

Comprehensive compositional study of torrefied wood and herbaceous materials by chemical analysis and thermoanalytical methods

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ABSTRACT

In this work the torrefaction of three biomass materials: wheat straw, rape straw and black locust wood was studied at five different torrefaction temperatures: 200, 225, 250, 275 and 300 °C. The evolutions of decomposition products as well as the thermal stability of the untreated and treated

samples were measured by TG/MS method. The cellulose, hemicellulose and Klason-lignin content of raw and torrefied biomass samples were determined by acidic hydrolysis and subsequent HPLC analysis. The inorganic ion contents of the biomass samples were analyzed by ICP-OES system. The degree of hemicellulose and cellulose decomposition at the different torrefaction temperatures were characterized by compositional analysis of the torrefied and untreated samples. The joint evaluation of the results obtained by various analytical methods revealed that at 225°C torrefaction temperature the acidic side groups of hemicellulose are partially split off, while the main mass of the hemicellulose does not degrade. At 250°C torrefaction temperature about 40% of the hemicellulose degrades and the remainder decomposes at higher temperature. No significant difference was observed in the thermal stability of hemicellulose in the three studied samples. Taking into consideration the significantly higher alkali ion content of the straw samples it was concluded that the alkali ion content of the sample does not modify the thermal stability of hemicellulose. Statistical analysis (PCA) have been used to present correlations between the torrefaction temperature, chemical composition and thermal parameters of the samples.

Keywords: Torrefaction, Pyrolysis, Wood, Herbaceous biomass, Cellulose, Hemicellulose, Lignin, Thermogravimetry, Mass spectrometry, Bomb calorimetry, Principal component analysis

ABBREVIATIONS

BL	Black locust
RS	Rape straw
WS	Wheat straw

BLU	Untreated black locust
BL 200	The torrefied black locust obtained from torrefaction at 200 °C
HHV	High heating value
MC	Moisture content
VM	Volatile matter
FC	Fixed carbon
DTG _{max}	Maximum value of the $-dm/dt$ curves
T _{peak}	Temperature belonging to the maximum of the $-dm/dt$ curves
T _{1%}	Temperature belonging to the 1% mass loss of the dried samples
T _{start}	Onset temperature extrapolated from the DTG curves
T _{end}	Extrapolated offset temperature
Char	Char residue at 950 °C temperature
PCA	Principal component analysis

1. INTRODUCTION

Biomass is a primary type of renewable energy source which is one of the most abundant energy sources on the Earth. In energetic applications, the untreated biomass has several disadvantages due to the high oxygen content, low calorific value, low energy density, hydrophilic nature and high moisture content. Furthermore, the agricultural production of biomass involves high logistics and transportation costs due to the low energy density of biomass. These disadvantages can be reduced by torrefaction, which is a mild thermal pretreatment between 200 and 300 °C in an inert atmosphere for the conversion of biomass.¹⁻² The torrefaction process can be classified into light, mild and severe torrefaction, where the temperatures are approximately 200-235 °C,

235-270 °C and 270-300 °C, respectively. The purpose of the pretreatment from a chemical point of view is the removal of water and the acidic groups of hemicelluloses or the whole hemicellulose fraction with minor degradation of cellulose and lignin in the biomass.³⁻⁴ During the process, water and a part of the volatiles are released, causing a decrease in mass, but an increase in the energy density, this way reducing the storing and transportation costs.⁵⁻⁷ In order to maximize the effectiveness of the energy extraction, we need to characterize the biomass materials as much as possible.

Several types of biomass materials have been torrefied ranging agricultural⁸⁻¹⁴ and forestry by-products.¹⁵⁻¹⁹ Torrefied wood and straw in the form of pellets can be directly co-fired with coal or natural gas in a relatively high ratio (about 30 %) hereby utilizing the processing infrastructures at existing coal and gas plants. Several factors may have influence on the thermal behavior of plant materials. As a consequence of the difference in the relative amount of cellulose, hemicellulose, lignin, and extractives, the woody and herbaceous materials behave differently during thermal decomposition.²⁰⁻²¹ The effects of inorganic ions on the thermal decomposition of lignocellulosic materials are well-known, the alkali ions catalyze the decomposition of cellulose²²⁻²⁹ and lignin³⁰⁻³¹ resulting in a lower decomposition temperature and a higher amount of char. Thermoanalytical and pyrolysis methods are useful to determine differences between the structures of biomass samples without separating the main fractions.³²⁻³³ More valuable information can be obtained about the composition of the biomass samples using coupled techniques, where the volatile decomposition products are monitored by a mass spectrometer³⁴⁻³⁶ or an infrared spectrometer.³⁷⁻³⁸

In this work the torrefaction of black locust wood (*Robinia pseudoacacia*), wheat straw (*Triticum aestivum*) and rape straw (*Brassica napus*) was studied, which are typical biomass products or

by-products in Hungary. Black locust wood is native to the southeastern United States, but it has been widely planted and naturalized elsewhere in temperate Europe, Southern Africa and Asia. It can be a promising biomass for future energy production because of its high growth rate and favorable fuel characteristics, such as low ash content and high heating value. Straw is a low value by-product of the agricultural industry and it is available in large quantities.

The purpose of this work is to study the thermal behavior of torrefied woody and herbaceous biomass materials and understand the chemical changes which take place during torrefaction at different temperatures. The evolutions of the decomposition products as well as the thermal stability of the untreated and treated samples were studied by thermogravimetry/mass spectrometry (TG/MS). The chemical composition (cellulose, hemicellulose and lignin content) of the untreated and torrefied samples was determined by a two-step acid hydrolysis. The obtained thermoanalytical and compositional data were evaluated by statistical analysis with the goal to present correlations between the temperature of the torrefaction pretreatment, the thermal behavior of woody and herbaceous samples and the chemical composition of the samples.

2. EXPERIMENTAL SECTION

Materials. A black locust wood and two herbaceous biomass materials (rape straw and wheat straw) were selected for the torrefaction study. The raw samples were dried at 105 °C for 8 hour in an oven to about 6% moisture content prior to the torrefaction experiment. The untreated samples were ground by a cutting mill to <1mm particle size.

Torrefaction. The torrefaction experiments were carried out in a tube furnace in nitrogen atmosphere using flow rates of 20 ml min⁻¹. About 12 g samples were treated in a glass sample

holder at 200 °C, 225 °C, 250 °C, 275 °C and 300 °C temperatures using one hour isothermal period.

Proximate and ultimate analysis. The samples were characterized before and after torrefaction, using proximate analysis and elemental (ultimate) analysis. The moisture and volatile content of the untreated and torrefied biomass samples were determined using thermogravimetry heating the samples up to 950 °C. The ash content was determined by the standard method developed by National Renewable Energy Laboratory (NREL/TP-510-42622). The fixed carbon content was determined by difference. The carbon and hydrogen contents of the untreated and torrefied biomass samples were measured by an elemental analyzer. The oxygen content was determined by difference.

High heating value determination. The high heating value (HHV) was determined using an automatic IKA C 5000 bomb calorimeter. The combustion of about 0.5 g sample in pure oxygen atmosphere was performed under 30 bar pressure. The heat capacity of the calorimeter system was determined by benzoic acid calibration. All heating values were calculated using the average of three replicates.

