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Comparative study on the thermal behavior of untreated and various torrefied bark, stem wood, and stump of Norway spruce

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Abstract

In this work, the torrefaction of different parts of Norway spruce (stem wood, bark, and stump) was studied. Three different torrefaction temperatures were applied: 225, 275, and 300 °C with 30 and 60 minutes isothermal periods. The thermal stability as well as the evolutions of the decomposition products of the untreated and torrefied samples were measured by thermogravimetry/mass spectrometry (TG/MS). The TG/MS results are interpreted in terms of the chemical composition, namely the cellulose, hemicellulose and Klason lignin content. The inorganic components of the samples were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) technique. It was found that the effect of torrefaction temperature was greater than the effect of residence time up to 275 °C, while at 300 °C the residence time had a significant influence on the

composition of the torrefied samples due to the intensive decomposition of cellulose. Principal component analysis has been applied to find statistical correlations between the torrefaction temperature, the residence time, the chemical composition and the thermal parameters of the samples. The results of the principal component analysis confirmed that the chemical composition and hence the thermal properties of the studied samples changed to a greater extent at higher torrefaction temperature than at lower torrefaction temperature.

Keywords: torrefaction, thermogravimetry/mass spectrometry, spruce, bark, stump, stem wood

Highlights:

- Comparative study on the thermal behavior of torrefied bark, stem wood and stump
- Thermal stability of the samples is interpreted in terms of the chemical composition changes
- The residence time has larger effect at higher torrefaction temperature
- Hemicellulose side groups are split at milder torrefaction conditions compared to the galactomannan chain
- Principal component analysis has been used to identify statistical correlations

1. Introduction

The Paris Agreement aims to involve all nations to combat climate change and to keep the global temperature rise this century well below 2 °C above the pre-industrial levels [1]. The Norwegian national energy strategy has a goal of reducing the domestic greenhouse gas emissions by 30% by 2020, and the long-term goal was to become climate neutral by 2050 [2], which was changed to 2030 later. This strategy indicates that the utilization of lignocellulosic biomass and biofuels (bioethanol, biodiesel, and biogas), as sources of energy, will have to increase substantially in the next few years. Biomass is a carbonaceous renewable energy source, and therefore, it has attracted considerable attention as a replacement for fossil fuels.

Various thermal conversion technologies exist to produce bioenergy from lignocellulosic biomass, such as combustion [3], gasification [4], pyrolysis [5], as well as co-firing of biomass and coal [6]. However, in energetic applications the properties of raw lignocellulosic materials create challenges for their efficient utilization. One of the main difficulties is the high moisture content of the untreated biomass, which reduces the efficiency of the conversion process and increases the fuel transportation costs. Some of the

other problems with raw biomass materials are the following: low calorific value, low energy density, hydrophilic nature, and high oxygen content. Furthermore, the transportation, storage, and grinding are costly due to the low density and the fibrous nature of lignocellulose. Torrefaction is a mild thermal treatment method performed between 200 and 300 °C in an inert atmosphere for reducing the mentioned disadvantages [7]. A major goal of torrefaction is to upgrade the quality of the solid product by decreasing the moisture content and increasing the hydrophobicity, grindability, and energy density of biomass. The volumetric energy density of torrefied biomass can be increased by a combined grinding and pelletizing step after torrefaction [8-9]. In this way, the torrefied material can be handled and stored like coal.

While pelletization of lignocellulose is an established technology, torrefaction is still a developable process for the production of solid energy carriers. Recent research papers focus on the viability of torrefaction as a part of integrated approaches [10-13]. The major technical challenges are the predictability and consistency of the product quality, the flexibility related with using different input materials, and the densification of torrefied biomass [14]. The applied torrefaction condition (temperature and residence time) and the moisture content have significant influences on the pellet production (e.g., compression and friction energy) and pellet quality (e.g., strength) [15]. In order to estimate the feasibility of a commercial torrefaction system in a particular region, local and abundant biomass resources should be investigated.

During tree harvesting, stem wood is the main product, while the other parts of the tree (including bark and stump) are considered as by-products. According to the literature, stump constitutes 23-25% of the stem volume of a coniferous tree [16] and bark can reach 6-20% of the total volume of the stems [17]. These forest residues represent an abundant and underutilized source of renewable energy. Many studies have been carried out on the thermal characteristics of stem wood [7, 18-19]. These papers focus on the effect of torrefaction on the properties of the solid product, such as mass yield, energy content, hydrophobicity, grindability, and particle-size distribution. Only a few papers are available on the thermal decomposition of forest residues, such as bark and stump. The thermal behavior of bark and wood of Eucalyptus tree has been studied during torrefaction [20-21]. Almeida et al. [20] concluded that the mass loss is an excellent indicator of the treatment severity. It was suggested [21] that the most feasible torrefaction temperature was between 298 and 310 °C for Eucalyptus wood and bark. The torrefaction of stump has been studied focusing on the kinetic evaluation [22] and the thermogravimetric results [16]. In the literature, there is a lack

of papers, which compare the thermal behavior of different parts of the coniferous tree during torrefaction. A profound understanding of the thermal behavior of stump and bark is essential for the efficient utilization of these abundant energy sources in the future.

Thermoanalytical methods are suitable to determine similarities and differences between the compositions of the lignocellulosic materials without separating the main fractions [23]. Several factors may influence the thermal decomposition of lignocellulosic materials. The alkali ions are known to exert a great influence on the thermal decomposition of cellulose [23-25] and lignin [23, 26-27]. As a consequence of the difference in the relative amounts of cellulose, hemicellulose, lignin, extractives, and inorganic materials, the different biomass materials behave differently during thermal decomposition. Therefore, monitoring the changes in the chemical composition is essential during torrefaction. Nevertheless, comparison of chemical analysis and thermal analysis results is rarely carried out in the biomass literature.

The aim of this work has been to gain information about the thermal behavior of untreated and various torrefied bark, stem wood and stump of Norway spruce, which is the most abundant wood species in Norway and in the Northern hemisphere. The thermal stability and the formation of the volatile products of untreated and torrefied samples have been studied by thermogravimetry/mass spectrometry (TG/MS). The main differences between the thermal decomposition of the studied samples are interpreted in terms of the chemical composition (cellulose, hemicellulose and Klason lignin) with the goal of understanding the mechanisms of the decomposition of biomass components during torrefaction. The obtained data were evaluated by principal component analysis (PCA) to identify correlations between the temperature of torrefaction, the residence time, the chemical composition and the thermal behavior of the studied samples.

2. Materials and Methods

2.1. Materials

Different parts of a representative single Norway spruce (*Picea abies*) tree were selected for the torrefaction study: bark, stem wood and stump. The samples originated from a Norway spruce forest in South Norway. The trees in the forest site have high ages, more than one hundred years old on average. After harvested, the trees were divided into three parts: trunk, stump, and forest residues. The trunk was further debarked to obtain stem wood and bark. The stem wood was first cut to strips, and then further chopped into cubes with sides of 1 cm. The bark was chipped into pieces and those with length of around 5-7 cm were used for the torrefaction experiments. The stump was shredded into pieces and the pieces with length of 3-5 cm were torrefied.

