



Characterization of the pyrolysis condensates of birch, spruce and pine bark: Impact of water leaching on the composition

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ABSTRACT

Biocarbon, produced via the pyrolysis of lignocellulosic biomass, is increasingly sought as a sustainable reductant in metallurgical industries. The production of biocarbon also generates significant amounts of condensable liquid by-products, which can be valuable materials subject to detailed characterization and proper upgrading. The current biocarbon production relies mainly on stem wood, but alternative biomass materials of sufficient quality, high availability, and low costs are needed. Bark, a major forestry residue, is a potential feedstock candidate for biocarbon production; however, its high mineral content is a drawback for several industrial applications.

In the present work, bark chips of birch, spruce, and pine wood were pyrolyzed in a fixed bed reactor collecting both solid and condensed liquid products. The amount of inorganic elements present in the barks was reduced by an industrially feasible static water leaching method. The chemical composition of the condensates of both leached and unleached bark samples were compared by using GC/MS analysis. A comparison of the composition of bark and stem wood condensates revealed that the summed organic content measured in the bark condensates was much less than that of stem wood. The analysis of bark condensates showed that the birch bark condensates had significantly higher acid content than the bark condensates of conifers, i.e., spruce and pine. The concentration of specific condensate components showed different changes depending on the leached feedstock type. The reduced mineral contents in the leached barks affected the thermal decomposition during pyrolysis, resulting in modest changes in condensate compositions.

1. Introduction

In recent years, increasing attention has been directed toward the production and application of biocarbon derived from biomass as a sustainable alternative to fossil-based reductants in metallurgical industries [1]. Biocarbon is typically produced through thermochemical conversion processes leading to carbonization, such as pyrolysis of lignocellulosic feedstocks. However, its large-scale deployment in metallurgical industries remains limited by inherent drawbacks, like relatively high contents of inorganic impurities and low mechanical strength. Reducing ash content prior to pyrolysis can be an effective way to enhance both the performance and economic viability of the resulting biocarbon as a final product with desired quality.

At present, stem wood is primarily used as feedstock for large-scale

biocarbon production, which is also in demand for the production of other higher-value products. In order to ensure a stable and sustainable supply of biocarbon for energy- and material-intensive metal industries, greater emphasis should be placed on utilizing low-grade biomass as an alternative feedstock [2,3]. Bark, which constitutes approximately 9–21% dry mass of a tree depending on species, is generated in large quantities as a by-product of forestry, sawmilling, and the pulp and paper industries [4]. Globally, millions of tons of bark are produced each year, yet its utilization remains limited, with much of it being landfilled, openly burned, or used as low-grade fuel [5]. Given its lignocellulosic structure and relatively high carbon content, bark represents a promising renewable feedstock for bioenergy production. Its effective utilization could provide a sustainable energy source, reduce waste, enhance resource efficiency in the forestry sector, and contribute to greenhouse

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gas mitigation [4]. However, compared to stem wood, bark typically has higher contents of inorganic elements and exhibits greater compositional variability. Stem wood of birch and spruce typically contains 39–44 % cellulose, 20–35 % hemicellulose, 20–31 % lignin, 1–2 % extractives and 0.1–0.4 % ash [6–9]. The composition of bark is considerably different than that of stem wood, especially in terms of extractive and inorganic content. Bark contains much higher amounts of extractives, which can vary from few percentages up to 40 % depending on the specific part of the bark (i.e., outer bark or inner bark) [10]. Birch bark contains less carbohydrates, and similar or slightly more lignin in comparison to birch stem wood [6,11]. Furthermore, bark has higher inorganic content compared to stem wood, which contributes to increased ash production during combustion [12–14]. These differences are influenced by several factors such as tree species, geographic origin, tissue type, harvesting season, and growth conditions.

The issue of high ash content is particularly acute when biocarbon is produced from unconventional or low-grade biomass feedstocks, which often have a high concentration of specific inorganic elements. Biomass naturally contains mineral matter originating from both intrinsic physiological accumulation and external contamination during growth and handling [2]. Alkaline and alkaline earth metals (AAEMs), together with phosphorus, are dominant, as they play essential roles in plant growth and nutrition. To mitigate the adverse effects of these inorganic constituents on biocarbon quality, a range of demineralization strategies has been explored, with washing and leaching emerging as the most effective approaches [2,15]. Among these procedures, water and acid leaching have been the most extensively investigated. In particular, water leaching is widely recognized for its simplicity, low cost, operational efficiency, and effectiveness in removing water-soluble inorganic species such as sodium, potassium, and sulfur. Numerous studies have demonstrated the benefits of washing pretreatments in improving biomass quality for thermochemical conversion. For example, studies on agricultural residues, grasses, and aquatic biomass have shown that water leaching can remove more than 90 % of potassium, chlorine, and sodium, while reducing 10–70 % of calcium, magnesium, phosphorus, and silicon [15]. The process also removes significant amounts of extractable organic material along with the inorganics [16].

