arise from lignin source in biomass, followed by the cellulose, and hemicelluloses. Considering biomass pseudo-components pyrolysis, it was

found that CH₄ was mainly released from lignin pyrolysis, because it contains more methoxyl-O-CH₃ chemical groups than hemicelluloses and celluloses. It was found that at temperatures higher than 450 °C, the H₂ formation can be attributed to secondary pyrolytic reactions. At lower temperatures, the H₂ emission was mainly generated from thermal decomposition of cellulose and hemicelluloses.

Acknowledgment

Authors would like to acknowledge financial support of Ministry of Education, Science and Technological Development of the Republic of Serbia under the Projects 172015 and III42010.

Conflict of Interest

The authors declare that they have no conflict of interest.

References

- [1] Ohlstrom, M., *et al.*, New Concepts for Biofuels in Transportation: Biomass-Based Methanol Production and Reduced Emissions in Advanced Vehicles., VTT (Technical Research Centre of Finland) Energy, Espoo, Finland, VTT Research Note, 3-94, 2001
- [2] Saxena, R. C., *et al.*, Biomass-Based Energy Fuel Through Biochemical Routes: A Review, *Renewable and Sustainable Energy Reviews*, 13 (2009), 1, pp. 167-178
- [3] Maniatis, K., Progress in Biomass Gasification: An Overview. Progress in Thermochemical Biomass Conversion, Blackwell Science Ltd., Hoboken, N. J., USA, 2001
- [4] Faaij, A., Modern Biomass Conversion Technologies, *Mitigation and Adaptation Strategies for Global Change*, 11 (2006), 2, pp. 343-375
- [5] Anwar, Z., *et al.*, Agro-Industrial Lignocellulosic Biomass a Key to Unlock the Future Bio-Energy: A Brief Review, *Journal of Radiation Research and Applied Sciences*, 7 (2014), 2, pp. 163-173
- [6] Garcia-Perez, M., *et al.*, Methods for Producing Biochar and Advanced Biofuels in Washington State, Part 1: Literature Review of Pyrolysis Reactors, First Project Report, Department of Biological Systems Engineering and the Center for Sustaining Agriculture and Natural Resources, Washington State University, Pullman, Wash, USA, p. 137, 2010
- [7] Czajczynska, D., *et al.*, Potential of Pyrolysis Processes in the Waste Management Sector, *Thermal Science and Engineering Progress*, 3 (2017), Sept., pp. 171-197
- [8] Jayaraman, K., Gokalp, I., Pyrolysis, Combustion and Gasification Characteristics of Miscanthus and Sewage Sludge, *Energ Convers Manage*, 89 (2015), Jan., pp. 83-91
- [9] Alipour, M. R., *et al.*, Investigation on Syngas Production Via Biomass Conversion Through the Integration of Pyrolysis and Air-Steam Gasification Processes, *Energ Convers Manage*, 87 (2014), Nov., pp. 670-675
- [10] Chaudhari, S. T., *et al.*, Production of Hydrogen and/or Syngas (H₂+ CO) via Steam Gasification of Biomass-Derived Chars, *Energy & Fuels*, 17 (2003), 4, pp. 1062-1067
- [11] Boll, W., *et al.*, *Gas Production, 3. Gas Treating, Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, Germany, 2011
- [12] ***, EN ISO 14780:2017. "Solid biofuels - Sample preparation", European Committee for Standardization (CEN), 2017, Brussels, Belgium
- [13] ***, EN ISO 18134:2015. "Solid Biofuels - Determination of Moisture Content - Oven Dry Method - Part 1: Total moisture - Reference method", European Committee for Standardization (CEN), 2015, Brussels, Belgium
- [14] ***, EN ISO 16948:2015. "Solid biofuels - Determination of Total Content of Carbon, Hydrogen and Nitrogen", European Committee for Standardization (CEN), 2015, Brussels, Belgium
- [15] ***, EN ISO 17225-1:2014. "Solid Biofuels - Fuel Specifications and Classes - Part 1: General Requirements", European Committee for Standardization (CEN), 2015, Brussels, Belgium
- [16] ***, EN ISO 18125:2017. "Solid Biofuels - Determination of Calorific Value", European Committee for Standardization (CEN), 2015, Brussels, Belgium
- [17] Demirbas, A., Hydrogen from Mosses and Algae via Pyrolysis and Steam Gasification, *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 32 (2009), 2, pp. 172-179
- [18] Mohan., D, Pittman, CU, Steele PH (2006) Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review, *Energy & Fuels*, 20 (2006), 3, pp. 848-889