2.2. Methods

Torrefaction experiments

The torrefaction experiments were carried out in a batch tube reactor placed in an electrical furnace in nitrogen atmosphere using flow rates of 1 L/min. Approximately 80 g samples were heated up at a heating rate of 15 °C/min to temperatures of 225, 275 and 300 °C in the tube reactor followed by 30 and 60 minutes isothermal periods, whereafter the reactor was cooled down to room temperature. For further experiments the untreated and torrefied samples were ground by a cutting mill to <1 mm particle size.

Higher heating value determination

The higher heating value (HHV) was determined using an automatic IKA C 5000 bomb calorimeter. The combustion of approximately 0.5 g dried 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)

Approximately 2 g biomass samples were ashed at 550 °C in a furnace according to CEN/TS 14775:2004 standard method. The ashes were fused at 920 °C with a fusion blend ($Li_2B_4O_7$:$LiBO_2$, 2:1) and digested by 25 mL 33% nitric acid. The calcium, potassium, sodium, and magnesium 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 according to the 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. [28] applying slight modifications. The milled samples (<1 mm) were dried at 40 °C for 1 day. The raw and torrefied biomass samples were treated in a two-step acid hydrolysis with 72% H_2SO_4 for 2 hours at room temperature, and then with 4% H_2SO_4 for 1 hour at 121 °C. The gained suspensions were filtered and washed with distilled water through G4 glass filter crucibles. The sugar concentrations (glucose, mannose and galactose) of the filtered supernatants were analyzed by high performance liquid chromatography (HPLC) using an Agilent 1260 system with a Hi-Plex H column (Agilent, CA, USA) at 65 °C. An eluent of 5 mM H_2SO_4 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 [29]. 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 analyzed in argon atmosphere. The samples were heated at a rate of 20 °C min^{-1} from 25 to 900 °C in a platinum sample pan. The evolved products were flushed through a glass lined metal capillary heated at 300 °C by argon gas using a flow rate of 140 mL min^{-1}. The ion source of the mass spectrometer 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 ^{38}Ar isotope of the carrier gas (used as an internal standard). Since the MS intensities of various products have different magnitudes, they have been scaled to gain comparable peak heights in the plots. The curves of the individual species developed from bark, stem wood and stump are plotted using the same scale in each of the TG/MS figures.

Principal component analysis (PCA)

Due to the large number of samples and experimental data, principal component analysis (PCA) using the Statistica 12 software (StatSoft, Inc. Tulsa, Oklahoma, USA), was employed. PCA has been used to reveal correlations between the TG data and the chemical composition of the studied samples. PCA is a technique for reduction of data dimensionality, which allows detecting patterns and visualization of patterns retaining as much important information present in the original data as possible [30-31]. The values that represent the samples in the space defined by the principal components (Factors) are the component scores. Factor loadings show the correlation between the original variables and the Factors, and it may help understand the underlying nature of a particular Factor.

3. Results and Discussion

3.1. Comparison of the three untreated samples

Table 1 summarizes the higher heating value, the ash content and selected data of the ICP-OES characterization of the untreated samples. As the results illustrate, the heating values are rather similar, while the bark has significantly higher ash content than stem wood and stump. The bark has an order of magnitude higher K^+ and Si contents than stem wood and stump. Furthermore, the Na^+ and Ca^{2+} contents of the bark are also higher compared to stem wood and stump.

Table 1. Characterization of the untreated samples.

	Bark	Stem wood	Stump
Higher heating value (MJ/kg, db[a])	20.14	19.78	19.51
Ash content (% m/m, ar[b])	2.43	0.31	0.43
Inorganic components (mg/kg, db[a])			
Ca^{2+}	7803	1030	1235
K^+	2011	272	245
Na^+	47	22	36
Si	3602	82	253

[a]dry basis, [b]as received

Fig. 1a shows the chemical composition of the three untreated samples. The sum of the mannan and galactan contents represents the hemicellulose fraction, whereas the glucan content of the samples mainly characterizes the cellulose fraction of biomass. The Klason lignin content is defined as the acid insoluble residue of the samples without the acid

insoluble ash. Besides the acid insoluble lignin, the Klason lignin contains all acid insoluble components of the sample, excluding ash. The fraction denoted by "Other" represents the sum of unquantified components and includes extractives, acid soluble lignin and acid soluble minerals. As Fig. 1a shows, the bark sample has the highest Klason lignin content, stem wood has the highest cellulose content and stump has the highest hemicellulose content. The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the untreated samples are shown in Fig. 1b. The main DTG peak is dominated by the decomposition of cellulose, while the shoulder at lower temperature (around 320 °C) can be attributed mainly to hemicellulose decomposition. The lignin decomposes at a lower rate in a wide temperature range (200–600 °C). The evaporation and decomposition reactions of extractives start at lower temperatures and it is visible as a shoulder on the main DTG peak from approximately 160 °C. The comparison of the three untreated samples shows that bark releases the most extractives, in the low temperature range. The untreated stump has the most characteristic hemicellulose shoulder, which is in agreement with the chemical composition results showing that stump has the highest hemicellulose content. The decomposition of bark starts at the lowest temperature, the DTG peak maximum occurs at the lowest temperature, and the maximum rate of decomposition is considerably lower than in the case of the stem wood and stump. The high lignin content (41%) of bark results in the formation of a high yield of char during thermal decomposition. The different thermal behavior of the different untreated samples can be explained by their different composition as well as by the fact that alkali ions have catalytic effects on the decomposition mechanism of cellulose [23-25] and the charring reactions of lignin [23, 26-27].

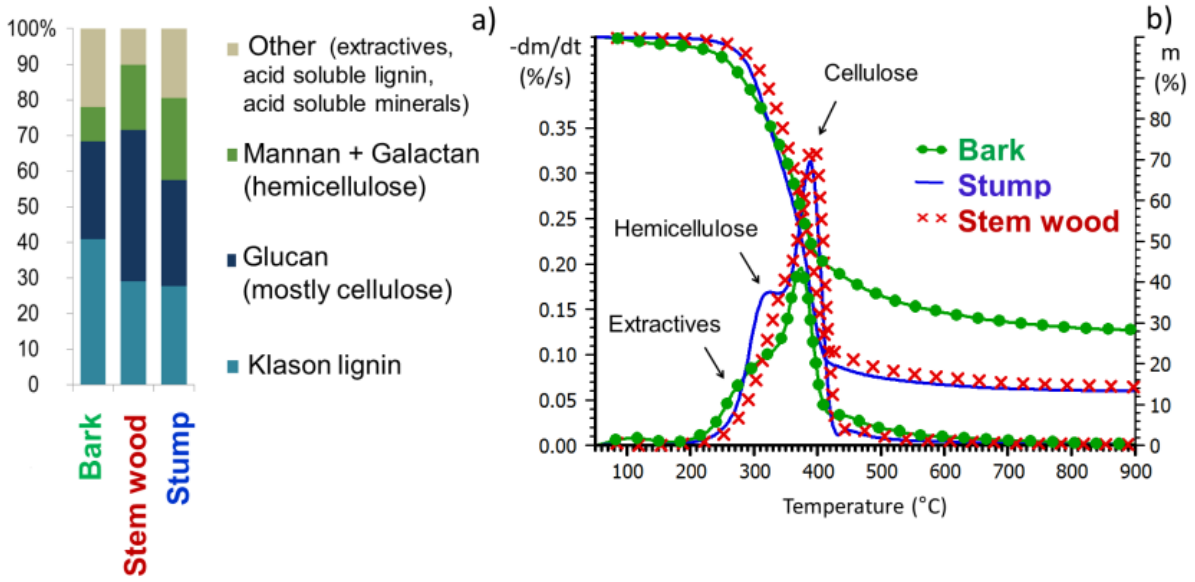

Fig. 1. (a) Composition and (b) TG and DTG curves of untreated bark, stem wood, and stump.