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) About 2 g biomass samples were ashed at 550 °C in a furnace according to EU standard method CEN/TS 14775:2004. The ashes were fused at 920 °C with a fusion blend ($\text{Li}_2\text{B}_4\text{O}_7$: LiBO_2 , 2:1) and digested by 25 mL 33% nitric acid. The potassium, sodium, calcium and silicon contents of the samples were determined by a Spectro Genesis ICP-OES (Spectro Analytical Instruments) with axial plasma observation. The amounts of the ashes have been determined using a CEN/TS 14775 EU standard method.

Carbohydrate and Klason lignin content determination. The contents of carbohydrates were determined according to the method of Sluiter et al.³⁹ applying slight modifications. The milled samples were dried at 40 °C for 1 day. The untreated and torrefied biomass samples were treated in a two-step acid hydrolysis with 72% H₂SO₄ for 2 hours at room temperature, and then with 4% H₂SO₄ for 1 hour at 121 °C. The obtained suspensions were filtered and washed with distilled water through G4 glass filter crucibles. The sugar concentrations (glucose, xylose and arabinose) of the filtered supernatants were analyzed with high performance liquid chromatography (HPLC) using an Agilent 1260 system with an Hi-Plex H column (Agilent, CA, USA) at 65 °C. An eluent of 5 mM H₂SO₄ was used at a flow rate of 0.5 mL min⁻¹. The solid residues obtained after washing were dried at 105 °C until constant weight. The dried residues consisted of acid-insoluble organics and acid-insoluble ash. The total ash, and acid-insoluble ash contents were measured by ashing the sample at 550 °C for 5 hours until the sample weight was constant.⁴⁰ The Klason lignin content was calculated by subtracting the acid insoluble ash content from the acid insoluble residue content. All experimental data were determined using three replicates.

Thermogravimetry/mass spectrometry (TG/MS). The TG/MS system consists of a modified Perkin-Elmer TGS-2 thermobalance and a Hiden HAL quadrupole mass spectrometer. About 5 mg samples were measured in argon atmosphere at a flow rate of 140 mL min⁻¹. The samples were heated at a rate of 20 °C min⁻¹ from 25 to 950 °C in a platinum sample pan. The evolved products were introduced through a glass lined metal capillary heated at 300 °C into the ion source of the mass spectrometer which was operated at 70eV electron energy. The mass range of 2-150 Da was scanned. The ion intensities were normalized to the sample mass and to the intensity of the ³⁸Ar isotope of the carrier gas.

Principal component analysis (PCA). Since we had a large number of samples and experimental data we employed a chemometric tool, principal component analysis (PCA) using Statistica 12 software (StatSoft, Inc. Tulsa, Oklahoma, USA). PCA has been used to reveal correlations between TG data, energy content and the chemical composition of the samples as well as to find further correlations between the thermogravimetry/mass spectrometry data of the untreated and torrefied samples.

3. RESULTS AND DISCUSSION

Characterization of untreated and torrefied biomass samples. The solid yield, the proximate and ultimate analysis data and the energy content of the untreated and torrefied samples are shown in Table 1. During torrefaction the moisture content and volatiles release from the sample resulting in a decrease of the sample mass. Up to the temperature of 250 °C, the yield of the solid residue was quite similar for the three investigated samples. Comparing the results obtained at 250 °C and 275 °C we can establish that a significant decrease of the solid yield occurred in rape and wheat straw samples (15 and 20%, respectively), while the solid yield reduced to a lesser extent in black locust wood (11%). This observation indicates the higher degree of decomposition of the herbaceous samples at about 275 °C.

The proximate analysis data of the torrefied samples present that the moisture content and volatile matter decreased, while the ash and fixed carbon content increased in the samples prepared at higher torrefaction temperature due to the progress of the thermal decomposition. Black locust wood had higher volatile matter content and lower fixed carbon yield than wheat and rape straw samples, prepared under the same torrefaction conditions.

The ultimate analysis shows that the increasing torrefaction temperature increased the carbon content and reduced the oxygen and hydrogen content of the torrefied materials. The calorific

value of the heat-treated samples increased with the increasing temperature. Torrefaction at 225 °C increased the HHV of the samples by at least 3.5% in comparison with the value of the untreated samples (17.6-18.2 MJ kg⁻¹). Torrefaction at 275 °C resulted in an increase of 19-27% in the HHV content. All of the proximate and ultimate analysis data as well as the calorific values verify the gradual thermal decomposition of the biomass samples by increasing temperature.

The alkali ion contents of the untreated samples have been determined using ICP-OES technique. Table 2 summarizes selected data of the ICP-OES characterization of the black locust, rape straw and wheat straw samples. As the results illustrate, wheat straw and rape straw samples have by an order of magnitude higher K⁺ content than the black locust sample. Furthermore, Na⁺, Ca²⁺ and Si contents of the two straw samples are also significantly higher comparing to the black locust sample.

Table 1. Characterization of the Studied Samples

Sample	Solid yield (%)	Proximate analysis (% m/m, as received)				Ultimate analysis (% m/m, dry basis)			HHV (MJ kg ⁻¹)
		MC	VM	Ash	FC	C	H	O	
Black locust									
BL U	100	6.08	77.85	1.75	14.32	48.10	4.74	45.41	18.17
BL 225	87	3.25	76.87	1.91	17.97	50.59	3.45	44.05	19.35
BL 250	79	3.23	69.79	2.16	24.82	52.77	4.39	40.68	20.38
BL 275	68	3.42	65.83	2.92	27.83	53.05	8.59	35.44	21.61
BL 300	49	3.78	56.34	4.2	35.68	60.65	8.30	26.85	
Rape straw									
RS U	100	7.16	71.16	6.04	15.64	46.3	5.46	42.2	17.68
RS 225	85	4.62	68.99	6.36	20.02	47.23	5.22	41.19	18.84
RS 250	76	4.11	66.01	7.26	22.62	48.86	5.79	38.09	20.21
RS 275	61	4.57	53.61	9.36	32.46	52.38	5.14	33.12	22.46
RS 300	47	3.76	40.73	11.84	43.67	60.84	4.81	22.51	
Wheat straw									
WS U	100	5.58	70.55	5.68	18.52	49.38	4.23	41.04	17.87
WS 225	89	3.68	69.69	5.80	20.83	47.68	4.10	42.42	18.48
WS 250	80	3.62	66.20	6.92	23.40	48.49	6.62	38.11	19.15
WS 275	60	3.53	54.84	9.28	32.34	56.12	4.63	29.97	21.73
WS 300	44	2.37	38.12	12.52	46.98	62.28	4.83	20.37	

Table 2. The Most Important Inorganic Components of the Studied Samples

Sample	Inorganic content (% m/m dry basis)				
	Si	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺
Black locust	* N. D.	0.12	* N. D.	0.085	0.017
Rape straw	0.03	1.86	0.072	0.503	0.158
Wheat straw	1.07	1.69	0.008	0.137	0.077

* N. D.: Not determined, below the detection limit

Carbohydrate and lignin content. The compositional analysis of each studied biomass was performed in order to understand better the thermal conversion process under torrefaction. The results are presented in Figure 1. The glucan content of the samples mainly characterizes the cellulose fraction of the biomass, whereas the sum of the xylan and arabinan content represents the hemicellulose fraction. The Klason lignin is defined as the acid insoluble residue content of the samples without the acid insoluble ash content. The fraction denoted “other” in Figure 1 represents the sum of the unquantified components and includes extractives, acid soluble lignin and acid soluble minerals. To compare the degradation degree of cellulose, hemicellulose and lignin in the torrefied samples, we have to take into consideration the mass loss during the torrefaction experiment as well. Therefore, Figure 1 also shows the amount of the mass loss during the torrefaction at the different temperatures.