Previous investigations have highlighted species-dependent responses to demineralization. For example, Liu and Bi [17] reported that water leaching of pine bark removed less than 10 % of total ash, whereas acid washing achieved reductions of 36–54 %. Similarly, Singhal et al. [15] found that static water leaching of spruce bark for 180 min reduced the total ash content by up to 18%, with removal efficiencies of 85 % for sodium, 57 % for potassium, 48 % for magnesium, and 20 % for phosphorus. Therefore, it has been shown that a static leaching method can make clear impacts on properties of biomass materials. A particular advantage of static leaching is that it can ensure the proper control of contact time of feedstock with water. If it is applied for wood chips, static leaching can be performed without considerable destruction of initial structure of feedstock and significant loss of material upon filtering. Although, the removal of water-soluble inorganics from wood bark (both powder and chips) is more effective with a long duration, no significant improvement can be expected if the leaching time is over 60 min [15,16]. Whereas the leaching temperature can play a more significant role. Therefore, static leaching of bark chips was conducted in this work with warm water for 60 min with the purpose of using an industrially feasible procedure regarding technological simplicity and cost effectiveness.

Besides reducing ash-forming elements, leaching significantly influences pyrolysis behavior by altering decomposition kinetics, product distribution, and the physicochemical properties of the resulting fractions. Water-leached biomass tends to decompose more slowly and releases volatiles at higher temperatures, highlighting the catalytic role of AAEMs in lowering pyrolysis activation energy [18].

The composition and yield of the carbonization products are primarily determined by feedstock chemical composition and pyrolysis

parameters (e.g., heating rate, pyrolysis temperature, type of reactor) [19,20]. Most studies focused primarily on the effects of leaching on the raw material and its carbonization products properties. However, only a few studies reported about how leaching pretreatments affect the bark-derived condensate products [21]. The detailed compositional analysis of bark condensates represents a critical knowledge gap, as the characteristics of the condensate directly determine its usability and the suitable upgrading method needed for its utilization, e.g., as a binder for use in metallurgical industry. The liquid by-products of biocarbon production can be valuable materials with detailed characterization and proper upgrading [22].

In this work, leached and unleached birch, spruce, and pine bark chips were pyrolyzed in a fixed bed reactor. This feedstock size and a simpler method for pretreatment as static water leaching were chosen as being feasible for a pilot-scale application. Although this leaching procedure is less effective for the mitigation of inorganics, the goal of this case study was testing an industrially feasible method for bark leaching regarding technological simplicity, resource intensity, and cost effectiveness. The liquid products from the pyrolysis experiments were condensed, collected, and analyzed by using a gas chromatograph coupled with a mass spectrometer (GC/MS). The GC/MS technique itself is insufficient for the complete chemical characterization of biomass condensates; however, it provides relevant information about a significant volatile fraction of this material, allowing for the identification of a broad range of compounds with different functional groups [23]. Based on the comparison of the chemical compositions of the different condensates, the effect of feedstock water leaching on the condensates produced was studied. Characteristic compositional differences between the condensates of bark and stem wood were also shown by examples of a broadleaf and a coniferous wood species, i.e., birch and spruce, respectively. The comparative analysis of the pyrolysis condensates produced from different raw materials under identical pyrolysis conditions revealed the significance of the feedstock type on the condensate composition and the effect of the leachable materials on the thermal decomposition process. The presented work aims to provide useful data for the biocarbon industry to widen feedstock selection and for the utilization of pyrolysis condensates.

2. Materials and methods

2.1. Materials

Birch wood (*Betula pubescens*), spruce wood (*Picea abies*) and Scots pine wood (*Pinus sylvestris*) samples originating from a forest in South Norway (Hobøl, 59°35'35"N 10°56'45"E) were studied. After harvest, the trunk was debarked to obtain separated stem wood and bark. The separated stem wood and bark were cut into chips. Approximately 3–5 cm pieces of stem wood and 2–3 cm pieces of bark were selected as feedstock for carbonization. The chips were air-dried at room temperature to about 15 % moisture, followed by oven drying at 105 °C for 16 h. The leaching and carbonization experiments were performed with chips of birch bark (BB), spruce bark (SB), and pine bark (PB). For comparison, the stem wood of birch (BW) and spruce (SW) was selected as feedstock for carbonization.

2.2. Water leaching

Static leaching of the bark chips was performed without mechanical agitation. In contrast to standard laboratory protocols using ground biomass, this leaching method was applied with the purpose of using an industrially feasible procedure regarding technological simplicity and cost effectiveness. Each batch of 100 g bark chips was immersed in 1000 mL deionized Milli-Q water (conductivity <1 µS cm⁻¹) and heated at 60 °C for 1 h without stirring. After leaching, the bark was filtered, oven-dried at 105 °C for 24 h and stored in an airtight container until the carbonization experiment or further analysis. The leaching experiments

were performed in triplicates under identical conditions. A total of 300 g of bark of each species was leached for subsequent analysis. The solid mass recovery of dried leached barks was 83–85 %. The abbreviation of sample names was extended with an additional letter to differentiate the unleached (U) and leached (L) samples.

2.3. Analysis of raw materials

The carbohydrate contents of the stem wood and bark samples were determined using a slightly modified NREL method [24]. 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), which was performed with Agilent 1260 system equipped with Hi-Plex H column (Agilent Technologies, USA) 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 measured according to ASTM D1102. Ashing of the feedstock samples and the acid-insoluble residues, respectively, was performed 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. The measurements were performed in triplicates.

