

Effect of Feedstock Water Leaching and Thermal Treatment on the Pyrolysis Condensate of Pine Bark

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There is a growing demand for biocarbon in metallurgical applications. While biocarbon is primarily produced from stem wood, it is crucial to diversify feedstock sources to ensure sustainability, high availability, and cost-efficiency. Pine bark, a significant forestry waste stream, represents a promising alternative. However, biocarbon production via pyrolysis generates significant condensable liquid by-products. Although often discarded, these condensates can become valuable resources through detailed characterization and upgrading. In this study, pine bark chips were pyrolyzed in a fixed-bed reactor. To mitigate the high inorganic content typical of bark, a portion of the feedstock underwent water leaching prior to pyrolysis. The impact of leaching on the resulting condensate composition was evaluated using gas chromatography/mass spectrometry (GC/MS) analysis. Since direct utilization of raw condensates is hindered by high water content, post-pyrolysis thermal treatments were applied to condensates from both leached and unleached samples. The thermal treatment of the condensate samples was performed in a muffle furnace at 140 and 160 °C for 2 hours. GC/MS analysis of the thermally treated condensates revealed that heating at 140 °C significantly enriched the organic content, evidenced by higher compound intensities compared to raw condensates. Treatment at 160 °C showed a similar trend but favored the retention of heavier compounds (e.g., levoglucosan) while significantly reducing highly volatile compounds (e.g., acetic acid). These findings provide critical data for the biocarbon industry, supporting the utilization of pine bark as a feedstock and offering strategies for the valorization of condensate by-products.

1. Introduction

The production and application of biocarbon derived from biomass have gained significant attention as a sustainable alternative to fossil-based reductants in metallurgical industries. Biocarbon is produced through thermochemical conversion processes like slow pyrolysis from raw biomass. While stem wood is the traditional feedstock, its high cost and limited availability, industries with large-scale energy use need to utilize lower-grade alternatives. Bark, a major by-product of the forestry and sawmilling industries, constitutes approximately 9–21 % of a tree's dry mass and represents an abundant, renewable resource (Sen et al., 2023). However, compared to stem wood, bark typically has a higher inorganic content (ash), which can reach 2–8 % depending on the species (Werkelin et al., 2005; Saarela et al., 2005). This high mineral content, dominated by alkaline and alkaline earth metals (AAEMs), is a significant drawback for metallurgical applications where biocarbon of low ash content is required. To mitigate these adverse effects, water leaching is a promising demineralization strategy due to its simplicity, low cost, and effectiveness in removing water-soluble species such as potassium, sodium, and chlorine (Singhal et al., 2023; Wang and Skreiberg, 2023). Studies on coniferous barks have shown that even static water leaching can significantly reduce alkali ion concentrations by 40–50 %, thereby improving the quality of the solid biocarbon for industrial processes (Babinszki et al., 2026). Beyond reducing ash-forming elements, leaching also influences the thermal decomposition of biomass by altering decomposition kinetics and product distribution (Branca and Di Blasi, 2024). While the primary focus of biomass carbonization is often the solid biochar, the process also generates significant amounts of condensable liquid by-products.

These pyrolysis condensates, or bio-oils, are complex mixtures consisting of water and various organic chemicals such as acids, phenols, ketones and anhydrosugars. Currently, the aluminum industry relies on coal-tar pitch (CTP) as a binder for carbon anode manufacturing, but CTP is non-renewable and contains carcinogenic polycyclic aromatic hydrocarbons (PAHs). Bio-pitch synthesized from upgraded bio-oil offers a potential "green" alternative due to its significantly lower PAH and sulfur content (Lu et al., 2020; Elkasabi et al., 2022).

However, raw bio-oil faces inherent challenges, including high oxygen (35–40 wt%) and water content (15–50 wt%), which lead to instability and high corrosiveness (Smets et al., 2011). To upgrade this liquid by-product into a suitable bio-binder, further treatments such as distillation and thermal polymerization can remove moisture and light volatiles while increasing the molecular weight and viscosity (Santos et al., 2025).