The comparison of the chemical composition of the three untreated samples shows that black locust has the highest Klason-lignin content (25.7%), while wheat straw has the highest hemicellulose (23%) content. The lignocellulose content (sum of cellulose, hemicellulose and lignin) of black locust and wheat straw samples is around 76%, while that of the untreated rape straw is only 66%. The reason could be the higher amount of extractive compounds and the higher acid soluble mineral content of the rape straw sample. The later assumption is supported by the highest alkali and alkali earth ion content shown in Table 2.

Under torrefaction the lignocellulose materials decompose to different degrees depending on the applied temperature. The variation of the amount of glucan, xylan and arabinan in the torrefied samples (see Figure 1) reflects the changes in the proportion of cellulose and hemicellulose in the samples. The decreasing carbohydrate yields indicate the progress of the thermal decomposition of hemicellulose and cellulose under torrefaction at various temperatures.

As the results present, hemicellulose (measured as the sum of arabinan and xylan) is the thermally least stable component of the lignocellulose fraction during torrefaction. The hemicellulose content of the torrefied samples is slightly decreased up to 225 °C for each studied samples. The samples torrefied at 250 °C have about half of the hemicellulose content of the untreated sample for each biomass. At higher torrefaction temperatures the relative amount of the hemicellulose drastically decreases, and only traces of hemicellulose were measured in the samples torrefied at 300 °C. The changes in the relative amount of hemicellulose show similar tendency as a function of torrefaction temperature for each sample indicating that the thermal stability of hemicellulose is similar in the studied wood and herbaceous samples. This observation can be explained by the conclusion that the alkali ion content of the samples does not modify significantly the thermal stability of hemicellulose.

The variation of the cellulose content in the untreated and torrefied samples is demonstrated by the amounts of glucan (Figure 1). As the bar diagram shows, the cellulose content of black locust wood does not decrease considerably up to 275 °C torrefaction temperature. In case of the two herbaceous samples, the degradation of cellulose is significant at this temperature; the relative decrease is almost 50% in both cases. At 300 °C torrefaction temperature, about 60% of the cellulose content of black locust decomposes, while cellulose almost disappears from rape and wheat straw samples. On the basis of this observation we can conclude that the thermal stability of cellulose in the herbaceous samples is lower by about 25 °C than in wood. The herbaceous samples have more than an order of magnitude higher alkali ion contents than wood. The catalytic effect of alkali ions on the thermal decomposition of cellulose is well-known²²⁻²⁹. The results obtained for the cellulose content of the torrefied samples confirm that the alkali ions have catalytic effect on cellulose decomposition even at low temperatures used in torrefaction.

As Figure 1 presents increasing the torrefaction temperatures resulted in a significant increase in the measured Klason-lignin content of the samples. Besides the acid-insoluble lignin, the Klason-lignin contains all acid insoluble components of the sample excluding ash. During the thermal treatment some parts of the extractables, cellulose, hemicellulose and acid soluble lignin were probably transformed into acid insoluble carbonaceous products by cross-linking and charring reactions. The increasing torrefaction temperature favors these reactions, resulting in the increased Klason-lignin value at higher temperatures.

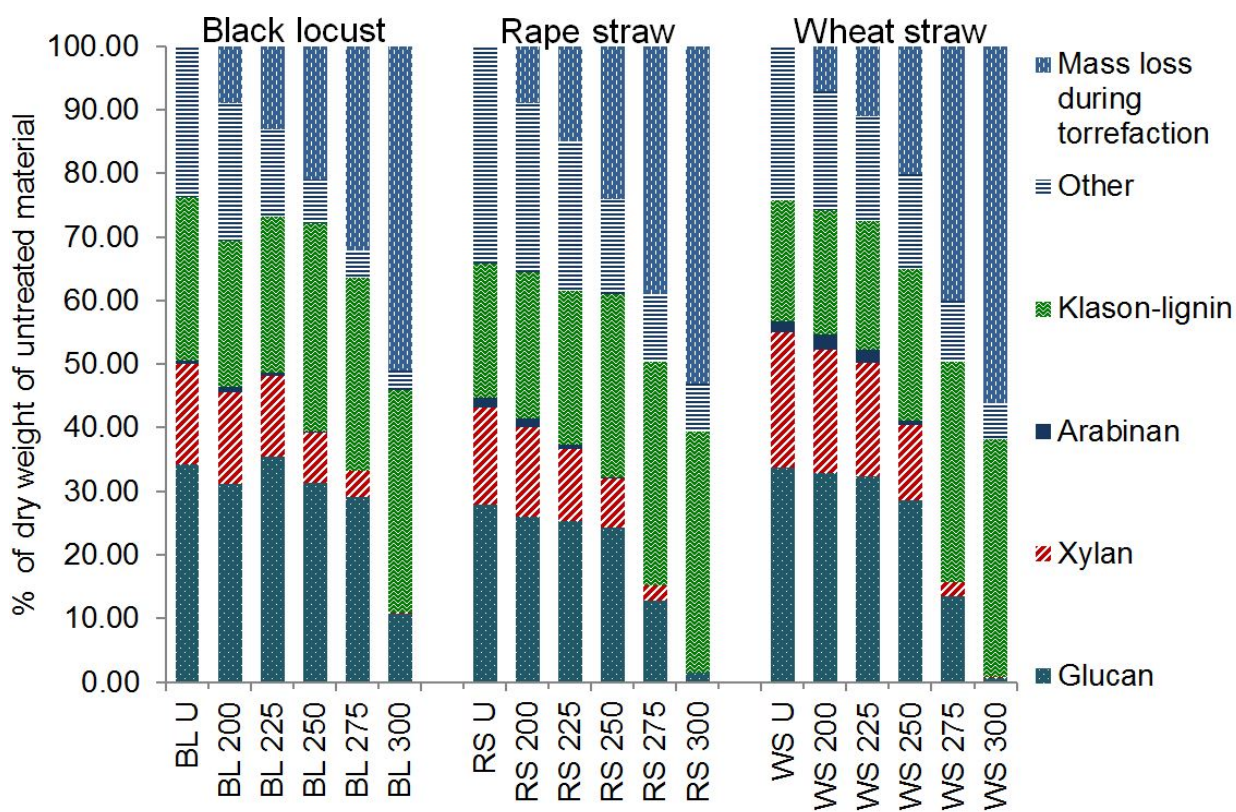


Figure 1. Composition of the untreated and torrefied black locust wood, rape straw and wheat straw (calculated on dry basis).

Thermogravimetric results. The thermogravimetry (TG) and derivative thermogravimetric (DTG) curves of the samples are shown in Figure 2. Comparison of the curves shows that the shape of the TG and DTG curves of rape straw and wheat straw samples are rather similar, while black locust wood behaves differently during thermal decomposition. It is well-known²²⁻²⁹ that the difference between the behavior of wood and herbaceous samples is due to the different alkali ion contents, which have significant effect on the thermal behavior of cellulose. The reason of the different thermal behavior of the torrefied woody and herbaceous biomass materials can also be interpreted by their different inorganic ion contents. In addition, the relative amounts of alkali ions further increased in the samples during the torrefaction.

