



# Effect of slow pyrolysis conditions on biocarbon yield and properties: Characterization of the volatiles

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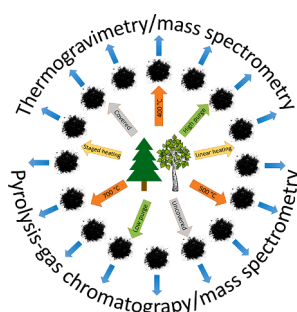
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## HIGHLIGHTS

- Low flow rate, staged pyrolysis or covered sample holder increase the char yield.
- Intense purging and sample holder lid effectively prevent adsorption of volatiles.
- Spruce biocarbons have more VM than birch biocarbons when prepared at 400 and 500 °C.
- Biocarbon prepared by staged pyrolysis at 700 °C releases less water above 800 °C.
- Share of aromatics in VM strongly reduces with increasing carbonization temperature.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Slow pyrolysis of spruce and birch was performed at various heating programs and conditions in a horizontal quartz tube reactor heated by an electric furnace. The effects of feedstock and carbonization conditions on the yield of biocarbon, liquid and gaseous products were studied. The thermal properties, volatile matter (VM) content and the evolution profiles of volatiles from the biocarbons were characterized by thermogravimetry/mass spectrometry. The composition of volatiles was analyzed in detail by pyrolysis–gas chromatography/mass spectrometry. Increased char yield was observed when staged pyrolysis program, low purging flow rate or covered sample holder were applied. Spruce produced more charcoal than birch due to the higher lignin content of softwood. The amount and the evolution profiles of the main gaseous products were similar from spruce and birch biocarbons prepared under the same conditions. The relative amount of aromatic and polyaromatic compounds in VM drastically decreased with increasing carbonization temperature.

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## 1. Introduction

Increasing the share of the renewable energy sources contrary to the currently dominating fossil fuels is an indisputable need to reduce CO<sub>2</sub> emission, the fundamental driver of climate change. Biomass is the most important source of renewable energy and the use of modern bioenergy should be increased (Elkasabi and Mullen, 2021). Thermochemical processes are considered as the most effective methods for lignocellulosic biomass utilization (Bhaskar and Pandey, 2015; Akhtar et al., 2018) including pyrolysis (Guedes et al., 2018; Zhang et al., 2017), hydrothermal carbonization (Fernández-Sanromán et al., 2021; Kumar et al., 2020; Nzediegwu et al., 2021), combustion, (Hupa et al., 2017) and gasification (Sarker et al., 2015). Pyrolysis is a thermal treatment performed in an inert atmosphere that converts the biomass into char, bio-oil, and gas. The solid product from biomass pyrolysis, so-called biocarbon, biochar or charcoal, has various applications besides heating and barbequing, like biochar for soil amendment, activated carbon for flue-gas cleaning, or substitution of the fossil carbon by renewable biocarbon in metallurgical processes. Each application requires large amount of carbonaceous material with certain properties; therefore, both high char yield and obtaining required properties are desirable.

The yield and physio-chemical characteristics of the char produced from slow pyrolysis depend on many factors like the composition of the feedstock, process temperature, heating rate, residence time and particle size (Wang et al., 2013). The char yield is determined primarily by the final carbonization temperature (Stimely and Blankenhorn, 1985); as the thermal degradation process develops at higher temperatures, the char yield decreases, while its carbon content increases. The thermal degradation of the carbohydrate components, namely hemicellulose and cellulose, are almost completed at 400 °C, therefore above this temperature the char yield reduces relatively slowly (Zhang et al., 2020). Further chemical changes take place up to 600 °C; the char produced at this temperature has relatively low oxygen and hydrogen content and high degree of carbonization. With increasing pyrolysis temperatures, changes in the physical properties of char dominate up to 800–1000 °C (Tintner et al., 2018). Slow pyrolysis at moderate temperatures and long residence times produces higher yield of charcoal (biocarbon), while fast pyrolysis and short reaction time favor bio-oil formation (Maggi and Delmon, 1994). It was found (Brunner and Roberts, 1980) that slow heating of cellulose resulted in a considerable increase in the yield of char, with reduced oxygen content. Improved char yield was observed by the two-step pyrolysis of eucalyptus (Elyounssi et al., 2012), when a slow pyrolysis step (2 °C min<sup>-1</sup>) was followed by a fast pyrolysis step (100 °C min<sup>-1</sup>). The yield increased to the greatest extent when the heating rate changed at 360 °C using eucalyptus, and only slight increase was observed when the heating rate changed in the 330–360 °C temperature range using cellulose. The gas flow also affects the char yield as low flow rate provides opportunity for the volatiles to interact with the solid carbonaceous residue and increase the char yield (Antal and Grønli, 2003). TGA studies on Avicel cellulose (Varhegyi et al., 1988) and woody biomass (Wang et al., 2013; Wang et al., 2016) performed in sample pans having a lid with a pinhole resulted in higher char yield than the experiments in open sample holders did. Both findings verified that the increased residence time of the reactive volatiles near the decomposing solid has a positive impact on the char yield. The chemical composition of the biomass is also an important factor, since the composition and yields of the produced biofuels are influenced by the properties of the feedstock (Leng and Huang, 2018).

The volatile matter content is one of the most general parameters measured in charcoal; its optimum value depends on the use of the charcoal (Antal and Grønli, 2003). In addition to the quantity of the volatile matter, the composition of the evolving products during heating is also important in various applications, e.g., in the metallurgical industry. TG/MS has proved to be a useful tool for understanding the devolatilization properties of chars (Varhegyi et al., 1998), characterizing the evolution profile of gaseous, and low molecular mass organic

products (Mészáros et al., 2007a). Pyrolysis-GC/MS technique provides a screening of the higher molecular mass volatiles; it was used successfully for biochar characterization, and a relationship was demonstrated between the pyrolysis fingerprint and the charring degree (Kaal et al., 2012).

In this work, the influence of the heating program, final temperature and residence time of the volatiles in the pyrolysis zone was studied on the carbonization process of the softwood, spruce (*Picea abies*) and the hardwood, birch (*Betula pubescens*), which are both abundant species in the Northern Hemisphere. The primary aim of this work was to investigate the effect of carbonization conditions on the yields and the composition of the solid products. In addition, the amount, the composition and the evolution behavior of volatile matter are critical indicators of thermal and environmental stability of biocarbon, which need to be carefully studied and assessed for further proper and efficient utilization. The composition and evolution profile of the volatile contents of the carbonized samples has barely been described in the literature. Therefore, the second objective of this work was to study the composition and evolution profiles of the volatiles using TG/MS and Py-GC/MS techniques. The detailed analysis of the volatiles provides insights into the structure of the biocarbon, thereby revealing information about the carbonization mechanism. Understanding the composition of the volatiles facilitates the selection and development of the appropriate biocarbon for industrial applications of special needs.