The inorganic contents of the leached and unleached bark samples was determined by inductively coupled plasma–optical emission spectrometry (ICP-OES) method. Each sample was digested with a mixture of nitric acid (65 %), hydrofluoric acid (40 %), and boric acid (4 %), according to CEN/TS 15290. The amount of inorganic elements in the resulting solution was determined by Thermo Scientific iCAP 6300 Duo View ICP Emission Spectrometer (Thermo Fisher Scientific, USA). The evaluated data is presented in Table S1 of the Supplementary material.

2.4. Production of the condensates

The carbonization of the biomass samples was performed using a laboratory-scale fixed-bed reactor system consisting of a cylindrical reactor housed within a tubular electric furnace with temperature and heating control at SINTEF Energy Research (Norway). The schematic diagram of the reactor system is presented in Fig. S1 of the Supplementary material. The reactor tube, constructed from Kanthal APM™ (FeCrAl alloy), can withstand temperatures up to 1250 °C. A nitrogen purging system and a condenser were integrated into the setup. For each experiment, about 300 g of dried bark (unleached or water-leached) or 700 g of wood chips was loaded into the sealed reactor, which was purged with nitrogen at a rate of 2 L min^{−1} for 1 h to remove the residual air. The reactor was then heated to 500 °C at a rate of 10 °C min^{−1} and held at this temperature for 1 h. The temperatures at the center of the biomass bed and at the reactor outlet were continuously monitored to ensure accurate control. During pyrolysis, the releasing volatiles passed through a metal condenser cooled to 5 °C, and the condensed fraction was collected in a metal container. After pyrolysis, the furnace was switched off, and the reactor was allowed to cool to room temperature under continuous nitrogen flow. When the temperature reached 50 °C, the reactor was opened, and the solid biocarbon and the condensed liquid fraction was collected. The yields of solid biocarbon were in a range of 26–37 % for bark and 23–25 % for wood. The yields of condensate fractions were between 28 and 38% from bark samples and 47–50% for wood samples. Note that similar yields were measured by other authors [21].

A portion of the pyrolysis condensates collected were sent to laboratory of HUN-REN RCNS (Hungary) for compositional analysis.

2.5. GC/MS analysis of the condensates

The pyrolysis condensate samples were dissolved in acetone and diluted to a 5 % solution. Prior to analysis, anisole was added to each sample as an internal standard at a concentration of 0.3 mg mL^{−1}. The chemical composition of the condensates was determined using an Agilent 7890A/5977B gas chromatograph/mass spectrometer (Agilent Technologies, USA). The GC injector was maintained at 280 °C. An aliquot of 1 µL solution was injected in split mode with a split ratio of 1:100. The compounds were separated on a DB-1701 capillary column (30 m × 0.25 mm, 0.25 µm film thickness; Agilent Technologies, USA) using helium as the carrier gas at a constant flow rate of 1 mL min^{−1}. The GC oven temperature program started with a 1 min hold at 40 °C, followed by a ramp of 6 °C min^{−1} to 280 °C, where it was held for 10 min. The mass range of *m/z* 14–550 was scanned by the MS in electron impact mode at 70 eV. The identification of the molecules was based on the combined Wiley Registry 9th edition/NIST 2011 mass spectral library and literature data [25,26]. Each sample was analyzed in triplicates. Semi-quantitative data for each compound as relative intensities were calculated from the peak integrals and divided by the peak integral of the internal standard. The list of the evaluated compounds is presented in Table S2 of the Supplementary material.

3. Results and discussion

3.1. Characteristic differences between bark and stem wood condensates

Stem wood and bark of a given wood species have distinct compositional profiles; hence the pyrolysis condensates produced from different feedstock types are expected to show certain differences in composition. However, the composition of a given wood or bark sample also varies in a range depending on many factors (origin and age of the wood, growth conditions, etc.). Therefore, Table 1 presents the organic compositions of the studied stem wood and bark samples of a broadleaf tree and a conifer, i.e. birch and spruce, respectively. These compositional data of the raw materials have been compared with the product yields of the pyrolysis condensates. The relative intensities of the identified compounds were grouped into specific compound categories, which is shown in Table 2.

In general, the organic composition of pyrolysis condensates produced from stem wood can be characterized as a mixture of anhydrosugars, short-chain carboxylic acids, aldehydes and ketones of open-chain and cyclic compounds, furan and phenol derivatives as illustrated in Table S3 of the Supplementary material. These compounds are mainly the volatile thermal decomposition products of carbohydrate and lignin components of stem wood [27].

Although the bark and stem wood condensates are qualitatively similar in chemical composition, they differ quantitatively in component concentrations. The sum of the volatile organic content was much less in bark condensates regardless of the species of biomass feedstock (i.e., broadleaf or conifer). Table 2 shows that the bark condensates contained lower amounts of cyclic and open-chain carbohydrate decomposition products including anhydrosugars, which is in agreement with the

Table 1

The organic composition and ash content of stem wood and bark samples of birch and spruce feedstock. Values are given in percentages by mass with standard deviation and are calculated on dry basis.

Content	BW	BBU	SW	SBU
Cellulose	38.6 ± 0.2	11.8 ± 0.1	40.1 ± 0.5	24.4 ± 2.6
Hemicellulose	24.2 ± 0.1	14.7 ± 0.1	20.3 ± 0.1	12.8 ± 1.3
Klason lignin ^a	19.5 ± 0.1	57.7 ± 1.1	31.1 ± 0.5	43.3 ± 0.5
Ash	0.44 ± 0.01	1.15 ± 0.02	0.35 ± 0.01	3.81 ± 0.02
Other ^b	17.3 ± 0.2	14.6 ± 1.1	8.0 ± 0.7	15.4 ± 3.0

^a Including acid-insoluble extractives.