The evaporation and decomposition of extractives in the untreated samples are visible on the DTG curve as a broad shoulder starting approximately at 180 °C. The higher weight loss of untreated rape straw comparing to wheat straw and black locust (Figure 2 a and b) between 200 and 300 °C indicates the highest extractive content of this sample. During torrefaction at 225 °C the extractive content of the samples mostly evaporated, therefore the above mentioned difference disappeared from the TG and DTG curves of rape straw (Figure 2 c and d) and the weight loss curves of the three torrefied biomass overlap up to 300 °C. This observation is in accordance with the results of compositional analysis, where higher amount of extractive and/or acid soluble inorganics was determined in the untreated rape straw sample (see “other” component in Figure 1) than in the other biomass samples studied.

The main DTG peak of the untreated samples (Figure 2 b) can be attributed to the decomposition of cellulose. The characteristic shoulder on the DTG curve of the untreated black locust sample (Figure 2 b) up to 350 °C presents the decomposition of hemicellulose. In case of herbaceous samples the hemicellulose shoulder is not pronounced because the cellulose decomposition shifted to lower

temperature due to the catalytic effect of the high amounts of alkali ions. O-Acetyl-4-O-methylglucuronoxylan is the main building block of hemicellulose in the hardwoods. In herbaceous biomass, arabinoxylans are the dominant hemicellulose polysaccharides. As the compositional analysis data demonstrates (Figure 1), the hemicellulose content of the samples did not degrade during torrefaction at 225 °C. Accordingly, the obtained DTG curve of black locust torrefied at 225 °C (Figure 2 d) has a significant shoulder presenting the decomposition of hemicellulose. After torrefaction at 250 °C (Figure 2e and f), the characteristic shoulder on the DTG curve of wood sample disappeared indicating that the hemicellulose decomposed or its structure changed as a result of the torrefaction. The results of the acidic hydrolysis revealed, that about 40% of the hemicellulose content decomposed during the torrefaction at 250 °C temperature. The significant hemicellulose content of the samples torrefied at 250 °C contradicts to the disappearance of the hemicellulose shoulder from the DTG curve. These results can be explained by the assumption that the thermally most labile side groups (e.g., acetyl groups) of hemicelluloses were split off under torrefaction; therefore the remaining hemicellulose chains became more stable and decomposed in a similar temperature range as cellulose.

Regarding the cellulose component of the heat-treated biomass samples, the thermogravimetric curves confirm the results of compositional analysis. Low-temperature torrefaction has small effect on the amount of cellulose. After torrefaction at 275 °C (Figure 2 g and h), the maximal rate of thermal decomposition of both straw samples decreased by about 50% indicating the high degree of cellulose decomposition during the torrefaction. In case of black locust sample, torrefaction at 275 °C still did not affect significantly the cellulose content. These observations also indicate the catalytic effect of alkali ions on the decomposition of cellulose, and are in agreement with the results of compositional analysis. After torrefaction at 300 °C, the DTG curve of black locust shows

significantly reduced, but still extant cellulose content; while the DTG curves of wheat straw and rape straw have (Figure 2 j) wide and flat shape, indicating the almost complete decomposition of cellulose. The lignin decomposition is not separated on the DTG curve due to its low decomposition rate and a broad temperature range of decomposition (from 250 to 600 °C). Lignin is a complex cross-linked methoxyphenol-based polymer built of so called monolignol subunits: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. The lignin of the herbaceous plants is composed of all three types of monolignols, while the hardwood lignin is built of only coniferyl alcohol and sinapyl alcohol. The char yield of the biomass samples is mainly influenced by the lignin content and the alkali ion content of the sample. The lignin produces about 30% char^{31,41}, while cellulose and hemicellulose yield only about 5% and 5-10% solid residue, respectively. It is well known that the alkali ion content has a catalytic effect on the charring reactions: the higher the alkali ion content of the biomass the higher the char yield and the evolution of gaseous products during thermal decomposition.⁴²

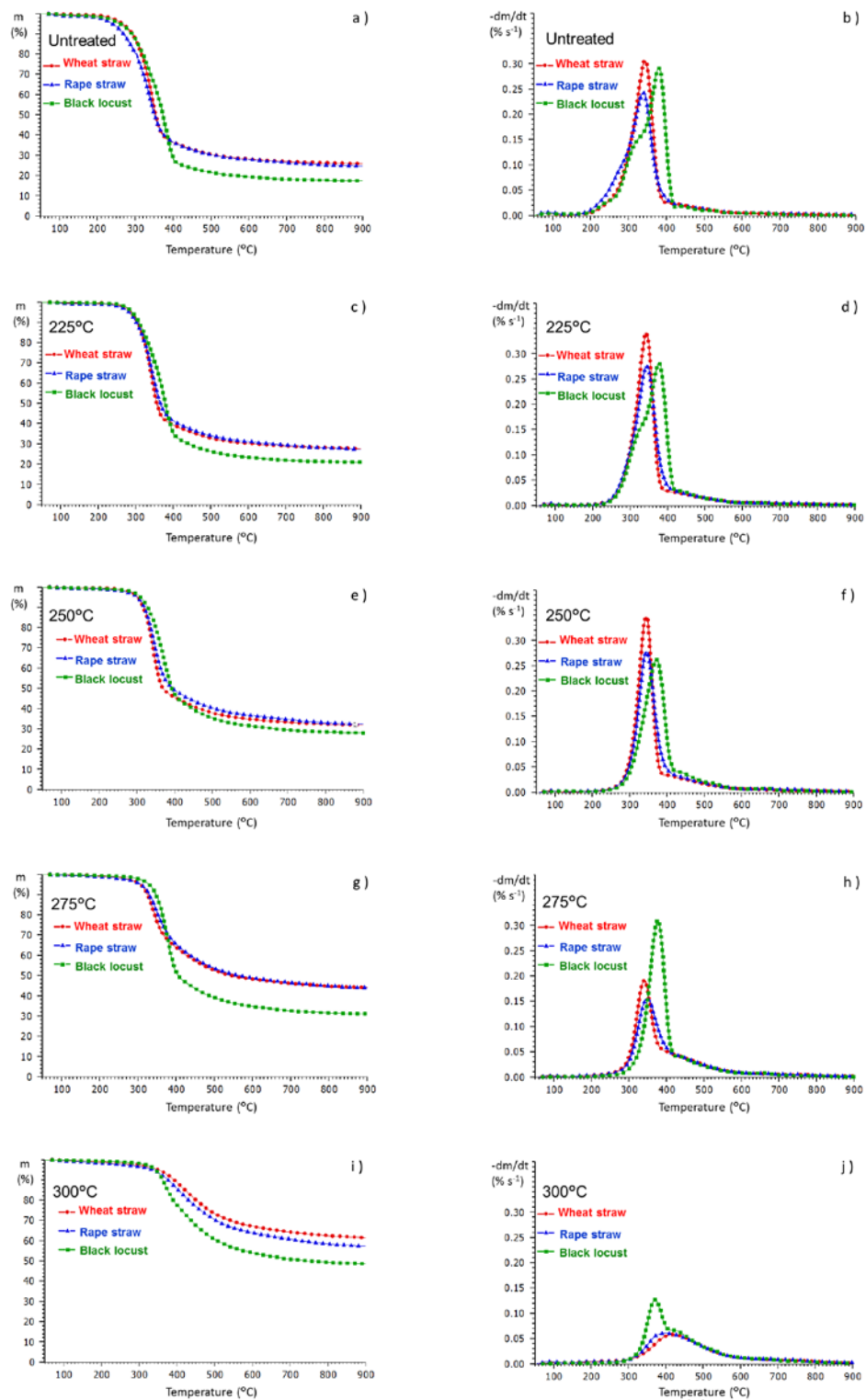


Figure 2. TG and DTG curves of black locust wood, rape straw and wheat straw before and after various torrefaction temperatures.