## 2. Materials and methods

### 2.1. Biomass materials

Spruce wood (*Picea abies*) and birch wood (*Betula pubescens*) samples originating from South Norway forests were studied. After harvest, the trunk was debarked to obtain stem wood. The stem wood was chipped into pieces and the pieces with a length of 3–5 cm were selected as feedstock. The chipped wood samples were sent to the laboratory of RCNS (Hungary), where the wood chips were ground by a cutting mill to <1 mm particle size. All carbonization experiments were performed using the milled (<1 mm) feedstock.

### 2.2. Carbonization process

The carbonization experiments of spruce and birch samples were carried out in a horizontal quartz tube reactor heated by an electric furnace. About 4 g samples were carbonized in a quartz vessel shaped as a boat. To ensure an inert atmosphere, nitrogen with a flow rate of 400 mL min<sup>-1</sup> purged the tubular reactor for 40 min before the experiments. During the heating program, a reduced (5 mL min<sup>-1</sup>) flow rate was applied to ensure an inert atmosphere or a high (400 mL min<sup>-1</sup>) nitrogen purge flow was used to flush the system rapidly. The carbonization experiments were performed applying 10 °C min<sup>-1</sup> heating rate and 400, 500 and 700 °C final temperatures with an isothermal period of 1 h at the final temperature. Staged pyrolysis experiments were carried out by inserting an isothermal period at 350 °C for 1 h into the temperature program. Most of the experiments were performed with an open boat. In four carbonization experiments, a rectangular plain quartz sheet was placed on the top of the quartz boat as a lid. Due to the imperfect fit of the lid on the sample boat, it hindered the escape of volatiles from the vessel, but was not pressure tight.

The completed experiments and the designation of the biocarbon samples are summarized in Table 1. The condensates were trapped in a U tube cooled by liquid nitrogen; however, the less volatile components were condensed on the cooler wall of the quartz tube reactor. The nitrogen flow (5 or 400 mL min<sup>-1</sup>) was maintained till the system was cooled to room temperature. Then the quartz sample holder with the solid biocarbon residue was measured to calculate the char yield. The mass of the quartz tube reactor and U tube was measured before and after the experiment to calculate the mass of the condensate. The gas

**Table 1**

The designation of the carbonized samples based on the raw material and the carbonization conditions.

No.	Experiment, Sample name <sup>a</sup>	Raw material	Carbonization conditions			
			Final temperature (°C)	Heating program <sup>b</sup>	N <sub>2</sub> flow rate <sup>c</sup>	Covered sample holder
1	S400-LR	Spruce	400	linear	reduced	no
2	S500-LR		500	linear	reduced	no
3	S500-LH		500	linear	high	no
4	S500-LRC		500	linear	reduced	yes
5	S500-SR		500	staged	reduced	no
6	S500-SRC		500	staged	reduced	yes
7	S700-LR	Birch	700	linear	reduced	no
8	S700-SR		700	staged	reduced	no
9	B400-LR		400	linear	reduced	no
10	B500-LR		500	linear	reduced	no
11	B500-LH		500	linear	high	no
12	B500-LRC		500	linear	reduced	yes
13	B500-SR		500	staged	reduced	no
14	B500-SRC		500	staged	reduced	yes
15	B700-LR		700	linear	reduced	no
16	B700-SR		700	staged	reduced	no

<sup>a</sup> Abbreviation of sample name: L, linear, S, staged (heating program); R, reduced, H, high (flow rate); C, covered (sample holder).<sup>b</sup> Heating program: linear, 10 °C min<sup>-1</sup>; staged, 10 °C min<sup>-1</sup> – 350 °C (1 h) – 10 °C min<sup>-1</sup>.<sup>c</sup> N<sub>2</sub> flow rate: reduced, 5 mL min<sup>-1</sup>; high, 400 mL min<sup>-1</sup>.

yield was calculated by difference (gas yield = 100% – char yield – condensate yield). The standard deviations of the biocarbon, condensate and gas yields were determined by performing triplicate carbonization experiments on the S500-LH sample. The standard deviation values of biocarbon, condensate and gas yields were 0.37%, 0.73% and 1.26%, respectively.

### 2.3. Analytical methods

#### 2.3.1. Compositional analysis of the raw material

The carbohydrate contents of the wood samples were determined using a slightly modified NREL method (Sluiter et al., 2012). The samples were treated in a two-step acid hydrolysis with 72% sulfuric acid for 2 h at room temperature and with 4% sulfuric acid for 1 h at 121 °C in an autoclave. The formed suspensions were filtered through G4 glass filter crucibles. The sugar concentrations of the filtrates were analyzed with high-performance liquid chromatography (HPLC) (Agilent 1260 system, Hi-Plex H column) at 65 °C. The solid residues obtained after washing with demineralized water were dried at 105 °C overnight. The dried samples consisted of the acid-insoluble organics and acid-insoluble ash. The amounts of total ash and acid-insoluble ash were obtained by ashing the original samples and the acid-insoluble residues, respectively, at 550 °C until the sample mass was constant (5 h). The Klason lignin content was calculated by subtracting the acid-insoluble ash content from the mass of the dry acid insoluble residue.

#### 2.3.2. Thermogravimetry-mass spectrometry (TG/MS)

The TG/MS measurements were performed by a TGS-2 thermobalance (Perkin Elmer, USA) used with a modified furnace and a Eurotherm temperature controller, which was coupled to a HiQuad quadrupole mass spectrometer (Pfeiffer Vacuum, Germany). Approximately 7 mg biocarbon samples prepared at 400 and 500 °C final temperatures, were measured in a platinum sample pan. Due to the low VM content of biocarbons produced at 700 °C, about 18 mg of these samples were analyzed by TG/MS to obtain an appropriate mass flow for the MS. After a 40 min inertization period, the samples were heated at a 20 °C min<sup>-1</sup> rate from room temperature to 950 °C under argon atmosphere. During the inertization and the measurements, the argon flow rate was 140 mL min<sup>-1</sup>. A portion of the evolved products was introduced into the MS ion source through a glass-lined metal capillary heated at 300 °C. The mass range of *m/z* 2–128 was scanned except some irrelevant ions and the most intensive ions of the argon gas. The ion source of the mass spectrometer was operated in electron impact mode at 70 eV electron

energy. The measured ion intensities were normalized for the mass of the sample and the intensity of the <sup>38</sup>Ar isotope of the carrier gas. The standard deviation of the char yield at 950 °C was 0.3%, which was determined by performing triplicates on the B400-LR sample.