Regarding the thermal behavior of the studied samples, further information is given by the mass spectrometry curves. The thermal decomposition of extractives, cellulose, hemicellulose and lignin results in a high yield of low molecular mass compounds at low heating rate, hence the evolution profiles of these products are characteristic to the decomposition of the different parts of the tree. Fig. 2a, c and e presents the DTG curves as well as the evolution of water and the main permanent gases, while Fig. 2b, d and f presents the evolution of some typical organic products measured by the mass spectrometer during the thermal decomposition of the three untreated samples.

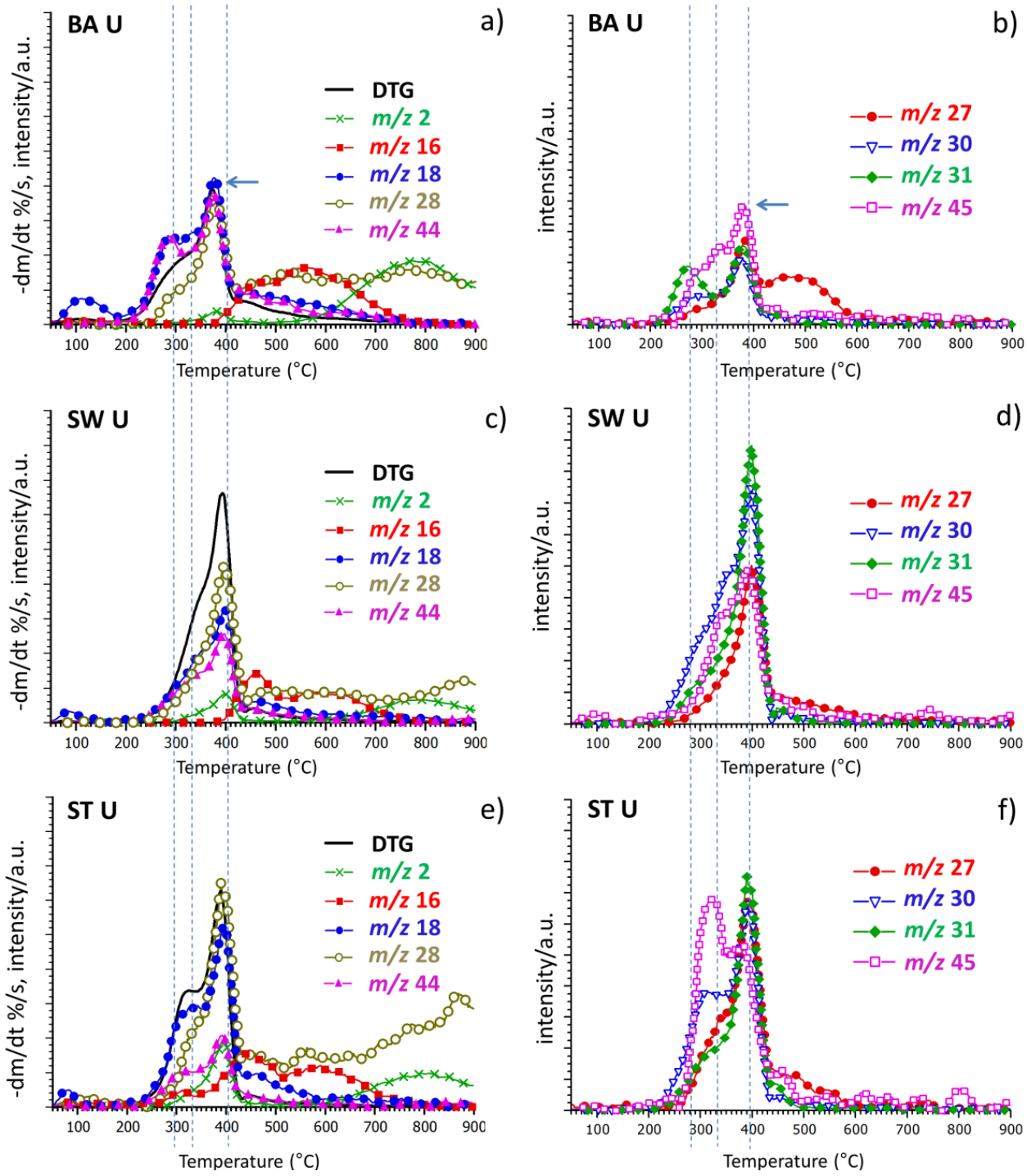

Fig. 2. The DTG curves and the evolution profiles of the most characteristic decomposition products and fragment ions released from untreated bark (BA U), stem wood (SW U) and stump (ST U) (*m/z* 2, hydrogen; *m/z* 16, methane; *m/z* 18, water; *m/z* 28, carbon monoxide; *m/z* 44, carbon dioxide; *m/z* 27, $C_2H_3^+$; *m/z* 30, formaldehyde; *m/z* 31, CH_3O^+; *m/z* 45, $COOH^+$).

Relatively large amounts of water (*m/z* 18), carbon monoxide (*m/z* 28) and carbon dioxide (*m/z* 44) are formed during the thermal decomposition of the untreated materials (Fig. 2a, c and e) due to the large number of hydroxyl and other oxygen-containing functional groups in the natural polymers (cellulose, hemicellulose and lignin). In the temperature range of 300-430 °C besides carbon monoxide the ion current *m/z* 28 represents the CO^+ mass spectrometric fragment ion of organic oxygen-containing volatile products as well (e.g., formaldehyde). In the temperature range of 500-900 °C, the charring processes are characterized by the evolution of carbon monoxide (*m/z* 28), methane (*m/z* 16) and hydrogen (*m/z* 2). Fig. 2 also shows the evolution of some characteristic organic volatile products and fragment ions from the untreated samples (Fig. 2b, d and f). Formaldehyde (*m/z* 30) is released during the thermal decomposition of cellulose, hemicellulose and lignin, as well. The fragment ion *m/z* 31 represents mainly the evolution of methanol during the thermal decomposition. On the other hand, *m/z* 31 is the main fragment ion of hydroxyacetaldehyde, which is a typical product of the cellulose decomposition. The evolution curve of the *m/z* 45 ion represents mainly $COOH^+$, which is the main fragment ion of acidic products released from hemicellulose and cellulose. The *m/z* 27 ion is a typical fragment ion of hydrocarbons.