Principal component analysis based on the calorific values, TG and chemical composition data.

The TG parameters (T_{peak} , DTG_{max} , $T_{1\%}$, T_{start} , T_{end} , char yield), glucan, xylan and lignin contents, and high heating values have been used in the calculation as input data to illustrate the similarities and differences between the untreated and the torrefied biomass samples (Table 1, Figure 1 and 2). Beside the extrapolated T_{start} value, the beginning of the decomposition was also characterized by $T_{1\%}$ data, which belongs to the temperature of 1% mass loss after the release of the adsorbed water. T_{start} is characteristic of the start of hemicellulose decomposition, while T_{end} reflects the end of cellulose decomposition. In the PCA calculation the first principal component (Factor 1) describes 67.26%, while the second and third principal components (Factor 2 and Factor 3) describe 14.67% and 9.86% of the total variance, respectively. These three factors are sufficient to characterize the major differences between the samples. The score plot for Factor 1 and Factor 2 (Figure 3 a) shows that the black locust (BL), rape straw (RS) and wheat straw (WS) samples can be found in different parts of the plot. The first principal component separates the untreated, the mildly and severely torrefied samples. As a function of the second principal component, the herbaceous samples are found in the upper, and the woody samples in the lower part of the score plot. This difference is apparently due to the different cellulose, hemicellulose, lignin, and extractive content of the samples; which is reflected in the different thermal behavior of woody and herbaceous materials.

The loading plot for Factor 1 and Factor 2 (Figure 3 b) shows that the values of glucan and xylan content and DTG_{max} data correlate negatively with the high heating value (HHV), lignin content, char yield and T_{start} and $T_{1\%}$ data. Factor 1 is composed of mostly these parameters and mainly differentiates the samples as a function of the torrefaction temperature. Figure 3 a shows that the herbaceous samples torrefied at 275 and 300 °C are separated essentially indicating the severe decomposition. T_{peak} and T_{end} data contribute mainly to Factor 2, these parameters are characteristic

of the cellulose decomposition. Untreated black locust and wheat straw have similar cellulose content (approximately 34%); however, straw samples have more than an order of magnitude higher K^+ and Na^+ content than black locust (Table 2). Due to the alkali catalysis, the characteristic temperatures of cellulose decomposition of the herbaceous samples shifted to lower temperatures. Mainly this effect is reflected in Factor 2.

Factor 3 describes almost 10% of the total variance. The loading plot (Figure 3 d) shows that the values of $T_{1\%}$, T_{start} , cellulose content and DTG_{max} contribute to Factor 3 and 1, as well. $T_{1\%}$ and T_{start} can be attributed to the hemicellulose decomposition in untreated and mildly-treated samples, while after severe torrefaction, i.e., after the decomposition of hemicellulose, these parameters belong to the cellulose decomposition. The samples formed two groups as a function of Factor 1 and 3 as shown in Figure 3 c. The severely torrefied samples are separated from the untreated and mildly torrefied biomass samples. As mentioned above, the maximum rate of thermal decomposition (DTG_{max}) of straw samples decreased by half between the torrefied samples at 250 °C and 275 °C, while the DTG_{max} data of black locust wood only differ significantly between the samples treated at 275 °C and 300 °C. It was found that the hemicellulose and cellulose content of the studied samples strongly decreased from 250 °C to 300 °C (see Figure 1). At the severe torrefaction temperatures (275-300 °C), the chemical composition of the samples significantly changed during torrefaction, therefore the thermal properties of the samples altered to a greater extent in this temperature range.

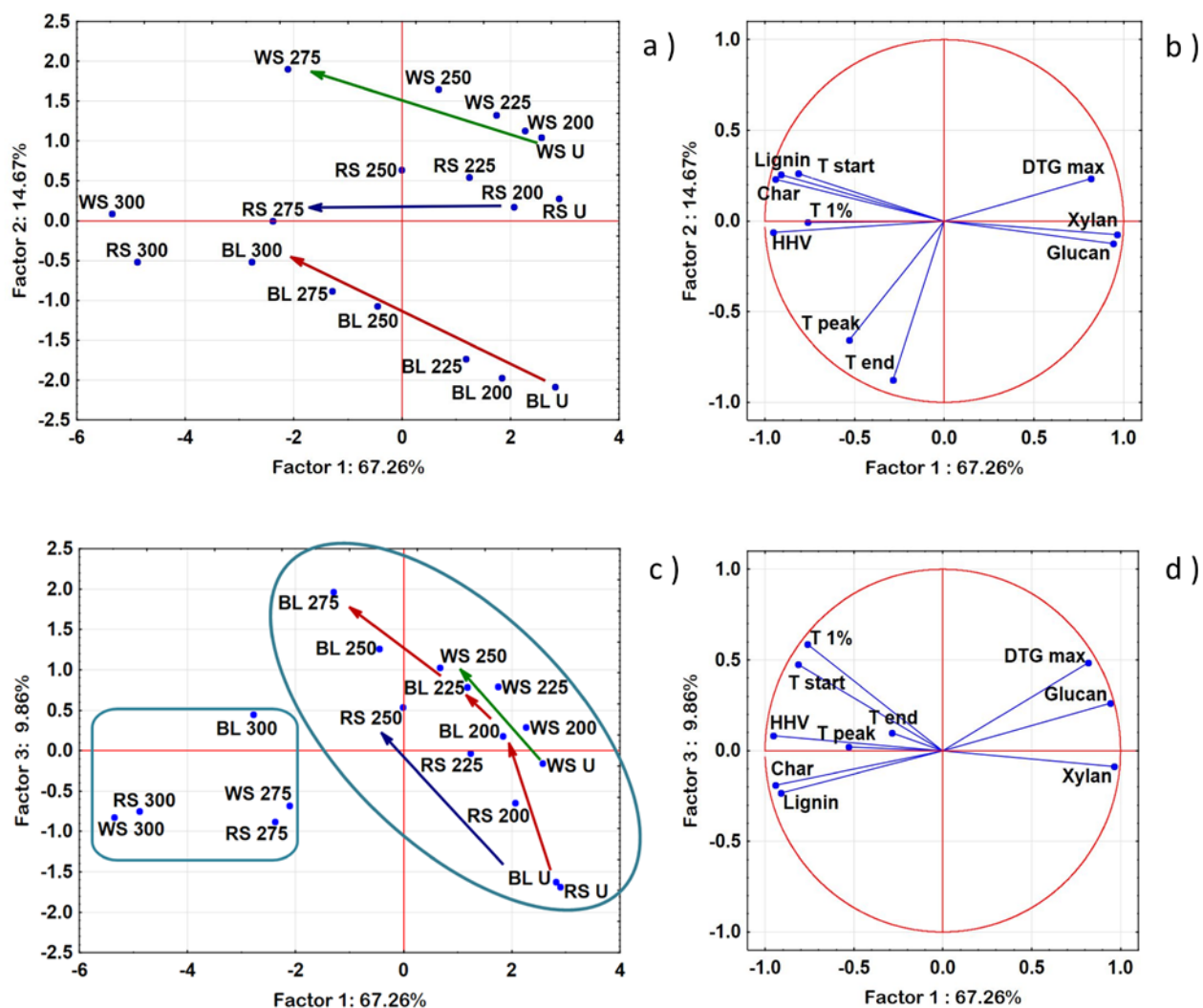


Figure 3. PCA score (a, c) and loading (b, d) plots based on the calorific values, thermogravimetric and chemical composition data. The arrows show the direction of the variation of the samples with increasing torrefaction temperatures. WS: wheat straw, RS: rape straw, BL: Black locust wood

TG/MS results. The evolution profile of the most characteristic decomposition products of the untreated and torrefied black locust and wheat straw samples are presented on Figure 4 and Figure 5. The scale for the individual species evolved from black locust wood and wheat straw are plotted on the same scale on each figures. The pattern of the ion intensity curves of rape straw are very similar to that of wheat straw, therefore it is not presented here.