#### 2.3.3. Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS)

Py-GC/MS measurements were carried out by using a CDS Pyroprobe 2000 pyrolyzer equipped with a platinum coil heater and a quartz sample tube. The pyrolyzer was coupled to an Agilent 6890/5973 GC/MS instrument. Approximately 5 mg samples were pyrolyzed for 180 s in a quartz sample tube using helium carrier gas. The biocarbon samples, prepared at 400 and 500 °C final temperatures, were pyrolyzed at 700 °C calibrated temperature (900 °C set value), while biocarbons, prepared at 700 °C final temperature, were pyrolyzed at 800 °C calibrated temperature (1050 °C set value). The temperature of the pyrolyzer chamber was set at 280 °C and the helium flow of the chamber was set at 20 mL min<sup>-1</sup>. The GC injector was held at 280 °C. The pyrolysis products were separated on an Agilent DB-1701 capillary column (30 m × 0.25 mm i. d., 0.25 µm film thickness). The GC oven was programmed to hold at 40 °C for 7 min and then increase to 280 °C at a rate of 6 °C min<sup>-1</sup>. The range of *m/z* 14–500 was scanned by the mass spectrometer in electron impact mode at 70 eV electron energy. The experiments were carried out in triplicates with each sample. The identification of the pyrolysis products was based on the combined Wiley Registry 9th edition/NIST 2011 mass spectral library. The relative yields of the compounds were estimated by calculating the peak integrals of the total ion chromatograms, with the exception of carbon dioxide, carbon monoxide, water, methane, acetone, 2-methylfuran, butan-2-one, acetic acid, and benzene. Due to the overlapping peaks, the quantitative data of the latter compounds were calculated based on peak integrals of single ion chromatograms, which were multiplied by a factor calculated based on the mass spectrum of the corresponding compound. The integrals of each measurement were normalized by the sample mass.

## 3. Results and discussion

### 3.1. Effect of wood species and experimental conditions on the product yields

The effects of carbonization temperature, heating program, flow rate, and open or covered sample holder on the solid, liquid, and gas yields were studied on spruce and birch samples, and the obtained results are illustrated in Fig. 1. As the figure presents, spruce produced

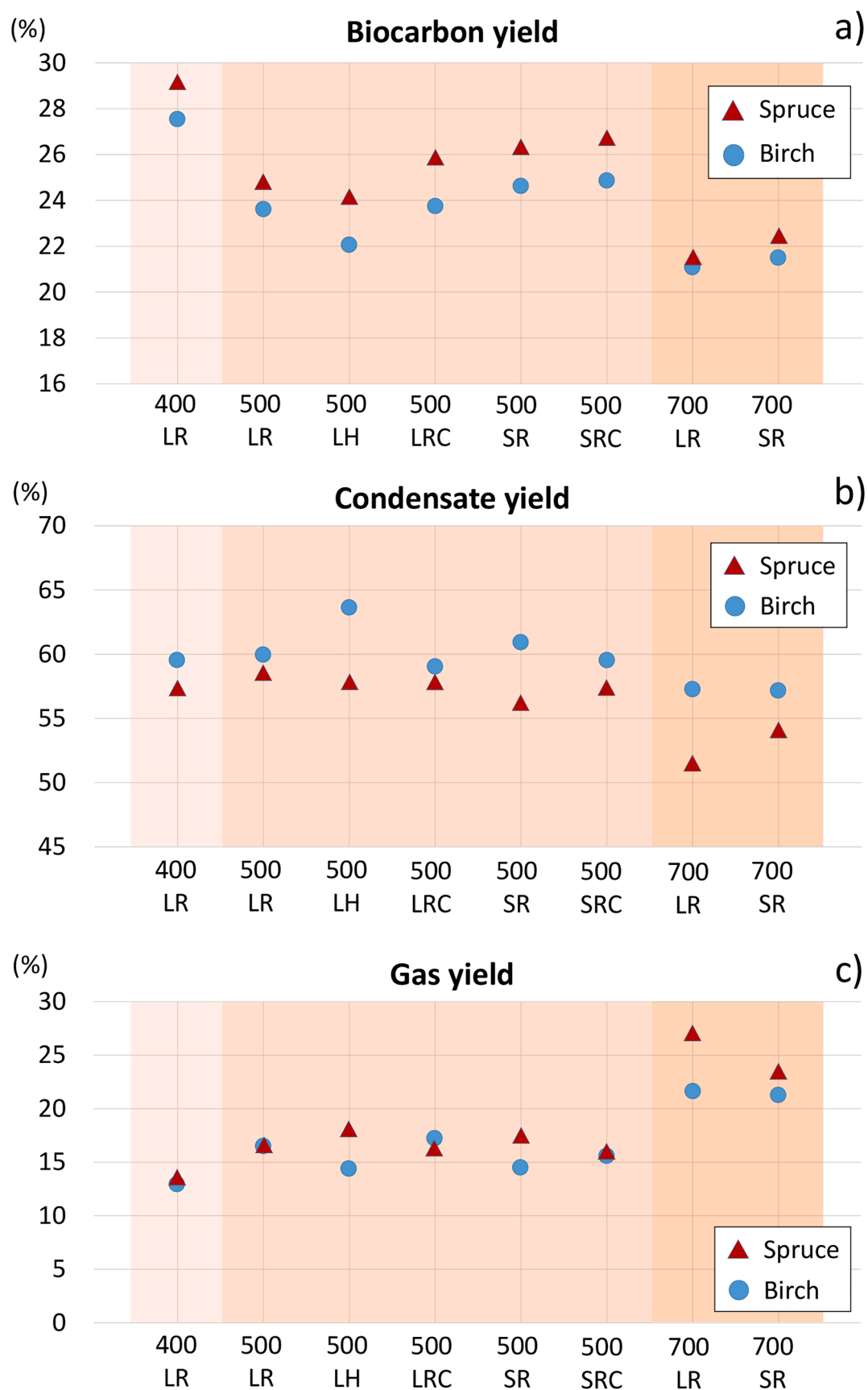


Fig. 1. Yields of (a) biocarbon, (b) condensate, and (c) gas yields of carbonization experiments. The designation of the samples can be found in Table 1.

higher biocarbon yield than birch (Fig. 1a), while the condensate yields from birch was higher than that from spruce in each case under the same experimental conditions (Fig. 1b). The gas yield of spruce and birch (Fig. 1c) was similar in the carbonization processes performed at 400 or 500 °C final temperatures, while spruce released higher amount of gas than birch when the final temperature was 700 °C. Table 2 summarizes the carbohydrate, Klason lignin and ash contents of the raw spruce and birch samples. The most significant compositional differences between spruce and birch were found in their Klason lignin content, which is one and a half times higher in spruce than in birch, in accordance with the usually higher lignin content of gymnosperms compared to angiosperms (Lourenco and Pereira 2018). The cellulose content of the two wood samples is similar, while spruce contains about 4% less hemicellulose than birch. The higher biocarbon yield of the softwood spruce compared to that of the hardwood birch can be explained by the significantly higher lignin content of spruce, as among the main biopolymer components of lignocellulosic materials, lignin contributes the most to the char formation (Raveendran et al., 1996). It is also in accordance with the finding that higher yield of charcoal can be obtained when species with high lignin and/or low hemicellulose content are used as feedstock (Mok et al., 1992).