The moisture content (*m/z* 18 in Fig. 2a, c and e) is released from the untreated samples up to 200 °C. The higher intensity and broader shape of this water peak for the bark sample indicate a higher moisture content of the bark sample, which may be bonded mostly to the inorganic content (Table 1) of the bark sample. As seen in Fig. 2, considerably higher amounts of permanent gases and lower amounts of organic volatiles are released from raw bark than from raw stem wood and stump. The characteristic peaks or shoulders of carbon dioxide, water, formaldehyde and methanol in the temperature range of 200-300 °C can be attributed to the thermolysis of extractives and scission of lignin side groups from the untreated samples. In case of stem wood and stump, the characteristic shoulder of formaldehyde, carboxyl group, carbon dioxide and water in the temperature range of 300-350 °C reveals the decomposition of hemicellulose (Fig. 2c and e). O-acetyl-galactoglucomannans are the main hemicelluloses in softwoods. The evolution profile of $COOH^+$ and carbon dioxide indicates the scission of the acidic groups from hemicellulose. As seen in Fig. 2, the untreated stump produces the highest amount of acid products as the *m/z* 45 fragment ion indicates, which can be explained by the highest hemicellulose content of the stump sample (Fig. 1). The hemicellulose shoulder of the untreated bark is not pronounced which is in agreement with the chemical composition results showing that bark has the lowest

hemicellulose content (Fig. 1). The main thermal decomposition product of cellulose is levoglucosan, which cannot be detected by TG/MS, but smaller decomposition products like formaldehyde (*m/z* 30), hydroxyacetaldehyde (*m/z* 31) and methanol (*m/z* 31) originating from cellulose can be monitored at around 390 °C as shown in Fig. 2b, d and f. Significant amounts of water vapor and carbon dioxide are released during cellulose decomposition, as well. Methane (*m/z* 16) is released in two main processes during the thermal decomposition of the untreated samples. In the first process at around 450 °C methane forms during the thermal decomposition of lignin by the scission of the methoxy groups [27]. The evolution of carbon monoxide, methane and hydrogen (Fig. 2a, c and e) above 500 °C takes place during the charring processes. As a result of the higher lignin content of bark (Fig. 1), the charring processes are more pronounced than in the stem wood and stump resulting in higher amount of methane, hydrogen, and char.

3.2. Effect of torrefaction temperature and residence time

During torrefaction the lignocellulosic materials decompose to different degrees depending on the applied temperature and residence time. Fig. 3 shows the TG and DTG curves of the various torrefied bark, stem wood, and stump samples. The carbohydrate and lignin contents of the untreated and torrefied biomass samples (Table 2) were also determined in order to understand better the thermochemical conversion process during torrefaction. As the mannan and galactan contents demonstrate in Table 2, the sugar units of hemicellulose did not degrade during torrefaction at 225 °C. However, the characteristic hemicellulose shoulder of the DTG curves decreased revealing the structural modification as a result of the torrefaction (Fig. 2 and 3a and b). These results can be explained by the hypothesis that the acidic side groups of hemicellulose were partially split off, while the main hemicellulose content did not degrade at 225 °C. As the result of the partial scission of acidic side groups, the hydrophilicity of the biomass decreases, and therefore it takes up less moisture during storage [7]. The biomass with less moisture has higher energetic value, giving lower transportation cost, and moreover it can be stored stably with a low risk of biological deterioration. The cellulose content of stem wood and stump did not reduce considerably up to 275°C, as the results show in Table 2, and Fig. 3, while the degradation of cellulose in the bark sample was significant at this temperature. At 300 °C, only trace amounts of cellulose were found in bark, and the cellulose content of stem wood and stump strongly decreased. As already mentioned, the presence of alkali ions modifies the thermal degradation of cellulose [23-25] and lignin [23, 26-27]. The reason for the promoted decomposition rate of bark during torrefaction is

most probably the catalyzed decomposition of its cellulose content. As Fig. 3 shows, the residence time had no significant effect on the composition of the torrefied samples up to 275 °C; therefore applying the longer residence time of 60 minutes in a real application is superfluous. At 300 °C, the torrefaction residence time had substantial effects on all parts of the spruce tree due to the severe decomposition reactions at this temperature.