- [19] James, A., *et al.*, Ash Management Review-Applications of Biomass Bottom Ash, *Energies*, 5 (2012), 6, pp. 3856-3873.
- [20] McKendry, P., Energy Production from Biomass (part 1): Overview of Biomass, *Bioresource Technology*, 83 (2002), 1, pp. 37-46
- [21] Novak, J. M., *et al.*, Compositional and Thermal Evaluation of Lignocellulosic and Poultry Litter Chars via High and Low Temperature Pyrolysis, *BioEnergy Research*, 6 (2013), 1, pp. 114-130
- [22] Conesa, J. A., *et al.*, Analysis of Different Kinetic Models in the Dynamic Pyrolysis of Cellulose, *Thermochimica Acta*, 254 (1995), Apr., pp. 175-192
- [23] Caballero, J. A., *et al.*, Pyrolysis Kinetics of Almond Shells and Olive Stones Considering Their Organic Fractions, *Journal of Analytical and Applied Pyrolysis*, 42 (1997), 2, pp. 159-175
- [24] Yang, H., *et al.*, Characteristics of Hemicellulose, Cellulose and Lignin Pyrolysis, *Fuel*, 86 (2007), 12-13, pp. 1781-1788.
- [25] Wu, S., *et al.* Intensive Interaction Region During Co-Pyrolysis of Lignin and Cellulose: Experimental Observation and Kinetic Assessment, *BioResources*, 9 (2014), 2, pp. 2259-2273
- [26] Sonobe, T., *et al.*, Pyrolysis Characteristics of Thai-Agricultural Residues of Rice Straw, Rice Husk, and Corn cob by TG-MS Technique and Kinetic Analysis, *Proceedings, 2nd Joint International Conference on "Sustainable Energy and Environment (SEE'06)*, Bangkok, Thailand, C-044. 2006, pp. 1-6
- [27] Breunig, M., *et al.*, Direct Liquefaction of Lignin and Lignin Rich Biomasses by Heterogenic Catalytic Hydrogenolysis, *Biomass and Bioenergy*, 111 (2018), Apr., pp. 352-360
- [28] Park, J., *et al.*, Understanding the Relationship Between the Structure and Depolymerization Behavior of Lignin, *Fuel*, 217 (2018), Apr., pp. 202-210
- [29] Gomez, C. J., *et al.*, Thermogravimetry/Mass Spectrometry Study of Woody Residues and an Herbaceous Biomass Crop Using PCA Techniques, *Journal of Analytical and Applied Pyrolysis*, 80 (2007), 2, pp. 416-426
- [30] Ozveren, U., Ozdogan, Z. S., Investigation of the Slow Pyrolysis Kinetics of Olive Oil Pomace Using Thermo-Gravimetric Analysis Coupled with Mass Spectrometry, *Biomass and Bioenergy*, 58 (2013), Nov., pp. 168-179
- [31] Jakab, E., *et al.*, Thermal Decomposition of Milled Wood Lignins Studied by Thermogravimetry/Mass Spectrometry, *Journal of Analytical and Applied Pyrolysis*, 40-41 (1997), May, pp. 171-186
- [32] Wang, T., *et al.*, Effects of Chemical Inhomogeneity on Pyrolysis Behaviors of Corn Stalk Fractions, *Fuel*, 129 (2014), Aug., pp. 111-115
- [33] Ferdous, D., *et al.*, Production of H₂ and Medium Btu Gas Via Pyrolysis of Lignins in a Fixed-Bed Reactor, *Fuel Processing Technology*, 70 (2001), 1, pp. 9-26
- [34] Widyawati, M., *et al.*, Hydrogen Synthesis from Biomass Pyrolysis with in Situ Carbon Dioxide Capture Using Calcium Oxide, *International Journal of Hydrogen Energy*, 36 (2011), 8, pp. 4800-4813