^b Calculated as a difference.

Table 2

The volatile organic composition of pyrolysis condensates produced from the stem wood and bark of broadleaf birch and conifer spruce. The numbers indicate the summed relative intensities of specific compound groups evaluated by GC/MS analysis.

Compound group	Birch		Spruce	
	BW	BBU	SW	SBU
Acids	5.5	5.1	2.4	1.8
Open-chain carb. ^a	2.6	1.4	3.2	1.4
Cyclic carb. ^a	3.3	0.7	2.4	1.0
Anhydrosugars	4.3	1.4	3.3	1.3
Lignin-derived decomp. ^b	5.2	1.0	2.7	0.4
Other phenolics	0.5	0.3	0.3	0.2
Other compounds	1.2	0.3	0.7	0.3
Sum	22.5	10.2	15.1	6.4

^a Carb., carbohydrate decomposition products.

^b Decomp., decomposition products.

significantly lower cellulose and hemicellulose content of the bark feedstock samples (Table 1). The lower yield of lignin-derived phenolics in the bark condensates indicate lower lignin contents. Nevertheless, it cannot be correlated with the Klason lignin content of the bark samples (Table 1). The Klason lignin content determined in this work includes not only the acid-insoluble lignin, but the acid insoluble extractives as well, which are significant components of barks.

Though the broadleaf and coniferous tree barks are different in feedstock composition (Table 1), their pyrolysis condensates resulted in a similar composition for most of the compound groups as shown in Table 2. It should be noted that the sum of volatile organic content of BBU and SBU mainly differed in the acid content. The condensates of birch stem wood and bark contained significantly higher amounts of carboxylic acids than the condensates of conifers. Unlike the hemicellulose of conifers, the major component of birch hemicellulose is *O*-acetyl-(4-*O*-methylglucurono)xylan [28], which releases more acetic acid during thermal decomposition than the other types of hemicellulose segments. Besides hemicellulose, lignin and extractives evolve also acetic acid during thermal decomposition, which contribute to the high acid content of each condensate.

3.2. Effect of leaching on the inorganic contents of bark samples

The ash content determination and ICP analysis of bark samples were performed to reveal the efficiency of static leaching applied to the bark feedstock samples. The measured data are presented in Table S1 of the Supplementary material. Fig. 1 shows the removed percentages of the ash content and specific water-soluble inorganic contents from the bark samples during the static water leaching procedure. The data present that the performed leaching of barks moderately reduced the total ash content, by about 10 %, while it significantly decreased the amounts of alkali ions (i.e., potassium and sodium) by 40–50 %. The reduced presence of alkali ions may have a considerable effect on the thermal decomposition of the leached bark samples [29]. However, the amounts of other inorganic elements (e.g., calcium, phosphorus, sulfur) decreased moderately with static leaching, by less than 20 %.

Singhal et al. [15] also performed static water leaching on spruce bark but on ground samples sieved to <5 mm. Leaching of ground sample is more effective regarding diffusion-controlled leaching processes, but grinding to low particle size of feedstock is industrially more cost and energy intense than preparing feedstock as wood or bark chips. However, considering their results with the same leaching duration (60 min) as a reference, the following leaching efficiency was achieved by the simpler method performed in this work: about 65 % in ash content removal, 70 % for K, 60 % for Na and P, and 40 % for S removal. This comparison shows that lower but considerable leaching efficiency of inorganic contents can be achieved with static leaching, which is more feasible and cost effective from an industrial point of view, using 2–3 cm

bark chips rather than ground feedstock.

3.3. Effect of leaching on the chemical composition of bark condensates

3.3.1. Characteristic changes in the volatile organic composition of bark condensates

The solid mass recovery of bark samples after static leaching and drying was 83–85 % by mass. Since the decrease in ash content was modest, a significant part of the substances removed by the leachate was organic material. Thermogravimetric analysis of similar leached bark samples presented in our previous study [16] showed that leaching affected the thermal behavior of barks mainly in the lower temperature range of 180–300 °C, which is related to the devolatilization of thermally labile water-leachable organic extractives. However, the overall changes in the leached feedstock, including the removal of dissolved components and fines, and the decreased inorganic contents, could affect the composition of the formed condensates produced by pyrolysis.

The GC/MS chromatograms of the leached and unleached bark condensates depicted in Fig. S2–4 of the Supplementary material show that feedstock leaching did not change the overall composition of the forming condensate during pyrolysis to a significant extent. However, there are some compounds, which were detected in different amounts in the condensates of leached bark samples and unleached ones. In the following, the effect of leaching on bark feedstock is presented by highlighting those condensate components, the concentration of which significantly changed in the comparison of the condensate pairs. It should be noted that our results are consistent with the findings of Sampaio et al. [30], who also reported that the amounts of specific thermal decomposition products, e.g., acids, aldehydes and phenol, changed differently in the pyrolyzates after leaching pretreatments with ethanol and water depending on the type of biomass feedstock.

The highlighted compounds of our work were selected from a larger group of condensate components, which were identified in the GC/MS analysis of the condensate samples. The list of these evaluated compounds is presented in Table S2 of the Supplementary material, and the summed intensity data of the grouped compounds are presented in Table 3.