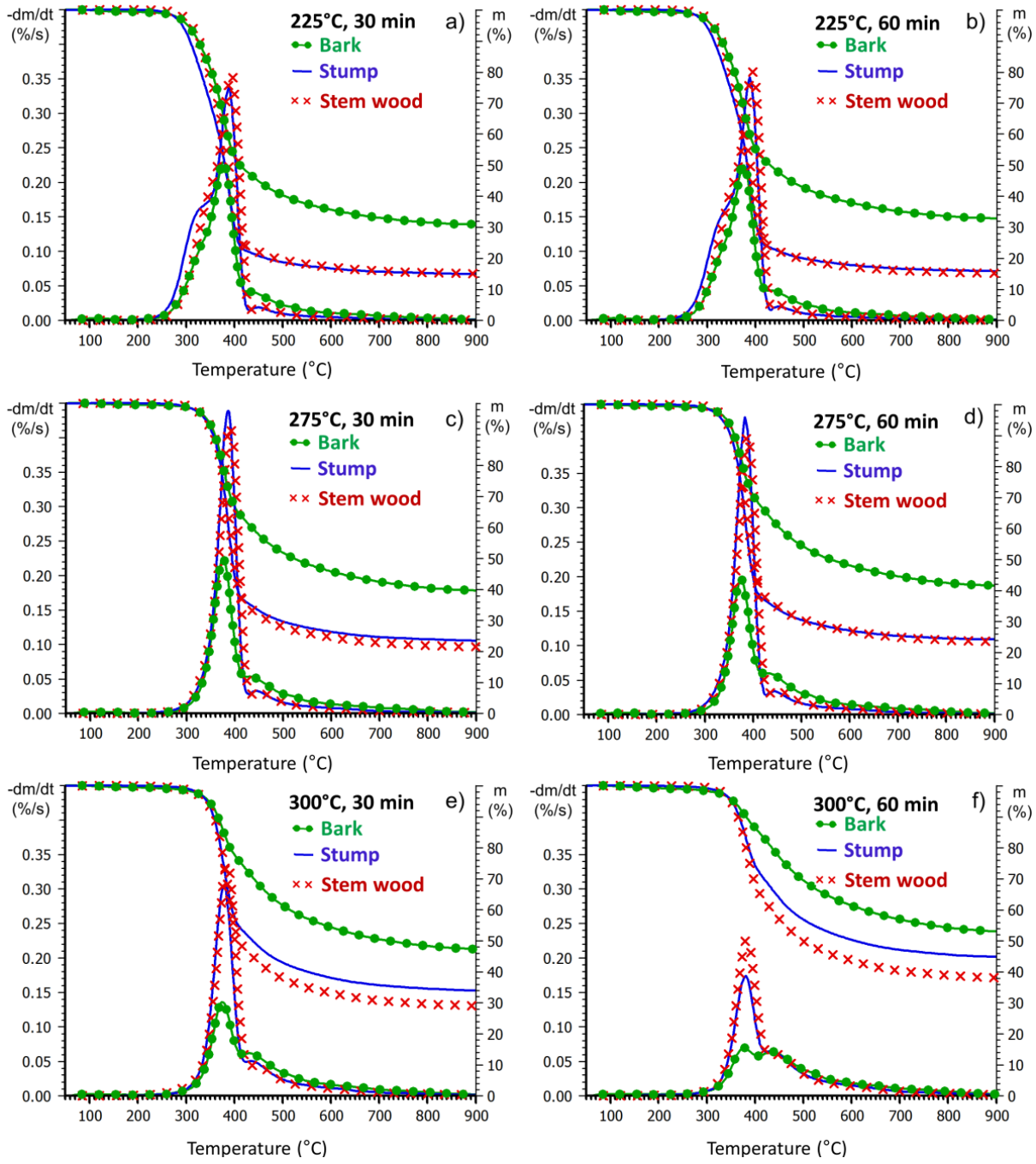

Fig. 3. TG and DTG curves of bark, stem wood, and stump after various torrefaction treatments.

Table 2. Solid yields of torrefaction and composition of the untreated and torrefied bark, stem wood, and stump (dry basis). Standard deviations are calculated from triplicates.

Sample	Solid yield (% m/m)	Glucan (% m/m)	Mannan + Galactan (% m/m)	Klason lignin (% m/m)
Bark				
BA U	100	27.5 ± 0.7	9.7 ± 0.2	40.8 ± 0.3
BA 225_30	90	28.4 ± 0.2	9.8 ± 0.2	49.6 ± 1.3
BA 225_60	82	24.4 ± 0.6	8.8 ± 0.1	56.7 ± 0.8
BA 275_30	73	12.3 ± 0.7	1.8 ± 0.1	78.8 ± 1.4
BA 275_60	69	7.7 ± 0.3	0.8 ± 0.0	86.0 ± 1.2
BA 300_30	63	2.7 ± 0.1	0.3 ± 0.0	90.0 ± 0.9
BA 300_60	61	1.5 ± 0.1	0.1 ± 0.0	92.0 ± 0.4
Stem wood				
SW U	100	42.5 ± 0.9	18.3 ± 0.5	29.0 ± 0.8
SW 225_30	92	44.7 ± 1.3	17.1 ± 0.4	30.6 ± 0.1
SW 225_60	91	43.5 ± 0.9	16.6 ± 0.0	31.2 ± 0.5
SW 275_30	79	45.6 ± 0.9	6.2 ± 0.3	42.7 ± 0.7
SW 275_60	76	42.2 ± 1.4	4.7 ± 0.2	47.8 ± 0.3
SW 300_30	70	12.8 ± 0.4	1.4 ± 0.1	80.2 ± 1.5
SW 300_60	58	8.3 ± 0.3	0.8 ± 0.0	87.3 ± 1.4
Stump				
ST U	100	29.8 ± 0.3	23.0 ± 0.3	27.7 ± 0.7
ST 225_30	93	28.2 ± 1.8	21.5 ± 0.4	34.3 ± 2.0
ST 225_60	90	28.9 ± 1.3	20.9 ± 2.3	37.7 ± 2.4
ST 275_30	72	29.7 ± 0.4	4.9 ± 0.2	57.2 ± 0.4
ST 275_60	70	29.0 ± 0.4	4.6 ± 0.2	59.6 ± 1.0
ST 300_30	56	25.6 ± 0.6	1.1 ± 0.0	68.6 ± 0.3
ST 300_60	46	13.7 ± 0.5	0.4 ± 0.0	82.3 ± 0.5

Figs. 4, 5, and 6 show the evolution of the most significant products from the torrefied bark, stem wood, and stump samples, respectively, in order to get a better understanding of the above discussed differences in the decomposition during torrefaction. The curves for the individual species released from bark (Fig. 4), stem wood (Fig. 5) and stump (Fig. 6) are plotted using the same scale in each of the figures. The pattern of the ion intensity curves of the samples torrefied at 225 and 275 °C for 30 minutes is very similar to that of the samples torrefied at 225 and 275 °C for 60 minutes; hence they are not presented here. As the water vapor evolution below 200 °C indicates, the moisture content of the torrefied bark samples is higher than that of the torrefied stem wood and stump samples. The reason could be the higher inorganic ion content, therefore the more hydrophilic nature of the torrefied bark samples. The torrefaction removes the moisture content of the samples; however, during sample handling the torrefied sample can take up some water from the ambient air depending on the degree of hydrophilicity of the torrefied sample. The torrefied bark samples release higher amounts of permanent gases and lower amounts of organic volatiles than torrefied stem wood and stump samples, prepared under the same torrefaction conditions. This observation indicates the catalytic effect of alkali ions on the decomposition of cellulose and is in agreement with the results of the compositional analysis, as well. The inherent alkali ion content of lignocellulosic biomass changes through a catalytic effect the thermal decomposition mechanism, giving increased char yield and increased amount of water and permanent gases, at the expense of the yield of organic volatiles [26]. During torrefaction at 225 °C, the extractives content of the samples strongly decreased, therefore the shoulder of the DTG curves at 290 °C is less pronounced for the torrefied samples at 225 °C (Figs. 4a, 5a and 6a) than for the untreated samples (Fig. 2). The main mass of the hemicellulose content of the bark, stem wood and stump samples was thermally stable during torrefaction at 225 °C; however, changes in the evolution pattern of $COOH^+$ (Figs. 4b, 5b and 6b) point to the scission of the most labile acetate groups from the hemicellulose chains at this temperature. The composition analysis revealed (Table 2) that 8-26% hemicellulose remained in the samples after the thermal treatment at 275 °C; however, the shoulder of the DTG curve disappeared. The TG/MS results indicate that the decomposition of the remaining part of hemicellulose takes place in the temperature range of cellulose decomposition.