The condensate contains the volatile extractives, their degradation products and the thermal degradation products of carbohydrates (cellulose and hemicellulose) and lignin. The studied birch sample contained higher amount of “other” compounds compared to spruce. This designation stands for all acid-soluble substances, except carbohydrates and ash, such as acid-soluble extractives and acid-soluble lignin content of the raw wood samples. According to the literature, the proportion of extractives is higher in the stem of birch compared to spruce (Routa et al., 2017). Extractives are low molecular mass compounds such as terpenes, phytosterols, flavonoids, alkaloids and phenol derivatives (Mészáros et al., 2007b). These compounds have relatively low molecular mass and may evaporate or decompose to volatile products and a small amount of char. Both the higher extractive content and the lower lignin content may have resulted in the higher amount of condensed products in the case of birch samples.

The comparison of the obtained biocarbon yields (Fig. 1a) of the same feedstock demonstrates that the final carbonization temperature was the most important factor influencing the char yield. By increasing the final temperatures, the carbonization processes proceeded with further decomposition of biomass sample, resulting in a decreased char yield in agreement with the results obtained on tea pruning litters (Borgohain et al., 2020). In term of gas yield (Fig. 1c), an opposite tendency was found by increasing the final temperatures, increased gas yield was measured. Similar tendencies were found in a 350–550 °C temperature range (Mašek et al. (2013)) pyrolyzing pine and spruce wood chips. The gas yield was more pronounced at 700 °C final temperature, since the carbonization processes produce higher yield of small molecular mass gaseous products at 700 °C, while the condensate yield was smaller than at 500 °C. However, it should be noted that the mass of condensates (Fig. 1b) was about twice as much as that of the gaseous products (Fig. 1c) at 700 °C.

The biocarbon yields obtained by using the same final temperature (500 or 700 °C), but different process conditions, indicate the effect of

the varied factors on the carbonization process (Fig. 1a). Increasing the nitrogen flow rate from 5 mL min<sup>-1</sup> to 400 mL min<sup>-1</sup> resulted in decreased solid yields for both spruce (S500-LR vs. S500-LH) and birch (B500-LR vs. B500-LH). Nevertheless, loosely covering the quartz sample vessel with a quartz lid (S500-LRC and B500-LRC) had an opposite effect and increased char yields were observed. The reason for the changed char yield in both cases could be the varied residence time of the releasing volatile compounds near the surface of the pyrolyzing solid char sample. The 80-fold higher flow rate (samples S500-LH and B500-LH) significantly shortened the residence time of the volatiles by rapidly flushing the volatile decomposition products away from the reaction zone. Covering the sample holder with a lid hindered the release of volatile products from the reaction zone, increasing their residence time in this way. The longer residence time enhanced the possibility of recondensation and secondary reactions of tarry vapors, which led to the higher solid yield. In the opposite way, the shortened residence time of the volatiles decreased the possibility of these reactions and reduced the char yield.

In order to slow down the reaction rate and extend the sample residence time, an isothermal period was applied at a temperature, where the thermal decomposition process is intense. Thus, the positive effect of slowing down the heating rate on the char yield (Williams and Besler, 1996) could prevail. Moreover, the selected temperature is in a range, where the greatest increase was found by two-staged pyrolysis (Elyounssi et al., 2012). Hence, a 1 h isothermal period was inserted at 350 °C into the pyrolysis programs, which had 500 and 700 °C final temperatures. This so-called staged pyrolysis had a positive effect on the char yield at both final temperatures and using either spruce (S500-SR and S700-SR) or birch (B500-SR and B700-SR) feedstock (Fig. 1a). The highest biocarbon yield was obtained at 500 °C final temperature by applying the staged pyrolysis program and covering the sample vessel with a lid (S500-SRC and B500-SRC).

### 3.2. Characterization of the biocarbon samples by TG/MS

The mass loss characteristics and the evolution profiles of the released products were characterized by TG/MS. Fig. 2 presents the TG and DTG curves of spruce and birch biocarbon samples produced applying linear heating program, reduced flow rate of purge gas and 400, 500 or 700 °C final temperatures. The moisture content was released up to 130 °C and the evolution of compounds strongly adsorbed in the pores of biocarbons took place before the start of the thermal degradation and further carbonization, which is indicated by the rising DTG curve. This carbonization step started at around the final

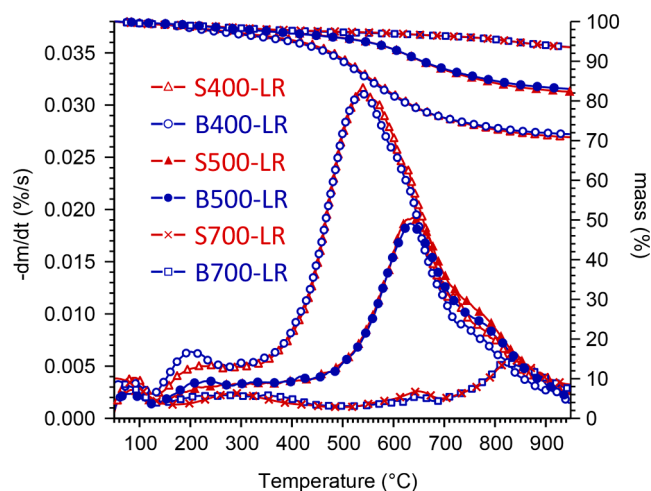


Fig. 2. TG and DTG curves of spruce and birch biocarbons produced at 400, 500 and 700 °C applying linear heating rate and 5 mL min<sup>-1</sup> nitrogen flow.

Table 2

Organic composition and ash content of raw spruce and birch biomass calculated on dry basis. Values are given in percentages with standard deviation.

Sample	Cellulose	Hemicellulose	Klason lignin	Ash	Other <sup>a</sup>
Spruce	40.1 ± 0.5	20.3 ± 0.1	31.1 ± 0.5	0.35 ± 0.01	8.0 ± 0.7
Birch	38.6 ± 0.2	24.2 ± 0.1	19.5 ± 0.1	0.44 ± 0.01	17.3 ± 0.2

<sup>a</sup> Calculated as a difference.



temperature of the carbonization process of the given biocarbon sample. The samples S400-LR and B400-LR started to decompose at around 400 °C; the samples S500-LR and B500-LR had enhanced degradation above 500 °C, and the increased devolatilization of samples S700-LR and B700-LR commenced over 700 °C. The dynamically decreasing DTG values of samples S500-LR, B500-LR and that of S700-LR and B700-LR clearly indicates the gradually developing carbonization process by increasing the final temperature of the carbonization.