Research has shown that thermal treatment of bio-oil results in polymerization, which can be adjusted to control properties like the softening point and coking value, essential indicators for binder quality (Lu et al. 2020). While the impact of feedstock water leaching on the initial chemical composition of bark condensates was established in our recent publication (Babinszki et al., 2026), a critical question remains regarding how this pretreatment influences subsequent upgrading stages. The usability and necessary upgrading methods for these liquids are directly determined by their chemical characteristics.

Thus, the major goal of this work is to reveal the effect of thermal posttreatment on the pyrolysis condensates of water-leached and unleached pine bark feedstock. The volatilization profile of both raw and posttreated condensates were characterized by TGA. The chemical compositions of the raw and thermally treated condensates were analyzed by GC/MS and compared. This study aims to provide essential data for the biocarbon industry to optimize the utilization of liquid by-products as high-value bio-binders in metallurgical applications.

2. Materials and methods

2.1 Feedstock and leaching pretreatment

Bark of Scots pine wood (*Pinus sylvestris*) originating from a forest in South Norway (Hobøl, 59°35'35"N 10°56'45"E) was used. After harvest, the trunk was debarked to obtain separated stem wood and bark. The separated bark was cut into chips and approximately 2–3 cm pieces were selected as feedstock. The chips were air-dried at room temperature to about 15 % moisture, followed by oven drying at 105 °C for 16 h.

Some of the bark samples were used for pretreatment of static leaching. Approximately 100 g of bark chips were immersed in 1 L deionized water and heated at 60 °C for 1 h without stirring.

After leaching, the bark was filtered, oven-dried at 105 °C for 24 h. In contrast to standard laboratory protocols applying ground raw material and stirring, the leaching method used in this study was designed to reflect an industrially feasible approach, regarding technological simplicity and cost-effectiveness (Babinszki et al., 2026).

2.2 Production and thermal posttreatment of the condensates

Both leached and unleached bark samples were pyrolyzed using a laboratory-scale fixed-bed reactor system consisting of a cylindrical reactor housed within a tubular electric furnace. For each experiment, about 300 g of bark chips was loaded into the sealed reactor, which was purged with nitrogen at a rate of 2 L min⁻¹ for 1 h. The reactor was then heated to 500 °C at a rate of 10 °C min⁻¹ and held at this temperature for 1 h.

During pyrolysis, the condensates were collected in an integrated condenser cooled at 5 °C. The designation used for raw pyrolysis condensates of unleached and leached pine bark is PBU and PBL, respectively.

The solid and condensate yields were 33–38 % and 29–33 %, respectively. Some of the collected condensates were additionally thermally treated in a muffle furnace. The posttreatments were performed with about 10 g of condensate sample, which was loaded into an open glass container and placed in a muffle furnace.

Then the sample was heated up at rate of 1 °C min⁻¹ to the final temperatures of 140 or 160 °C and held for 2 h. Abbreviations of PBU140, PBL140, PBU160, and PBL160 are used for the samples, accordingly. The posttreatment solid yields of PBU140, PBU160, PBL140, and PBL160 were 20.4 %, 14.6 %, 23.8 %, and 19.3 %, respectively.

2.3 Thermogravimetric analysis (TGA)

Thermogravimetry (TGA) measurements were performed using a TGS-2 thermobalance with a modified furnace (Perkin Elmer, USA). Approximately 3 mg samples were measured into a platinum sample pan. After the furnace was closed, the heating program was immediately started to avoid partial evaporation of the sample. The furnace was continuously purged by argon at a flow rate of 140 mL min⁻¹ during the measurement. The samples were heated at a rate of 20 °C min⁻¹ from room temperature to 600 °C.

2.4 GC/MS analysis of condensate compositions

The condensate samples were dissolved in acetone and diluted to an 8 % solution by mass. 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. Each sample was analyzed in triplicates. Relative intensities for each compound were calculated from the peak integrals and divided by the peak integral of the internal standard for the comparison of the samples.

3. Results and discussion

The characterization of the samples was performed by determining thermal behavior as volatilization profile (TGA) and the organic volatile composition (GC/MS analysis).