In case of stem wood and stump, the ion intensities describing the decomposition of cellulose (in the temperature range of the main DTG peak) do not decrease due to the thermal treatment up to 275 °C torrefaction temperature. This is in agreement with the chemical composition results showing that the cellulose content of the stem wood and stump samples only slightly decrease up to this temperature. The cellulose content of the bark sample decreased by half between the torrefied samples at 225 and 275 °C, resulting in a reduced evolution of all cellulose decomposition products. These observations show the more extensive degradation of the cellulose in bark at 275 °C. As shown earlier, the evolution of methane shows a wide bimodal shape. In the temperature range of 350-500 °C, methane forms during the thermal decomposition of lignin by the scission of the methoxy groups [27]. The reason for the different methane evolution profiles from the bark, stem wood and stump samples in this temperature range could be the different methoxy group content of the studied samples. After severe torrefaction (275-300 °C), the relative amount of Klason lignin significantly increased in the samples due to the strong degradation of carbohydrates. It can be observed that the evolution of hydrogen, methane, and carbon monoxide above 430 °C are increasing, while the intensities of the hemicellulose and cellulose decomposition products are decreasing when raising the torrefaction temperature and residence time. The charring reactions are more pronounced in case of the bark sample. In the temperature range of 400-700 °C, the evolution of small hydrocarbon molecules were detected, denoted by the *m/z* 27 ion curves in Figs. 4, 5 and 6. The relative intensity of the hydrocarbon evolution is increasing with the torrefaction temperature for all the bark, stem wood and stump samples. These hydrocarbon molecules could be released by secondary reactions involving the decomposition products of cellulose, hemicellulose and lignin. At 300 °C, the hemicellulose content of each studied sample almost completely decomposes during 30 minutes; the torrefaction residence time has a significant effect owing to the severe decomposition of cellulose. The torrefaction at 300 °C for 60 minutes results in reduced evolution of all cellulose decomposition products, decreasing by half in the stem wood and stump samples, while only traces of cellulose were measured in the bark sample. The severe decomposition of hemicellulose and cellulose results in the relatively low solid yield (43-70%) due to the significant dry matter loss during thermal degradation, therefore this temperature is too high for most real applications.

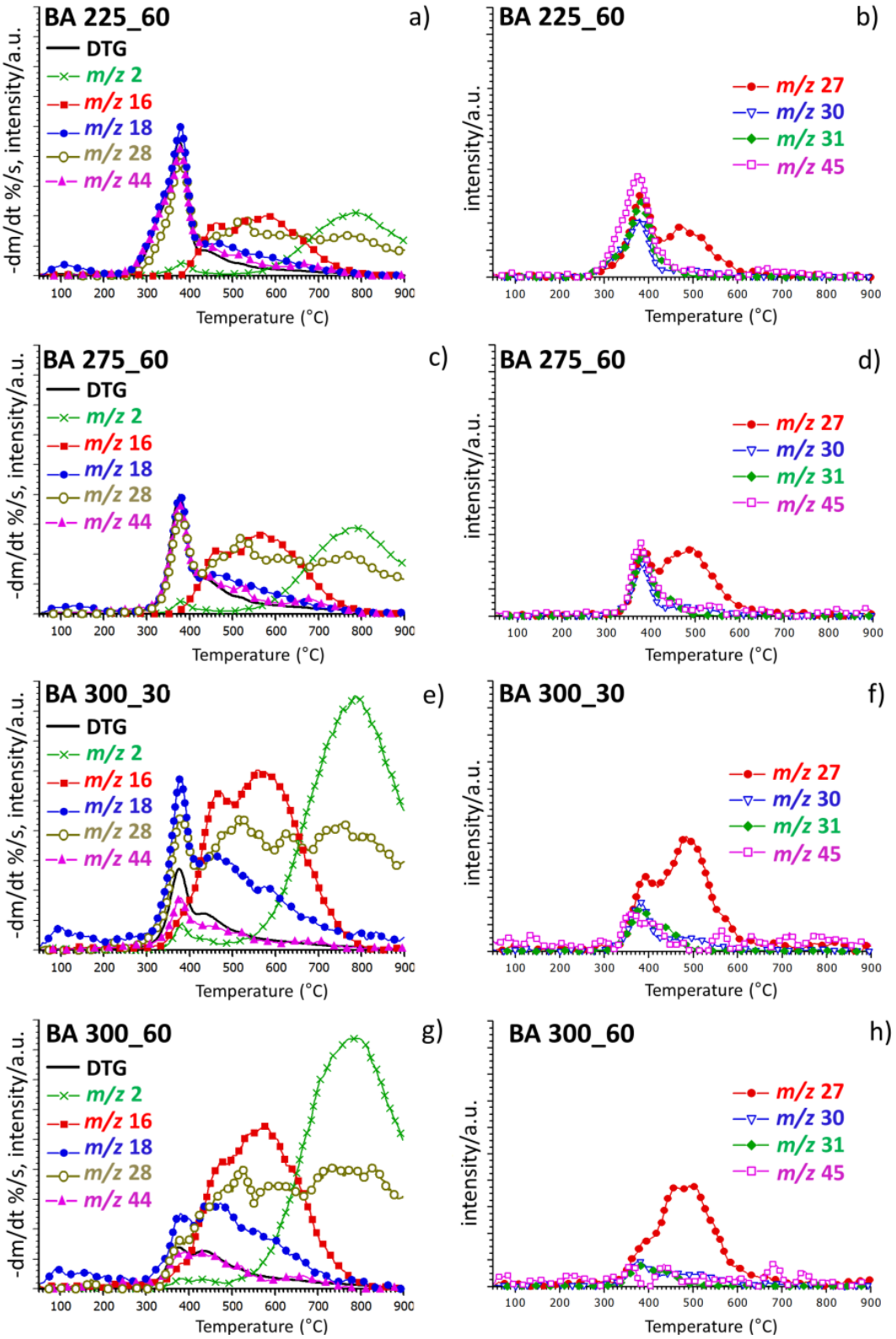

Fig. 4. The DTG curves and the evolution profiles of the most characteristic decomposition products and fragment ions released from torrefied bark samples (*m/z* 2, hydrogen; *m/z* 16, methane; *m/z* 18, water; *m/z* 28, carbon monoxide; *m/z* 44, carbon dioxide; *m/z* 27, $C_2H_3^+$; *m/z* 30, formaldehyde; *m/z* 31, CH_3O^+; *m/z* 45, $COOH^+$).