Fig. 3 compares the volatile matter content of the biocarbon samples. As expected, the residual VM content of the biocarbons decreased with increasing carbonization temperature. Spruce samples prepared at 400 and 500 °C contained slightly more VM than the birch samples did (by 0.7–2.3%) comparing biocarbons prepared under the same process conditions. The possible reason of these findings could be the difference in the lignin contents of the spruce and birch wood. Lignin decomposition takes place in a wide temperature range, and it is not completed by 500 °C. Therefore, the thermal degradation of the higher amount of lignin residue in spruce samples might result in a slightly higher VM content. However, during the carbonization process performed at 700 °C, the lignin content is almost fully decomposed, and the VM contents of both spruce and birch biocarbons became similar.

The evolution profiles of the released gases and vapors from the biocarbon samples under gradual heating are presented in Figs. 4 and 5. The TG/MS ion intensity curves of biocarbons produced at 400 °C (S400-LR and B400-LR) and 500 °C (S500-LR and B500-LR) are visible in Fig. 4. The  $m/z$  18 ion intensity curve indicates that the moisture content was released up to about 130 °C from the samples. Evolution of water adsorbed in the pores was detected up to 400 °C from both spruce and birch biocarbons prepared at 400 °C (Fig. 4a and b). The raised evolution profile of carbon dioxide below 400 °C indicates that besides water the adsorption of this compound is also significant on the surface and in the pores of the char. The samples experienced at least 400 °C for 1 h isothermal period during carbonization; therefore, the evolution of decomposition products in significant amount is not expected below the carbonization temperature. No volatile products were released below the heat treatment temperature when the biomass sample was heat treated in the thermobalance and the TG experiment was performed after cooling down without removing the sample from the furnace, while the system was continuously purged (Babinszki et al., 2020). Both spruce and birch biocarbons produced at 500 °C released water and

carbon dioxide continuously up to higher temperatures (Fig. 4e and f).

Raised decomposition rate was observed from birch biocarbon (B400-LR) compared to spruce biocarbon at around 200 °C, indicated as a characteristic hump on the DTG curve (Fig. 4c and d). The ion intensity curve of  $m/z$  60 represents the molecular ion of acetic acid, which was evolved in this temperature range. During the thermal decomposition of lignocelluloses, the main acetic acid sources are the acetyl groups of hemicellulose and lignin. *O*-acetyl-4-*O*-methylglucuronoxylan is the principal hemicellulose component of birch (Sjöström, 1993), which releases significant amount of acetic acid during its thermal decomposition. The maximal rate of acetic acid evolution from the B400-LR sample was at around 200 °C, which is a much lower temperature than the sample experienced during the carbonization experiment (400 °C). Therefore, the eluting acetic acid probably formed during carbonization and condensed on the cooler part of the quartz reactor tube before being adsorbed on the surface of the biocarbon during the cooling period. Spruce hemicellulose consists of galactoglucomannan, arabinoglucuronoxylan, and some other types of hemicelluloses (Sjöström, 1993), which contain less *O*-acetyl groups in the structure; hence, release less acetic acid during thermal decomposition. The signal of acetic acid evolution from the S400-LR sample was below the noise level of the mass spectrometer.

At higher decomposition temperatures, besides water and carbon dioxide, carbon monoxide, methane (Fig. 4a and b), and aromatic compounds like benzene, toluene and phenol (Fig. 4c and d) were also released from biocarbons produced at 400 °C, similarly to other high VM charcoals (Mészáros et al., 2007a). The intensities of the evolved aromatic compounds were higher from spruce biocarbon compared to birch biocarbon. Phenol is a degradation product of the lignin residue of carbonized samples. The higher lignin residue of spruce biocarbon sample resulted in higher phenol yield during the TG/MS experiment in comparison with birch biocarbon sample. In the final stage of the decomposition of the biocarbons, further carbonization took place indicated by the evolution of hydrogen above 500 °C and a slightly increased carbon monoxide formation at about 800 °C.

The TG, DTG and the evolution profile curves of the biocarbon samples produced at 500 °C under various conditions are barely different; therefore, only the results of S500-LR and B500-LR samples are presented in Fig. 4e and f. Besides the formation of gases and water, only benzene evolution was detected by TG/MS from these samples,