The relative intensities in Fig. 2 and the first row of Table 3 show that a moderate increase was measured in the amounts of carboxylic acids in the condensates of leached conifers (i.e., SB, PB), while the yield of acetic acid was slightly lower in the condensate of BBL than in that of BBU. Note that the absolute amount of pyrolytic acetic acid is much higher in birch condensates than that of conifers. As mentioned earlier, the hemicellulose of broadleaf birch is different than that of conifers. The hemicellulose of birch mainly contains *O*-acetyl-(4-*O*-methylglucurono)xylan, which has numerous acetoxy side-groups [28]. The thermal cleavage of these side-groups resulted in a significantly higher amount of acetic acid in the birch condensates in addition to the amounts acetic acid, which is formed in the thermal decomposition of

Table 3

The volatile organic composition of pyrolysis condensates produced from the unleached (U) and leached (L) bark of birch (BB), spruce (SB), and pine (PB). The numbers indicate the summed relative intensities of specific compound groups evaluated by GC/MS analysis.

Compound group	BBU	BBL	SBU	SBL	PBU	PBL
Acids	5.11	4.84	1.81	2.06	2.04	2.60
Open-chain carb. ^a	1.39	1.05	1.39	1.72	1.36	1.70
Cyclic carb. ^a	0.69	0.78	0.96	1.35	1.11	2.12
Anhydrosugars	1.37	1.44	1.29	0.97	1.23	1.52
Lignin-derived decomp. ^b	1.02	1.09	0.42	0.54	0.62	0.66
Other phenolics	0.27	0.35	0.21	0.14	0.18	0.24
Other compounds	0.31	0.42	0.31	0.37	0.33	0.59
Sum	10.2	10.0	6.4	7.2	6.9	9.4

^a Carb., carbohydrate decomposition product.

^b Decomp., decomposition product.

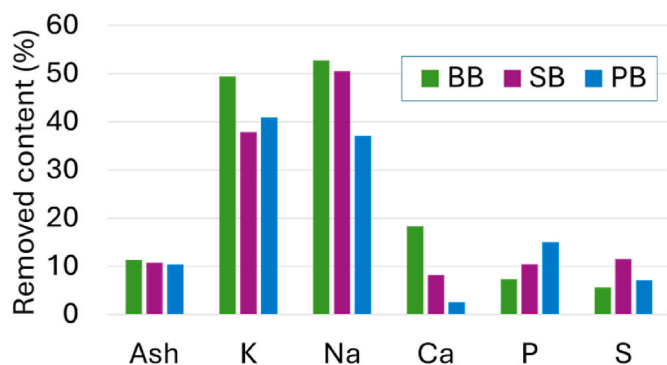


Fig. 1. The efficiency of leaching reflected by the ratio of specific inorganic contents removed by leaching in percentages.

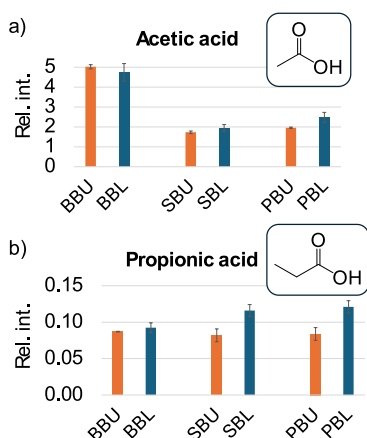


Fig. 2. The relative intensity of carboxylic acids, i.e. (a) acetic acid and (b) propionic acid measured in the bark condensates.

the biomass components (e.g., carbohydrates, lignin, extractives) in the cases of both broadleaves and conifers [27,31]. The evaluated data show that the sources of acetic acid in birch bark were barely affected by static water leaching. Since the hemicellulose content of birch bark is considered as the major source of acetic acid, such a minor difference in the acetic acid content between the condensates of BBU and BBL indicates that static water leaching had a limited impact on the hemicellulose content. On the other hand, leaching pretreatments of biomass feedstock with acids or alkaline solutions extensively break down the hemicellulose content [32].

It should be noted that most of the acetic acid content present in the condensates is in free form, but some of the acids interact with other condensate components forming esters. Since ester compounds are thermally labile [33], esters present in the condensates are presumably formed after condensation due to component interactions. A few ester compounds were identified, evaluated and listed in Tables S2 and S4 of the Supplementary material, i.e., ethane-1,2-diol monoacetate, acetoxycetone, 1-acetoxybutan-2-one. The relative intensity of these esters was measured similarly in the leached and unleached condensate pairs for each type of bark, correlating with the related relative intensity of free acetic acid.

3.3.2. Characteristic changes in the formation of carbohydrate decomposition products

Similar observations in relative intensities were obtained for a group of smaller carbohydrate decomposition products as shown in Fig. 3. Hydroxyacetaldehyde, hydroxyacetone, 1-hydroxybutan-2-one, cyclopent-2-en-1-one, 2-acetylfuran, and furan-2(5H)-one formed in

lower amounts from BBL than from BBU. But similar or slightly higher concentrations were measured in the condensates of leached conifer barks (i.e., SBL, PBL) than in the condensates of their unleached pair (i.e., SBU, PBU). The formation of these molecules can be related to the fragmentation of carbohydrate contents during pyrolysis, which is known to be catalyzed by the presence of alkali ions [27]. In the case of BBL, significant decrease in the alkali contents was achieved by leaching, which could result in lower yields of decomposition products formed by fragmentation. Although in the cases of conifers a similar leaching efficiency was measured as shown in Fig. 1, the concentration of potassium in the unleached feedstock was much higher (Table S1 of the Supplementary material). Therefore, the decreased level of potassium content of leached coniferous barks may not reach a critical level [34], which could influence the catalytic effect on fragmentation processes.