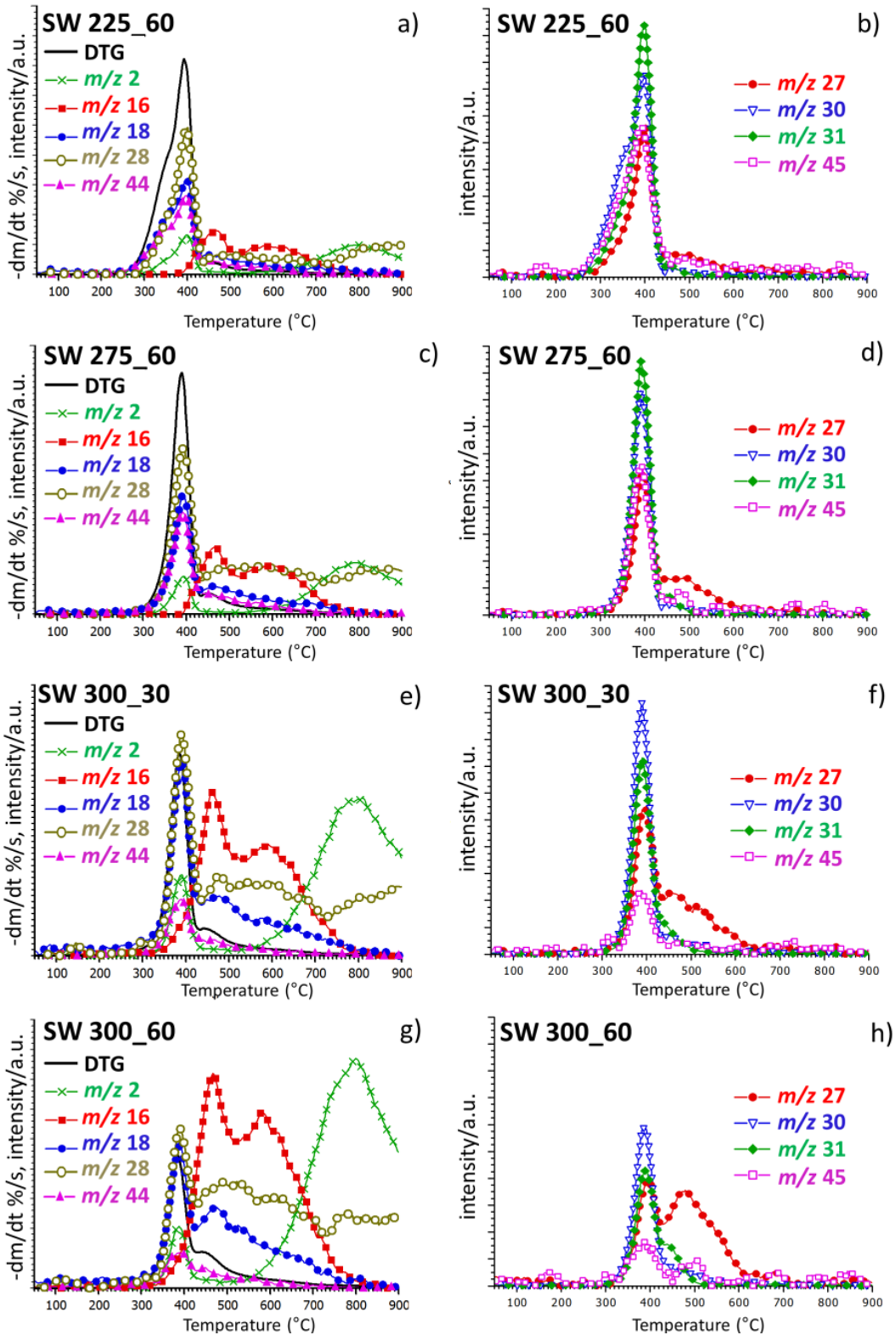

Fig. 5. The DTG curves and the evolution profiles of the most characteristic decomposition products and fragment ions released from torrefied stem wood samples (*m/z* 2, hydrogen; *m/z* 16, methane; *m/z* 18, water; *m/z* 28, carbon monoxide; *m/z* 44, carbon dioxide; *m/z* 27, $C_2H_3^+$; *m/z* 30, formaldehyde; *m/z* 31, CH_3O^+; *m/z* 45, $COOH^+$).

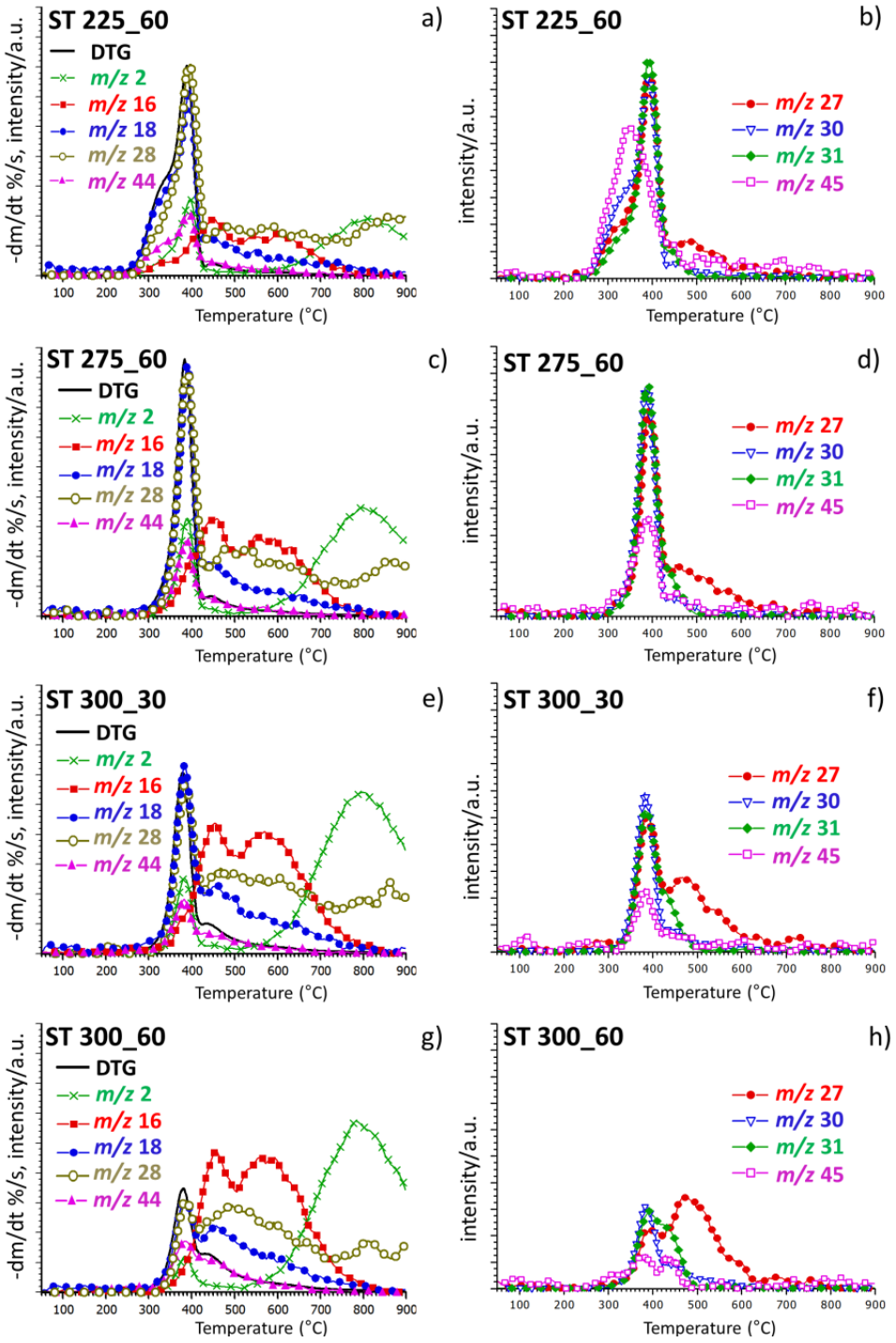

Fig. 6. The DTG curves and the evolution profiles of the most characteristic decomposition products and fragment ions released from torrefied stump samples (*m/z* 2, hydrogen; *m/z* 16, methane; *m/z* 18, water; *m/z* 28, carbon monoxide; *m/z* 44, carbon dioxide; *m/z* 27, $C_2H_3^+$; *m/z* 30, formaldehyde; *m/z* 31, CH_3O^+; *m/z* 45, $COOH^+$).