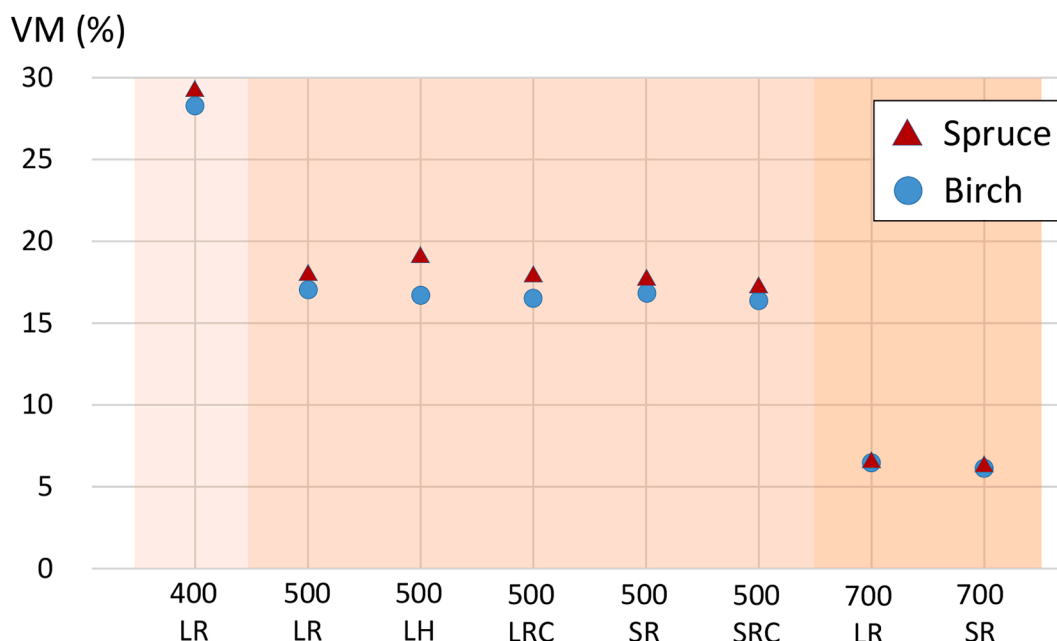
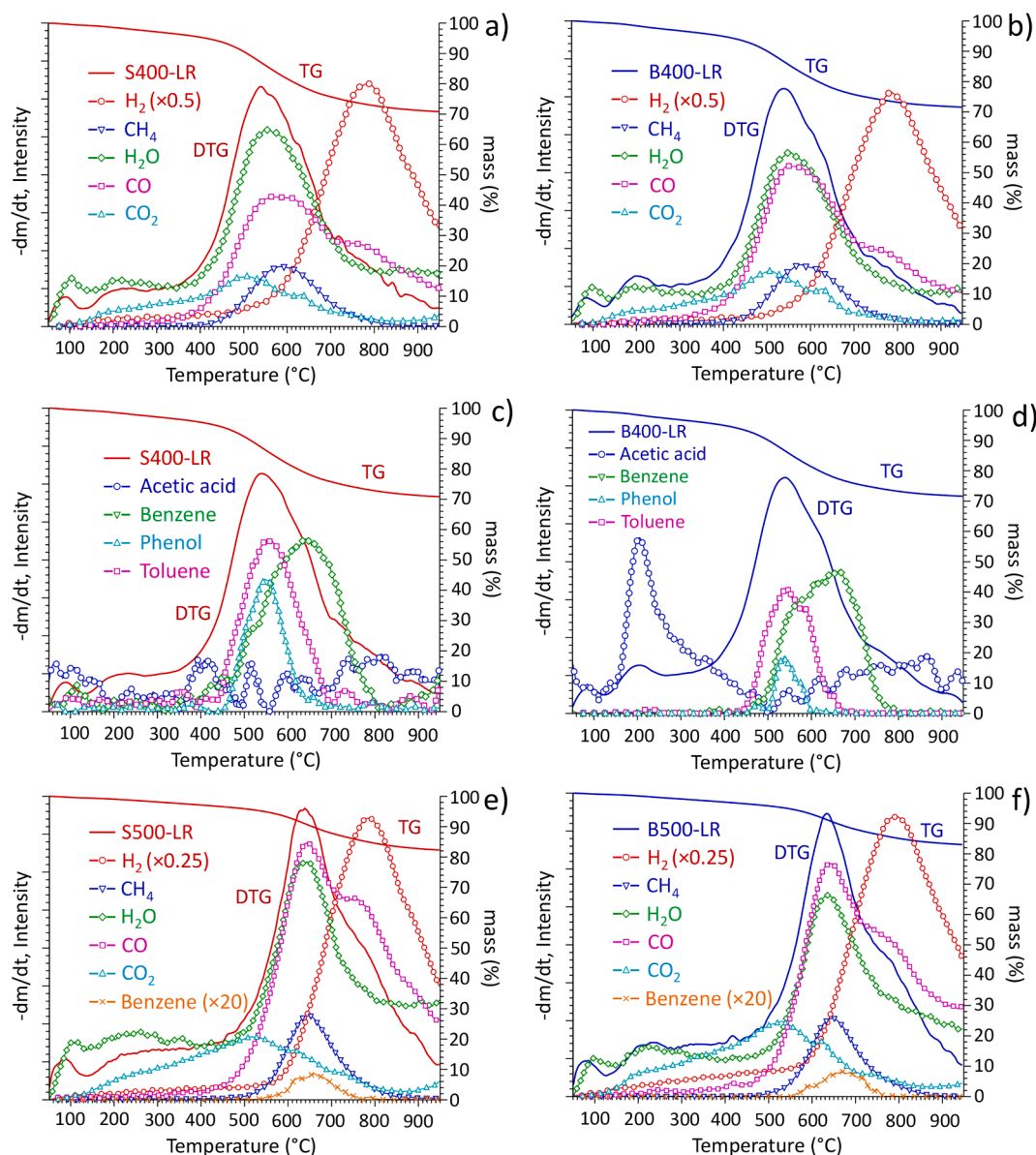


Fig. 3. Volatile matter (VM) content of the biocarbons measured up to 950 °C.



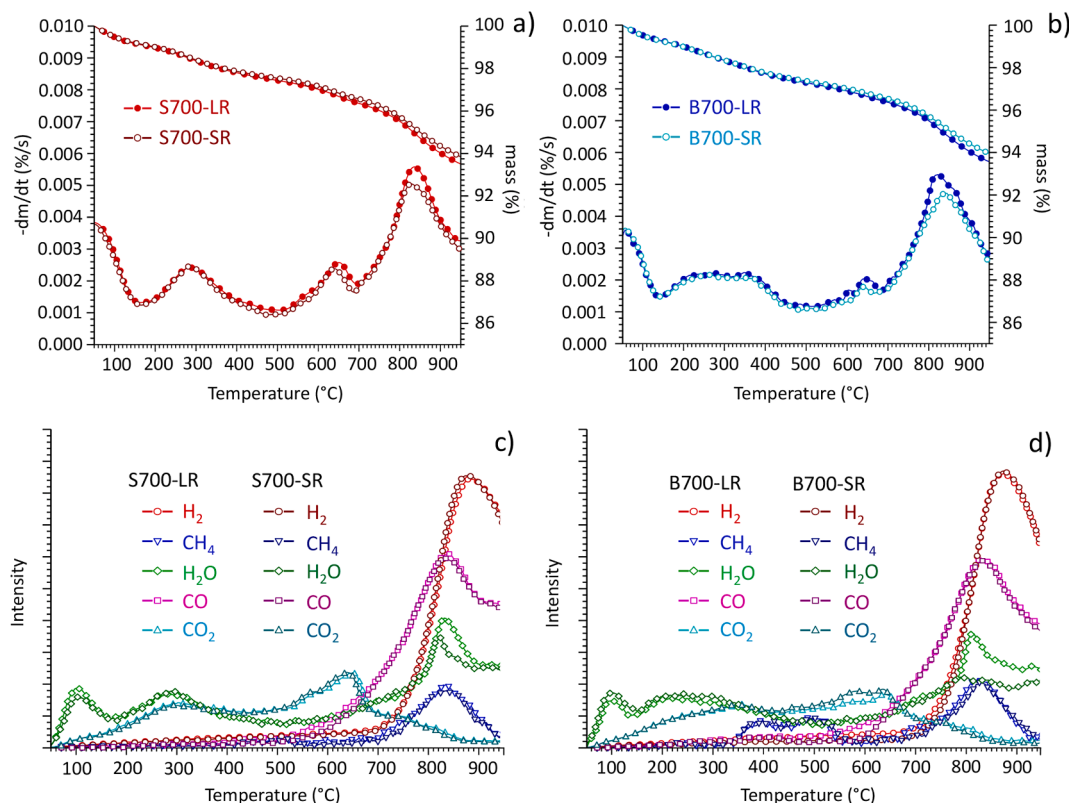
**Fig. 4.** TG, DTG and ion intensity curves of (a, c, e) spruce and (b, d, f) birch biocarbons produced at 400 and 500 °C final temperature applying linear heating rate and 5 mL min<sup>-1</sup> nitrogen flow.

while the yield of phenol was under the detection limit due to the advanced degradation of lignin at the carbonization temperature of 500 °C.