In the cases of specific cyclic carbohydrate decomposition products, different changes were observed. The intensity of furfural, 5-methylfurfural, 5-hydroxymethylfurfural, cyclopentane-1,2-dione, and 3-methylcyclopent-2-en-1-one showed a uniform increase in the condensates of leached barks in comparison to the data of unleached samples as presented in Fig. 4. As of 3-methyl-2-hydroxycyclopent-2-en-1-one (Fig. 4f), the significant increase was present in the cases of conifer condensates, but the difference in concentration between BBL and BBU was marginal. It should be noted that in the case of PBL, the relatively great increase of these cyclic carbohydrate decomposition products significantly contributed to the increased sum of volatile organic content measured in PBL condensate (Table 3). On the other hand, the net difference of the carbohydrate decomposition products formed from BBL resulted in a similar sum of volatile organic contents as it was measured in the condensate of BBU (Table 3).

It is well-known that polysaccharides consisting of hexose units (e.g., cellulose and softwood hemicelluloses) produce significant amounts of 5-hydroxymethylfurfural (5-HMF) upon flash pyrolysis, while polymers of pentose units (e.g., xylan, the most important hardwood hemicellulose) release substantial amounts of furfural [27,35]. As Fig. 4 and Table S4 show, the furfural yield was higher in the coniferous bark condensates than in the birch bark condensate. On the other hand, the intensity of 5-HMF followed a similar tendency, but its yield is about 10 % of that of furfural. These unexpected results can be explained by the established thermal instability of 5-HMF [36]. Due to the relatively large particle size of the bark samples and the applied fixed-bed reactor, the residence time of the decomposition products in the hot zone was significant, therefore the primary products of less stability decomposed. Based on this assumption, the decomposition of 5-HMF could contribute to the higher furfural yield. As the compositional data in Table 1 indicates, coniferous bark contains a significantly higher amount of cellulose than birch bark, hence spruce and pine barks evolved higher yields of cyclic carbohydrate decomposition products during carbonization (Table 3). The increased relative intensity of the cyclic carbohydrate decomposition products measured in the leached bark condensates may be also related to the AAEM contents, which can enhance the formation of these compounds during the thermal decomposition of both hemicellulose and cellulose [37]. The water-leachable inorganic salts are present as precipitated minerals in harvested biomass [38]. Although the amounts of these elements were modestly decreased, leaching could also have a dispersing effect during soaking of bark chips, which could have an increased net catalytic effect of specific components but in different extent of the different leached bark samples.

The third main group of carbohydrate decomposition products involves anhydrosugars. As shown in Table 3, the summed relative intensity of this group was measured slightly higher in BBL and PBL condensates, which is in correlation with the moderate decrease of alkali ions having smaller catalytic effect against depolymerization [27]. However, in the case of SBL, unexpectedly lower intensity was measured than in SBU. Studies of Miranda et al. [39] and Kemppainen et al. [40] performing leaching of spruce bark demonstrated that a few percentages

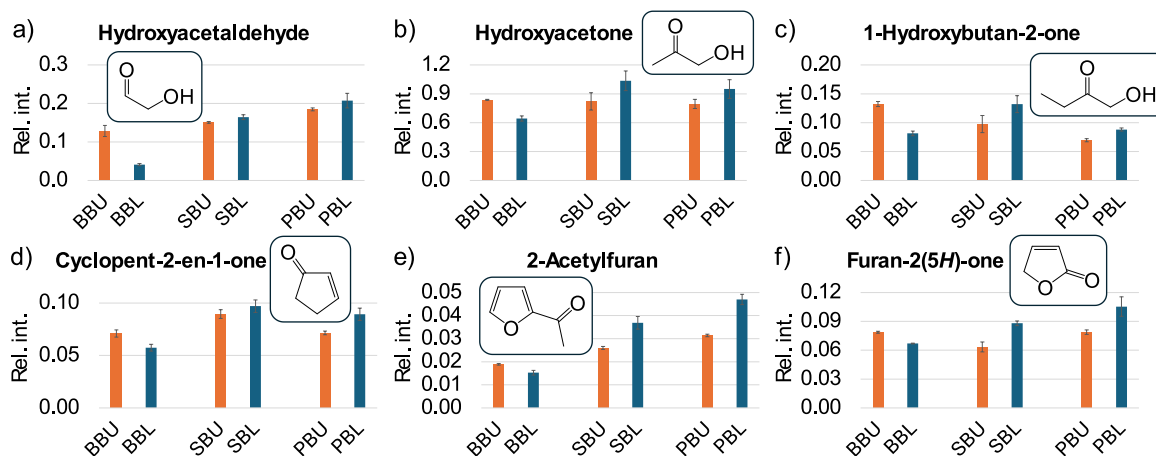


Fig. 3. The relative intensity of (a) hydroxyacetaldehyde, (b) hydroxyacetone, (c) 1-hydroxybutan-2-one, (d) cyclopent-2-en-1-one, (e) 2-acetylfuran, and (f) furan-2 (5H)-one measured in the bark condensates.