3.3. PCA calculation based on chemical composition and TG data

Principal component analysis has been applied to identify the similarities and differences between the untreated and various torrefied stem wood, bark and stump samples. In the PCA calculation, the characteristic thermogravimetric parameters (T_{start}, T_{peak}, DTG_{max}, T_{end}, and char yield) and the chemical composition data (glucan, sum of mannan and galactan, as well as Klason lignin contents) have been used as input variables. T_{start} denotes the start of hemicellulose decomposition in the untreated and mildly torrefied samples, while after severe torrefaction, this parameter belongs to the cellulose decomposition. T_{end} reflects the end of the cellulose decomposition. The T_{start} and T_{end} values have been determined by extrapolation of the DTG curve. In the PCA calculation the first principal component (Factor 1) and the second principal component (Factor 2) account for 64% and 21% of the total variance, respectively. These two factors can adequately characterize the major differences between the untreated and torrefied samples. The score plot (Fig. 7a) shows that the studied samples are located in four well separated groups. The untreated and mildly torrefied (at 225 °C) stem wood and stump samples belong to the same group, indicating that the torrefaction at 225 °C does not modify significantly the thermal properties of these samples compared to the untreated samples. The second group is formed from the stem wood and stump samples treated at 275 °C. The untreated and mildly torrefied (at 225 °C) bark samples are separated from the other samples, while all of the severely torrefied samples can be seen in the fourth group. These differences are mainly due to the different hemicellulose, cellulose and lignin content of the samples; which is reflected by the different thermal behavior of the studied samples, as well. The chemical composition and consequently the thermal behavior of the stem wood, stump, and bark samples have been changed to a greater extent at higher torrefaction temperature than at lower torrefaction temperature. The loading plot (Fig. 7b) shows that the values of glucan, sum of mannan and galactan, T_{peak} and DTG_{max} data correlate negatively with the lignin content and the char yield. Factor 1 is composed mainly of these parameters and primarily separates the samples as a function of the torrefaction temperature and residence time. As the PCA calculation shows (Fig. 7a), the effect of torrefaction temperature is greater than the effect of residence time. T_{start} and T_{end} data contribute mainly to Factor 2, and separates mostly the untreated and mildly torrefied bark samples from the others. The thermal decomposition of bark differs from the other samples due to the different composition (high lignin and alkali ion content).

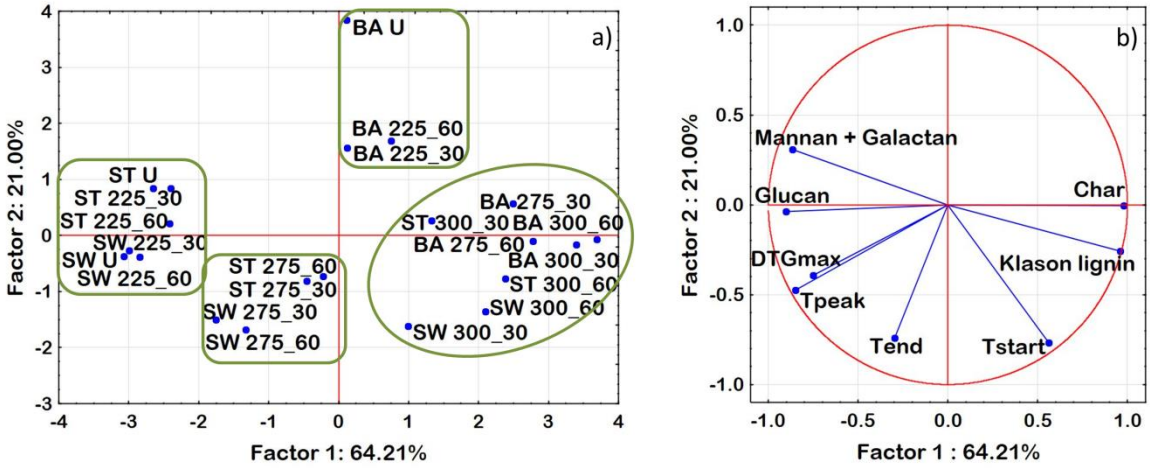

Fig. 7. PCA (a) score and (b) loading plots based on the TG and the chemical composition data. The score plot denotes the samples in the space defined by the Factors. The Factor loading shows the correlation between the original variables and the principal components.

4. Conclusion

A comparative study on the thermal behavior of untreated and various torrefied bark, stem wood, and stump of Norway spruce has been performed to better understand the thermal degradation process taking place during torrefaction. TG/MS and chemical composition analysis were applied to provide information about the structural changes of the main components and to compare the effects of different torrefaction conditions. Depending on the biomass feedstock properties and the needs of product applications, different torrefaction conditions will be optimal. The moisture content and the extractable compounds evaporate at first during torrefaction; the volatile extractive content strongly decreased in the samples torrefied at 225 °C. The comparison of the mannan and galactan content with the TG/MS results shows that the decomposition of hemicellulose starts with the cleavage of the functional groups, while the scission of the polysaccharide chains occurs at higher temperature. The thermally less stable acidic side groups are cleaved at this temperature, increasing the hydrophobicity of the product in this way, which is an important goal during the practical application of torrefaction. The hemicellulose chain of each sample was thermally stable during torrefaction at 225 °C; however, it degraded to a great extent at 275 °C as indicated by the chemical analysis. Significant decomposition of cellulose started as low as at 275 °C torrefaction temperature for the bark sample, while it was found to be stable for stem wood and stump, which can be explained by the high alkali ion content of bark.

Therefore, lower torrefaction temperature should be applied for bark, than for stem wood and stump to obtain products degraded to a similar degree. The torrefaction residence time (30 vs. 60 minutes) did not have significant influence up to 275 °C on the thermal behavior of the samples. However, at 300 °C the composition of the torrefied samples changed substantially with the torrefaction residence time due to the intensive decomposition of cellulose. Torrefaction at 300 °C temperature induces severe changes in all biomass components, resulting in significant mass and energy losses; hence this temperature is too high for most of the applications.

Abbreviations

BA	Bark
ST	Stump
SW	Stem wood
SW U	Untreated stem wood
SW 225_60	Torrefied stem wood obtained by torrefaction at 225 °C for 60 minutes isothermal period
DTG_{max}	Maximum value of the –dm/dt curves
T_{start}	Extrapolated temperature of the beginning of decomposition (on the DTG curve)
T_{peak}	Temperature belonging to the DTG_{max}
T_{end}	Extrapolated temperature of the end of cellulose decomposition (on the DTG curve)
Char	Char residue at 900°C temperature
% m/m	Mass percent
PCA	Principal component analysis
TG/MS	Thermogravimetry/mass spectrometry

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