The TG, DTG curves and the evolution profiles of the biocarbon samples produced at 700 °C temperature are presented in Fig. 5. The formation of gaseous products and water was only detected, as Fig. 5c and d illustrate. The comparison of the TG/MS curves of biocarbons in Figs. 4 and 5 shows that unambiguous tendencies can be observed as a function of the carbonization temperature. The higher the carbonization temperature, the higher the temperature of the maximal rate of evolution of methane, water, and carbon monoxide from the biocarbons. The temperature of the maximal rate of hydrogen evolution was at around 780 °C from the samples carbonized at 400 and 500 °C, while it was about 880 °C from the samples produced at 700 °C. At higher temperatures, carbon dioxide formed by the degradation of residual organic moieties from samples prepared at 400 and 500 °C, but it could be the decomposition product of carbonates at about 600–700 °C. Above 600 °C, the intensity of carbon dioxide decreased in favor of carbon monoxide formation due to the Boudouard reaction (Rao et al., 1982).

The TG and DTG curves of spruce and birch biocarbon samples prepared using linear and staged pyrolysis programs and 700 °C final temperature are compared in Fig. 5a and b. The comparison of the samples prepared by linear and staged pyrolysis shows that the TG and DTG curves coincide up to 600 °C, then slightly diverge at higher temperatures in the case of both spruce and birch biocarbon samples. In both cases, the difference in the VM content was about 0.4% at 950 °C final temperature; the samples prepared using staged pyrolysis program had a lower VM content. The difference was small, but reproducible. The DTG curves indicate that the higher decomposition rate difference was at around 800 °C for the studied spruce and birch biocarbon samples.

Fig. 5c and d present the evolution profiles of water and the main gaseous products of spruce (S700-LR, S700-SR) and birch (B700-LR, B700-SR) biocarbons. The evolution curves of carbon monoxide, carbon dioxide, methane and hydrogen coincide in the whole temperature range in the case of both spruce (S700-LR, S700-SR) and birch (B700-LR, B700-SR) biocarbon samples. This finding indicates the very similar degradation rate and adsorption properties of the samples in ambient air. In addition, the figure indicates the good reliability of the TG/MS ion



**Fig. 5.** (a, b) TG, DTG and (c, d) ion intensity curves of spruce and birch biocarbon samples produced by using linear and staged pyrolysis programs and 700 °C final temperature.

curves. The evolution curves of water were also very similar up to about 750 °C, while more water was released at higher temperatures from the S700-LR and B700-LR biocarbons than from the S700-SR and B700-SR biocarbons, respectively. This difference indicates that probably less hydroxy groups remained in the biocarbon samples prepared by staged carbonization program than in the samples produced by linear heating program. It is in agreement with Brunner's and Roberts' (1980) results, that cellulose char prepared under slow heating rate has lower O/C ratio compared to the char produced at high heating rate. Our finding provides additional information about the chemical form of the decreased oxygen content, and may explain why low heating rate has a positive effect on the biochar stability particularly at high pyrolysis temperature (e.g., at 650 °C) (Crombie et al., 2015).

### 3.3. Characterization of the volatiles by Py-GC/MS

The detailed volatile content analysis of the produced biocarbon samples was performed by Py-GC/MS analysis. The decomposition of the wood samples was fairly advanced during carbonization performed at and above 400 °C. However, the volatile content of the carbonized wood prepared at various temperatures differed both in the number and in the amount of the released organic compounds in agreement with the results of thermogravimetry (Fig. 3) and literature data (Fabbri et al., 2012; Conti et al., 2016).

Py-GC/MS showed that the major volatile degradation products were carbon dioxide, carbon monoxide, water, methane, benzene, toluene, and naphthalene from each biocarbon. Additionally, only traces of biphenyl and methyl-naphthalenes were detected during the pyrolysis of biocarbon prepared at 700 °C. Pyrolysis of S500 and B500 samples evolved more compounds than S700 and B700 samples did, but yet in small amounts, which were uniformly aromatic compounds and their methylated derivatives: dibenzofuran, aromatic hydrocarbons with 3 and 4 fused rings, phenol, and xylenes. The pyrolyzate of S400-LR and

B400-LR also contained phenol, methylphenols, and xylenes in significant amounts. Remarkable amount of acetic acid was released especially from B400-LR. In addition, birch biocarbon evolved small amounts of furfural, which is a characteristic carbohydrate decomposition product (Kaal et al., 2012), while spruce biocarbon did not. Probably, birch biocarbon contained more carbohydrate residue than spruce charcoal in agreement with the higher hemicellulose content of birch.

The pyrolysis results of the biocarbon samples confirmed that the benzene/toluene ratio showed good positive correlation with the carbonization temperature (Rathnayake et al. 2020), while the decreasing benzofuran/naphthalene ratio indicated the development of deoxygenation (Conti et al., 2016) at higher temperature.

A total of 80 compounds was detected in the pyrolyzate of S400-LR and B400-LR samples. In order to compare the volatile compositions of the produced biocarbons, the detected compounds were grouped into several classes based on structural similarity. The relative amounts of the compound groups including the identified decomposition products are presented in Table 3. The data shows the effect of carbonization temperature on the compound yields, when the same experimental conditions were applied except the final temperature. Both S400-LR and B400-LR contained much more volatile organic compounds than biocarbons produced at higher temperatures. Beside the presence of aromatic hydrocarbons, the ratio of phenolics was significant. It should be noted that the characteristic decomposition products of lignin (Brebu et al. 2013; Jiang et al., 2010), the methoxyphenols were not evolved from these biocarbons. Only methylphenols were detected, which can be related to the degradation of lignin during carbonization. Despite spruce and birch wood differ in composition, the fingerprint and distribution of volatiles in S400-LR and B400-LR samples presented small differences. However, the higher lignin content in spruce resulted in a significantly higher yield of phenolics in S400-LR than in B400-LR (Table 3).

S500-LR devolatilized less organic compounds in each group than B500-LR did. In general, all of the biocarbons prepared at 500 °C



**Table 3**

Relative peak integral values of the pyrolysis products of spruce and birch biocarbons prepared under the same experimental conditions at 400, 500, and 700 °C.