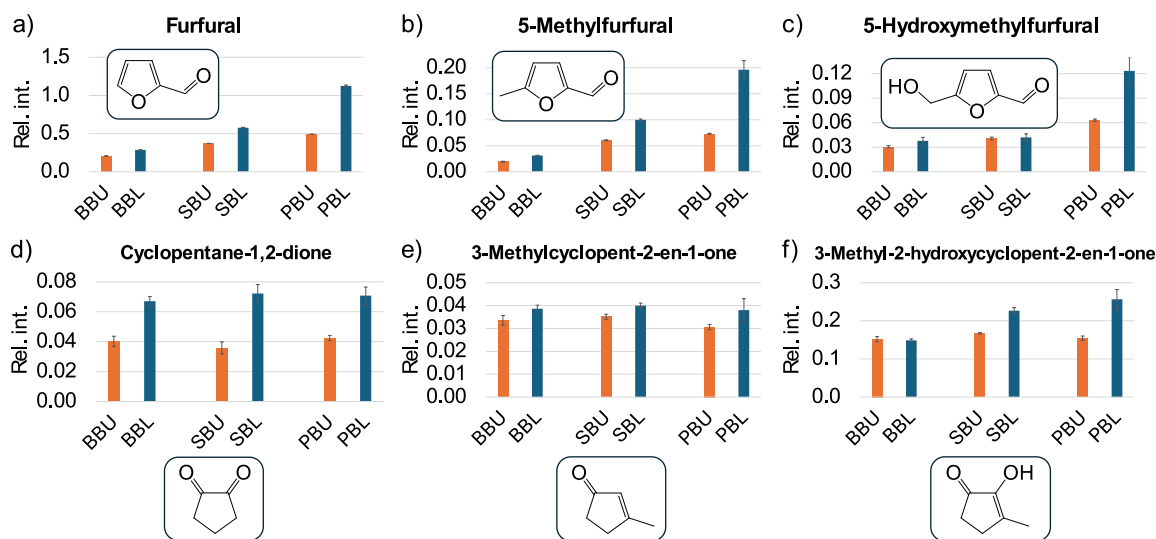


Fig. 4. The relative intensity of (a) furfural, (b) 5-methylfurfural, (c) 5-hydroxymethylfurfural, (d) cyclopentane-1,2-dione, (e) 3-methylcyclopent-2-en-1-one, and (f) 3-methyl-2-hydroxycyclopent-2-en-1-one measured in the bark condensates.

of spruce bark mass are water-leachable sugars, the removal of which could primarily lower the sources of carbohydrates before pyrolysis. Hydrothermal liquefaction performed by Feng et al. [41] on leached and unleached spruce bark showed that a fraction of decomposition products with smaller molecular weight appeared in the bio-oil of leached spruce bark, while the average molecule weight was also lower than that of unleached spruce bark. These results also indicate that the thermal decomposition of leached spruce bark may result in a different distribution of decomposition products than expected.

3.3.3. Characteristic changes in the formation of lignin decomposition products

As a result of leaching, a slight increase in the summed amounts of lignin decomposition products was observed in the GC/MS measurements of the leached bark condensates as shown in Table 3. As detailed examples, the relative intensity data of a few guaiacyl-type lignin decomposition products are presented in Fig. 5. These monoaromatic phenolics were measured in a higher concentration in the leached bark condensates than in the unleached ones of each wood type. However, the syringyl-type lignin decomposition products, which are characteristic of broadleaves, but not of conifers, changed differently. The amount of syringol formed from BB was lower after water leaching, while the

relative intensities of 4-methylsyringol and 4-ethylsyringol were similar in the condensates of BBU and BBL as shown in Table S4 of the Supplementary material.

3.3.4. Effect of leaching on species-specific extractives-related decomposition products

Dihydroconiferyl alcohol present in the bark condensates is also one of the lignin decomposition products [42,43]. As shown in Fig. 6, the condensates of PB contained much higher amounts of this compound than those of BB and SB as shown in Fig. 6. Dihydroconiferyl alcohol is likely a specific lignin-related decomposition product of PB. This compound is not normally associated with the lignin biosynthetic pathway, but Ralph et al. [44] demonstrated that loblolly pine lignin contains dihydroconiferyl alcohol subunits in about 3 %. Routa et al. [45] identified dihydroconiferyl alcohol in both free and glycoside form in the extract of fresh Scots pine bark; however, the latter one (dihydroconiferin) decomposes during a few days of storage. Borg-Karlson et al. [46] did not find dihydroconiferyl alcohol in the extracts of fresh Scots pine phloem, but it was present in considerable amounts in the gut of the pest of pine bark as a digestive product. The GC/MS analysis of the bark condensates of this work showed that leaching affected the sources of dihydroconiferyl alcohol in PB and therefore this