Figure 4 shows the evolution of the main permanent gases and water from black locust wood and wheat straw. Relatively large amounts of water and carbon dioxide are produced during the thermal decomposition of the samples due to a various types of hydroxyl groups and oxygen containing functional groups in the natural polymers that make up the cell walls (cellulose, hemicellulose, and lignin). Figure 5 shows the evolution of some characteristic organic volatile products and fragment ions from black locust wood and wheat straw samples. Formaldehyde (m/z 30) forms during thermal decomposition of cellulose, hemicellulose and lignin as well. The release of methanol can be monitored by the m/z 31 ion furthermore, it is the main fragment ion of hydroxyacetaldehyde, which is a significant product of cellulose decomposition. The evolution curve of m/z 60 ion can represent either acetic acid formed mostly by hemicellulose decomposition or hydroxyacetaldehyde released mainly during cellulose decomposition. The m/z 27 ion is a typical fragment ion of hydrocarbons.

The moisture content (m/z 18 on Figure 4) releases from the samples up to 120 °C. During torrefaction the moisture content of the sample releases, however after the pretreatment during sample handling the torrefied sample can take up some water from the humidity of the air depending on the degree of hydrophilicity of the torrefied sample. The moisture content of the torrefied straw samples is higher than that of the torrefied wood samples, which may be explained by the higher inorganic ion, therefore more hydrophil nature of the torrefied straw samples.

The evolution of water, formaldehyde and methanol (Figure 4 a and b, Figure 5 a and b) in a temperature range of 200-250 °C reveal the thermolysis of extractives and scission of lignin side groups from the untreated samples. These processes start at around 200 °C and the significant shoulder at 230 °C on the DTG and ion curves of untreated black locust can be attributed to the decomposition of extractives.⁴³ During 1 hour thermal pretreatment at 225 °C the extractive content of the sample decompose, therefore the shoulder at 230 °C disappear from the torrefied samples (Figure 4 c and Figure 5 c).

The characteristic peak or shoulder of formaldehyde, acetic acid, methanol, carbon dioxide and water in a temperature range of 280-350 °C of untreated wood sample (Figure 4 a and Figure 5 a) presents the decomposition of hemicellulose. In case of the herbaceous samples the shoulder is not pronounced due to the higher alkali ion content, therefore lower thermal stability of its cellulose content. Acetic acid and carbon dioxide indicates the scission of the acidic groups from the hemicellulose. The composition analysis revealed that the hemicellulose content of the samples does not decrease during thermal treatment at 225 °C. However, the ion intensities of significant decomposition products of hemicellulose slightly decreased in case of wood sample (Figure 4 c and Figure 5 c), while this effect is less conspicuous in case of the straw sample torrefied at 225 °C (Figure 4 d and Figure 5 d). This observation may indicate somewhat modified structure (e.g. scission of the most labile acidic groups) as a result of torrefaction at 225 °C. The TG/MS curves of the samples torrefied at 250 °C (Figure 4 e and Figure 5 e) verify our assumption on the basis of the DTG curve; the decomposition of remaining part of the hemicellulose takes place in a temperature range of cellulose decomposition.

The main thermal decomposition product of cellulose is levoglucosan, which cannot be detected by TG/MS, but smaller decomposition products like hydroxyacetaldehyde (m/z 60), formaldehyde (m/z

30) and methanol (m/z 31, which is also a fragment ion of hydroxyacetaldehyde) can be monitored (Figure 5). Significant amount of water and carbon dioxide released during cellulose decomposition as well (Figure 4). The ion intensities describing decomposition of cellulose (in a temperature range of the main DTG peak) does not decrease due to the thermal treatment up to 250 °C torrefaction temperature. Increasing the temperature of the torrefaction to 275 °C resulting in decreased evolution of all cellulose decomposition product by about 40% in wheat straw sample, while it does not decreased significantly in case of black locust sample. This observation shows the more developed degradation of the cellulose at 275 °C in case of the herbaceous wheat straw. After torrefaction at 300°C the ion intensity curves of black locust sample (Figure 4 i and 5 i) shows the significant, but not complete degradation of cellulose, while in case of the wheat straw sample (Figure 4 j and 5 j) the ion curves proves the almost complete degradation of cellulose and hemicellulose, in accordance the results of compositional analysis (Figure 1).

The evolution profile of methane (m/z 16 on Figure 4) shows a wide double humped shape. In a temperature range of 370-500 °C methane forms during the thermal decomposition of lignin by the scission of the methoxy groups. The slightly higher methane evolution from black locust in this temperature range is in accordance with the higher methoxy group content of the hardwood lignin comparing to the herbaceous lignin. After torrefaction, the relative amount of lignin was increased in the samples due to the release of extractives, degradation of hemicellulose and cellulose at higher torrefaction temperatures. The increased evolution of methane originating from the decomposition of lignin presents this process. This effect is more pronounced in case of the wood sample. In a temperature range of 400-600°C evolution of small hydrocarbon molecules were observed, presented by the m/z 27 ion curve on Figure 5. The relative intensity of the hydrocarbon evolution is increasing by the torrefaction temperature in case of both wood and straw sample. These hydrocarbon molecules

may produce by secondary reactions from decomposition products of cellulose, hemicellulose and lignin.

Methane over 500°C and hydrogen (m/z 2 on Figure 4) over 600°C eliminates during the charring reactions. Comparing the of intensities of the selected ions in a function of torrefaction temperature, it can be note that the evolution of hydrogen and methane increasing, while the intensity of the other presented lignocellulose decomposition products decreasing by raising the torrefaction temperature. These changes indicate the progress of the thermal decomposition during the torrefaction. In case of the black locust sample the ion intensity curve of carbon dioxide has two small sharp peak at 530 °C and at 670 °C, indicating the presence of calcium oxalate originating from the bark of the black locust wood.