Pyrolysis products	S400-LR	S500-LR	S700-LR	B400-LR	B500-LR	B700-LR
Gases <sup>a</sup> and water	71 ± 4	48 ± 3	50 ± 7	73 ± 7	67 ± 2	44 ± 4
MAH <sup>b</sup>	9.7 ± 0.6	3.7 ± 0.3	0.06 ± 0.01	8.7 ± 1.1	5.0 ± 0.2	0.11 ± 0.03
PAH <sup>c</sup>	5.1 ± 0.3	1.1 ± 0.1	0.02 ± 0.00	4.8 ± 0.5	1.5 ± 0.1	0.04 ± 0.01
Phenolics	9.6 ± 0.4	0.11 ± 0.01	BDL <sup>d</sup>	6.9 ± 0.7	0.15 ± 0.01	BDL <sup>d</sup>
Heteroaromatics	2.6 ± 0.1	0.21 ± 0.03	BDL <sup>d</sup>	2.3 ± 0.2	0.32 ± 0.01	BDL <sup>d</sup>
Ketones	1.0 ± 0.0	BDL <sup>d</sup>	BDL <sup>d</sup>	1.2 ± 0.1	BDL <sup>d</sup>	BDL <sup>d</sup>
Acetic acid	0.9 ± 0.1	0.03 ± 0.01	BDL <sup>d</sup>	1.8 ± 0.3	0.51 ± 0.04	0.01 ± 0.00
Sum	100 ± 5	53 ± 3	50 ± 7	99 ± 9	75 ± 2	44 ± 4

Data are related to the values of S400-LR. Abbreviation of sample name: L, linear heating program; R, reduced flow rate.

<sup>a</sup> Including carbon dioxide, carbon monoxide, and methane.

<sup>b</sup> Monocyclic aromatic hydrocarbons.

<sup>c</sup> Polycyclic aromatic hydrocarbons.

<sup>d</sup> Less than 0.01% or below the detection limit.

released a sharply reduced amount of oxygen-containing molecules. Biocarbons of both spruce and birch produced at 700 °C had the lowest content of aromatic hydrocarbons (Table 3). It should be noted additionally that both S700-SR and B700-SR had a reasonably similar volatile composition than S700-LR and B700-LR had, respectively, showing that the application of linear heating program or staged pyrolysis up to 700 °C did not affect the composition of biocarbons.

The effect of experimental conditions on the volatile composition is presented for samples prepared at 500 °C in Table 4, which shows data of the organic decomposition products given in area-% values. It can be established that the aromatic compositions of the pyrolyzates are very close to each other and benzene represents more than half of the pyrolyzate amount in all cases. Nevertheless, the yields of acetic acid shed light on some essential differences.

As the TG/MS results revealed, acetic acid is supposed to be a desorbing product of the pyrolysis of biocarbon. It could be formed during the biocarbon preparation, and was partially adsorbed by the solid product. A changing acetic acid yield was measured from the studied biocarbons produced at different carbonization conditions, but the series of spruce and birch biocarbon samples change uniformly in the extent of acetic acid release: LH < LRC < SRC < SR < LR. The highest acetic acid content was in the samples prepared at linear heating rate and reduced flow of nitrogen purge gas (LR), when the low flow rate, the free diffusion, and the open sample container allowed the adsorption of tar components. The use of a relatively high flow rate of purge gas (LH) sharply reduced the adsorption of the decomposition product formed during the carbonization. Covering the vessel at a low flow rate of nitrogen (LRC, SRC) was also effective in keeping acetic acid at bay. The major part of acetic acid forms in the lower temperature range due to biomass degradation, which is then removed by the intense release of decomposition products from the vessel at higher temperatures. Finally, the lid of the sample holder hinders the back diffusion into its volume, thereby hampers also the adsorption of tar components. It should be noted that the yields of furfural are also in correlation with the low and high purge gas rates (LR and LH), hence furfural is supposed to be an adsorbed carbonization product. However, its intensity is an order of magnitude smaller than that of acetic acid.

We can establish that the experimental conditions may affect the volatile content of the produced biocarbon by adsorbing a small portion of the volatile decomposition products of biomass especially when a low

**Table 4**

Comparison of volatile compositions (area-% without gases and water) of spruce and birch biocarbons prepared at different experimental conditions, but at the same final temperature (500 °C).

Pyrolysis products	S500-LR	S500-LRC	S500-SR	S500-SRC	S500-LH
Benzene	54 ± 3	55 ± 0	58 ± 6	60 ± 7	56 ± 2
ASB <sup>a</sup>	17.8 ± 1.0	19.2 ± 0.5	17.3 ± 1.6	15.9 ± 1.6	19.5 ± 0.6
PAH <sup>b</sup>	21.2 ± 1.8	20.3 ± 0.2	17.9 ± 1.9	18.4 ± 1.1	18.4 ± 0.7
Phenolics	2.1 ± 0.3	1.6 ± 0.2	2.7 ± 0.7	2.3 ± 0.1	2.4 ± 0.2
Heteroaromatics	4.1 ± 0.5	3.7 ± 0.3	3.8 ± 0.6	3.2 ± 0.2	3.7 ± 0.2
Acetic acid	0.6 ± 0.2	0.08 ± 0.06	0.3 ± 0.1	0.17 ± 0.01	0.04 ± 0.01
Sum (%)	100.0	100.0	100.0	100.0	100.0
Pyrolysis products	B500-LR	B500-LRC	B500-SR	B500-SRC	B500-LH
Benzene	53 ± 1	52 ± 2	55 ± 9	55 ± 5	57 ± 2
ASB <sup>a</sup>	14.4 ± 0.4	17.1 ± 0.9	13.0 ± 1.8	15.2 ± 0.4	19.4 ± 0.2
PAH <sup>b</sup>	19.7 ± 0.4	22.9 ± 0.9	20.0 ± 1.6	21.2 ± 1.0	18.9 ± 0.1
Phenolics	2.0 ± 0.1	1.9 ± 0.4	2.0 ± 0.4	2.5 ± 0.0	1.4 ± 0.1
Heteroaromatics	4.3 ± 0.1	3.7 ± 0.3	3.5 ± 0.3	3.4 ± 0.2	2.8 ± 0.1
Acetic acid	6.8 ± 0.5	1.9 ± 0.5	6.5 ± 1.4	2.6 ± 0.2	0.01 ± 0.00
Sum (%)	100.0	100.0	100.0	100.0	100.0

Abbreviation of sample name: L, linear, S, staged (heating program); R, reduced, H, high (flow rate); C, covered (sample holder).

<sup>a</sup> Alkyl and alkenyl substituted benzenes.

<sup>b</sup> Polycyclic aromatic hydrocarbons.

flow rate of purge gas is applied. In addition, a biomass producing relatively high acetic acid level during carbonization (e.g., birch wood) might result in a biocarbon containing unexpectedly high acid content, which can cause corrosion during utilization of the produced biocarbon.

#### 4. Conclusions

Staged pyrolysis, low flow rate or covered sample holder increased the char yield of spruce and birch. Spruce biocarbons prepared at 400 and 500 °C had higher VM content due to their higher lignin residue, as verified by TG/MS. Biocarbons prepared by staged pyrolysis using 700 °C final temperature had lower VM and released less water above 800 °C. There were minor differences in the VM content of birch and spruce biocarbons. More acetic acid and less phenol were released from birch biocarbons. The relative amount of aromatic and polyaromatic pyrolysis products drastically decreased by increasing the carbonization temperature.

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#### CRediT authorship contribution statement

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## Declaration of Competing Interest

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

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.biortech.2021.125567>.

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