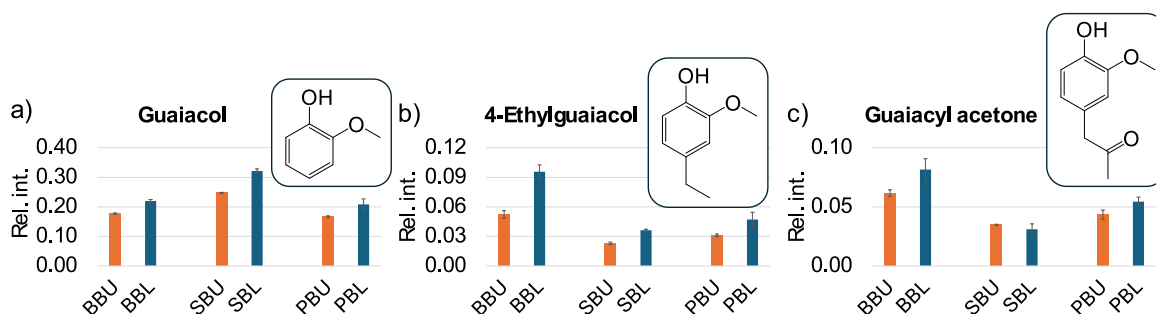


Fig. 5. The relative intensity of (a) guaiacol, (b) 4-ethylguaiacol, and (c) guaiacyl acetone measured in the bark condensates.

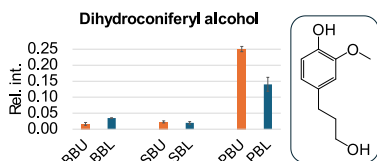


Fig. 6. The relative intensity of dihydroconiferyl alcohol measured in the bark condensates.

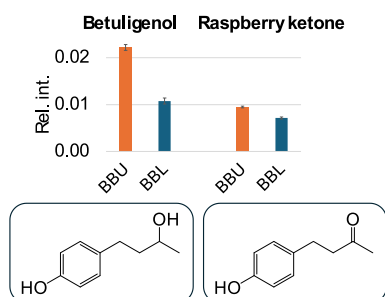


Fig. 7. The relative intensity of betuligenol and raspberry ketone measured in the birch condensates.

compound formed in a much lower amount from PBL than from PBU.

Betuligenol and raspberry ketone were identified uniquely in the condensates of BB. The compounds are specific thermal decomposition products of glycosides (e.g., platyphylloside, rhododendrin), which are characteristic components of BB [47]. The analysis of the birch condensates showed that a considerable portion of these glycosides was removed during the leaching procedure as lower amounts were measured in BBL than in BBU, especially for betuligenol, as presented in Fig. 7.

4. Conclusion

The effects of an industrially feasible water leaching procedure were evaluated on the composition of pyrolysis condensates produced from birch, spruce, and pine bark samples. The liquid by-products were collected during the pyrolysis of leached and unleached bark feedstock performed in a fixed bed reactor, and the comparison of the condensates was established by the results of GC/MS analysis. The compositional characteristics of bark condensates were also shown relative to stem wood condensates using the feedstock of broadleaf birch and conifer spruce as examples.

The total volatile organic content of the bark condensates, excluding carboxylic acids, was substantially lower than that of stem wood condensates, regardless of the feedstock. The composition of the three bark condensates was similar based on the comparison of summed compound

groups, and the sum of volatile organic contents mainly differed in the acid content. Due to the specific hemicellulose of birch bark, its condensate contained more than twice the concentration of acids, particularly acetic acid than the bark condensates of conifers, i.e., spruce and pine.

Inorganic content analysis showed that the simple static water leaching of barks led to a significant reduction in the amounts of alkali ions, while it moderately decreased the amounts of other inorganic elements in the feedstock including the total ash content. The leaching efficiency was compared with that of a more effective, but cost-intensive static leaching method applied on ground feedstock.

As a result of leaching, the overall composition of bark condensates showed modest changes. The observed differences in the condensate compositions are related to the removal of dissolved organic components and altered thermal decomposition of the remaining structures as an effect of decreased inorganic contents. The leached bark condensates contained higher amounts of specific cyclic carbohydrate derivatives, e.g., furfural and furfural derivatives, and a slight increase in the amounts of lignin-derived phenolics was observed. The amounts of smaller open-chain carbohydrate decomposition products, e.g., hydroxyacetaldehyde and hydroxyacetone, were measured lower in the condensate of water-leached birch bark, whereas increased amounts were detected in the condensates of leached conifer barks.

The thermal decomposition products of water-leachable organic substances were present in a lower ratio in the condensates of leached barks. For example, less birch-specific betuligenol and raspberry ketone were measured in BBL than BBU, while the amount of dihydroconiferyl alcohol also was considerably lower in PBL than in PBU.

The comparative analysis of the pyrolysis condensates produced from different leached and unleached barks revealed the similarities and differences depending on the feedstock type, while the impact of the removal of the leachable components on the condensate compositions was also shown. The results obtained can contribute to the pyrolytic utilization of bark biomass and its condensate by-product through the provided information.

CRediT authorship contribution statement

Bence Babinszki: Writing – original draft, Formal analysis, Data curation. **Liang Wang:** Writing – review & editing, Investigation, Conceptualization. **Øyvind Skreiberg:** Writing – review & editing, Funding acquisition. **Zoltán Sebestyén:** Data curation. **István Sándor Czírok:** Data curation. **Zsuzsanna Czégény:** Writing – review & editing, Funding acquisition, Conceptualization.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.biombioe.2026.109075>.

Data availability

Data will be made available on request.

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