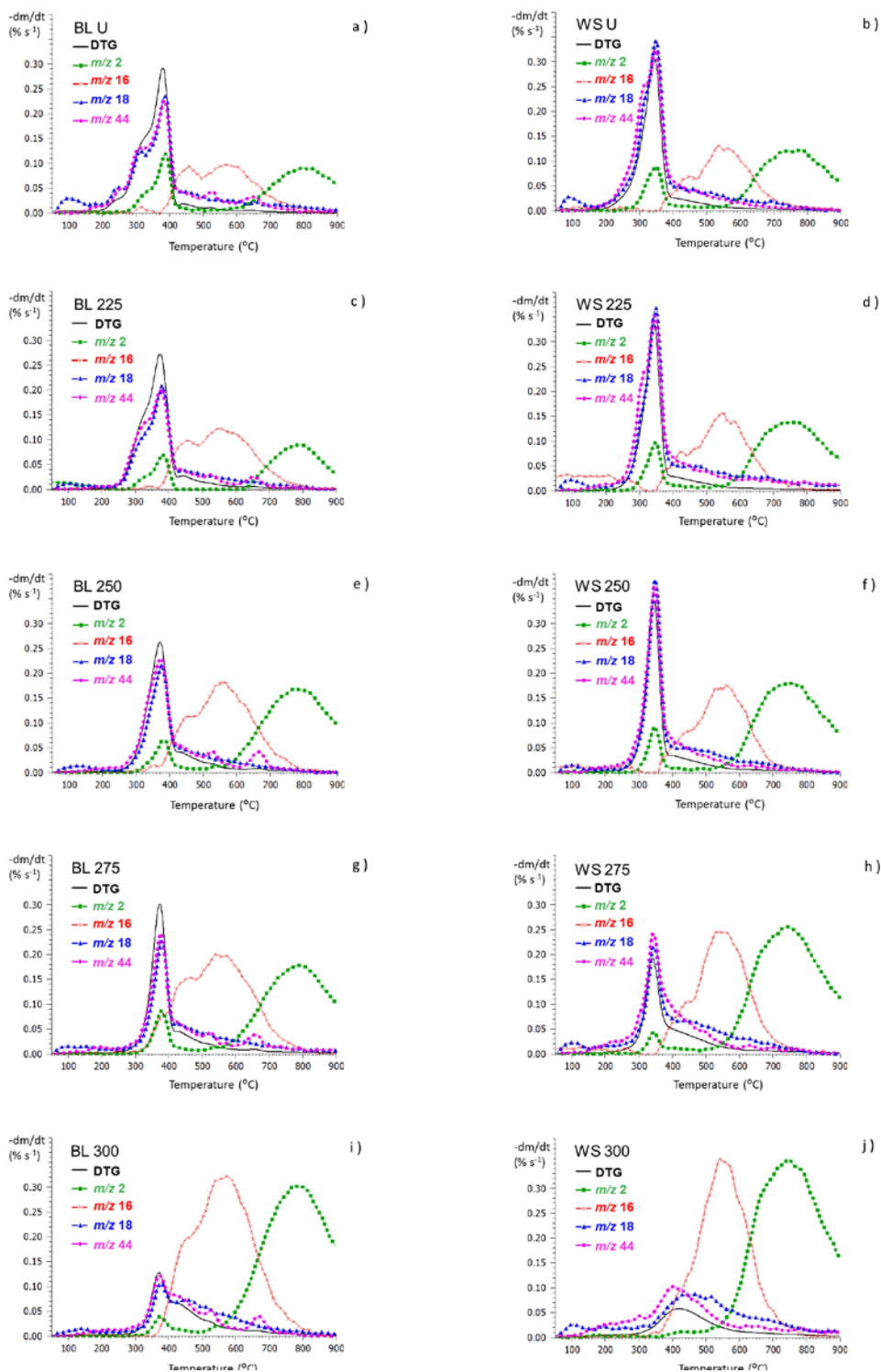


Figure 4. The DTG curves and the evolution profiles of the main permanent gases and water from black locust wood and wheat straw

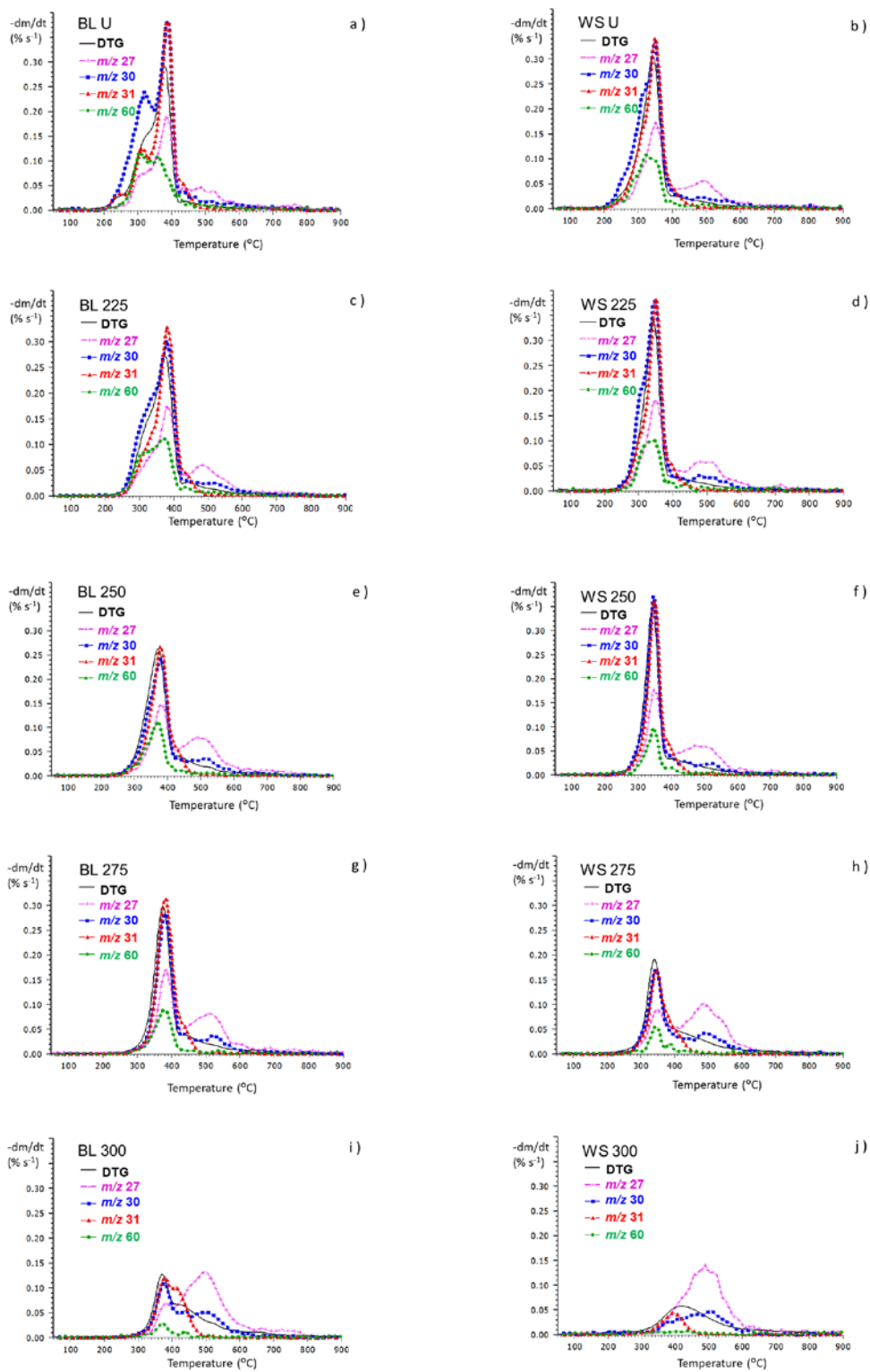


Figure 5. The DTG curves and the evolution of some characteristic organic volatile products and fragments from black locust wood and wheat straw.

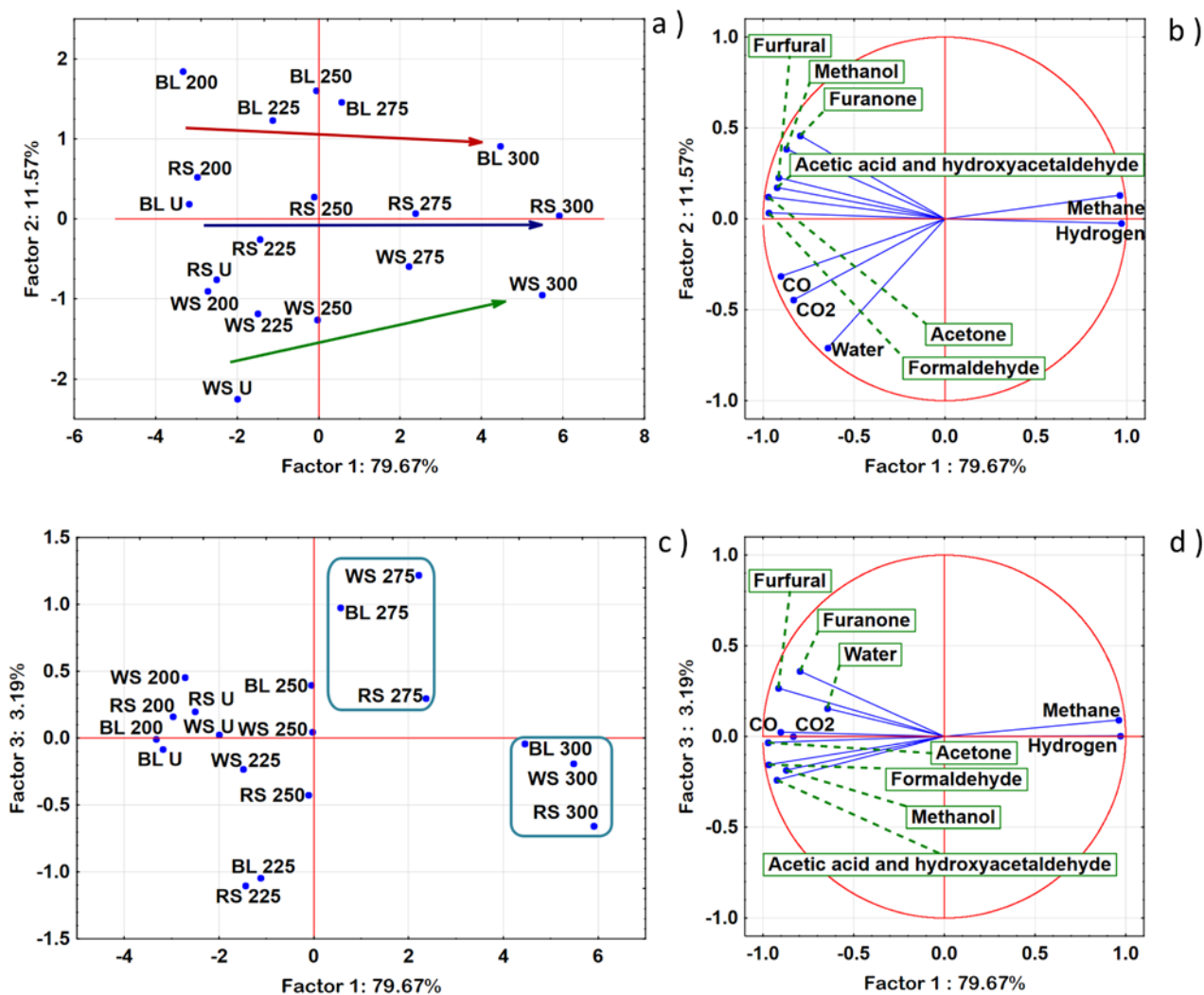


Figure 6. PCA score (a, c) and loading (b, d) plots based on TG/MS data. The arrows show the direction of the variation of the samples with increasing torrefaction temperature. WS: wheat straw, RS: rape straw, BL: Black locust wood

Principal component analysis based on the TG/MS data. Principal component analysis has been applied to reveal further correlations between the ion intensity data of the main decomposition products obtained by TG/MS technique. The integrated intensities of the characteristic mass spectrometric ion curves have been used in the PCA calculation (Figure 6). The first principal component (Factor 1) describes 79.67% of the total variance of the TG/MS data, and the second and

third principal components (Factor 2 and Factor 3) described 11.56% and 3.19% of the total variance, respectively. The first principal component separates the untreated and light torrefied samples from the mild and severe torrefied samples. The higher potassium and sodium ion content in the herbaceous samples promote the char formation during torrefaction at 275 and 300 °C (Figure 6 a and c). The loading plot for Factor 1 and Factor 2 (Figure 6 b) reveals that the yields of CO (m/z 28), CO₂ (m/z 44) and water (m/z 18) play the most significant role in determining the second principal component. As we seen earlier, more gaseous product and water are released from the herbaceous plants than from the hardwood. These differences can be explained by the different alkali ion contents of the studied samples. The higher alkali ion content promotes gas formation during torrefaction of wheat straw and rape straw via fragmentation, while the depolymerization reactions are dominant during the torrefaction of black locust wood. On the other hand, the loading plots suggest that the yield of furanone (m/z 84), furfural (sum of m/z 95 and 96), methanol (m/z 31) as well as acetic acid and hydroxyacetaldehyde (m/z 60) also play role in determining the second and third principal component. At the given torrefaction temperatures, the yields of these molecular mass products are higher during the decomposition of black locust wood than of wheat straw and rape straw. The second and third principal components may be attributed to the effect of both different chemical composition and inorganic contents of the studied samples.

4. CONCLUSIONS

Comprehensive compositional analysis of untreated and torrefied wood and herbaceous samples have been performed with the goal of understanding deeper the thermal degradation processes takes place during torrefaction. The hemicellulose, cellulose and Klason-lignin content of native and torrefied samples were determined after acidic hydrolysis. The changes in the thermal stability and in the evolution profile of volatile products were followed by TG/MS measurements. The joint

interpretation of the changes in the chemical composition, thermal stability and evolution profile of typical lignocellulose decomposition products as a result of thermal treatment revealed new information about the thermal degradation of the lignocellulose materials.

The main mass of the hemicellulose content of both wood and herbaceous samples was found thermally stable at 225°C during 1 hour torrefaction, however changes in the evolution pattern of acetic acid indicates the partial degradation, the scission of the most labile groups at this temperature. About 40% of the hemicellulose content decomposes at 250°C in case of black locust wood, rape and wheat straw samples as well. The thermal decomposition of the hemicellulose after mild thermal treatment shifted to higher temperature, indicating the modified structure of the torrefied hemicellulose. No significant difference was found in the thermal stability of the high inorganic-containing straw samples and the low inorganic-containing wood samples. Therefore, it can be concluded that the thermal stability of hemicellulose does not influenced by the inorganic content of the sample contrary to cellulose, where the significant catalytic effect of the alkali ion content on the thermal decomposition is a well known phenomena. The hemicellulose content of samples torrefied at 275°C is strongly reduced. The degree of cellulose decomposition at 275°C torrefaction temperature is significant for herbaceous samples, while it is not degraded in the studied wood sample at this temperature.

The results of the proximate and ultimate analysis, HHV values, compositional analysis data and TG/MS experiments all in correspondence demonstrate the progress of the thermal decomposition during torrefaction in a temperature range of 200-300°C.

Statistical correlations have been found between the torrefaction temperature, chemical composition and TG/MS data of the untreated and torrefied samples using Principal Component Analysis.

5. ACKNOWLEDGEMENT

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