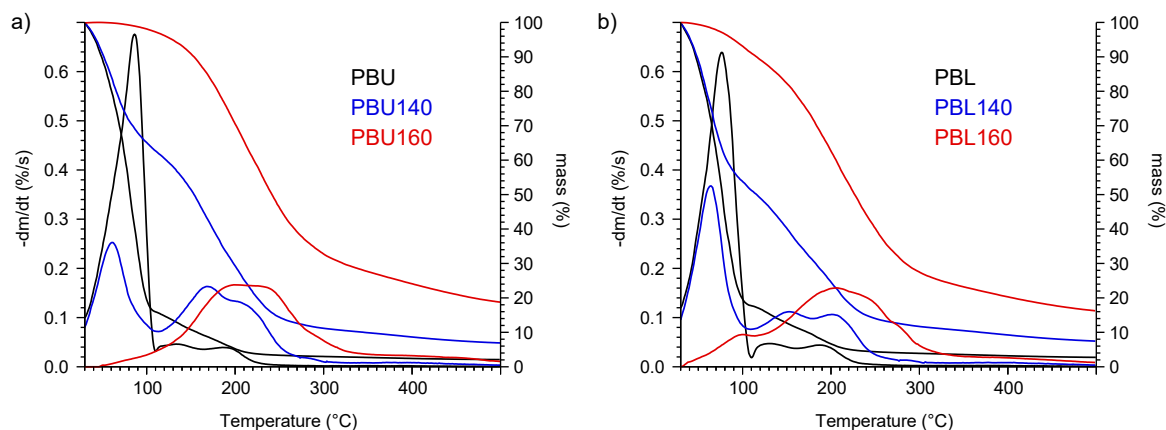


Figure 1: TG and DTG curves of (a) unleached and (b) leached pine bark condensates.

3.1 Volatilization profile of the samples

The volatilization profile of the samples was followed by TGA measurements and shown in Figure 1. The volatilization processes can be divided into two phases based on the shape of the DTG curves. Large amounts of water and highly volatile organic molecules were released from the condensates up to 120 °C as it is indicated by a significant distinct peak on the DTG curves of raw condensates PBU and PBL. This observation underscores the unsuitability of the raw condensate for direct application as metallurgical binder due to excessive water content. The height of the DTG peak below 100 °C of both PBU140 and PBL140 is lower, which indicates the partial evaporation of these volatile compounds and the significant decrease of water content as a result of thermal posttreatment performed at 140 °C for 2 h. The mass loss of PBU160 and PBL160 is much lower up to 120 °C, below 10 %, indicating almost complete evaporation of water and other volatile compounds. The evaporation of medium-to-heavy organics with lower volatility started over 120 °C and mainly finished up to 300 °C for all samples. At the same time, the thermally labile compounds also decomposed by releasing other volatile molecules. The relative portion of higher molecular weight compounds with lower volatility was higher in the posttreatment samples, as it is reflected by the higher DTG values in the temperature range of 120–300 °C than by that of raw condensates. Additionally, the wide DTG peak corresponding to the second volatilization step shifted to higher temperatures in the cases of both leached and unleached posttreated pine bark condensate samples. Beyond the increase in higher molecular weight compounds due to the evaporation of lower molecular weight and more volatile species, this shift also suggests the formation of additional higher molecular weight compounds through polymerization, which is in agreement with the findings of Lu et al. (2020). It can be concluded based on the TGA measurements that thermal posttreatments performed at 160 °C effectively reduced the moisture content of the condensates and promoted condensation, polymerization and cross-linking reactions, which are advantageous processes in the production of a potential bio-binder with increased organic content suitable for metallurgical industry.

3.2 Organic volatile composition of the samples

The evaluation of the condensate composition of pine bark and the effect of feedstock leaching on the condensate composition was described in detail in our previous publication (Babinszki et al., 2026). GC/MS analysis of the samples presented in the work revealed characteristic compositional changes of the condensates of both leached and unleached pine bark due to thermal posttreatments as shown in Figure 2. The comparison of the GC/MS chromatograms directly reflects on the increasing peak intensities as the thermal posttreatments significantly increased the total relative organic content of the posttreated samples. Furthermore, the temperature of the thermal treatment also showed considerable impact on the sample composition. However, the individual components were not uniformly affected. The evaluation of compound relative intensities showed that the concentration of specific compounds increased during the posttreatment, while other compounds behaved differently. Based on the changes observed, four different behaviors are described as the following, and the relative intensities of a few compounds evaluated are shown as examples in Figure 3.

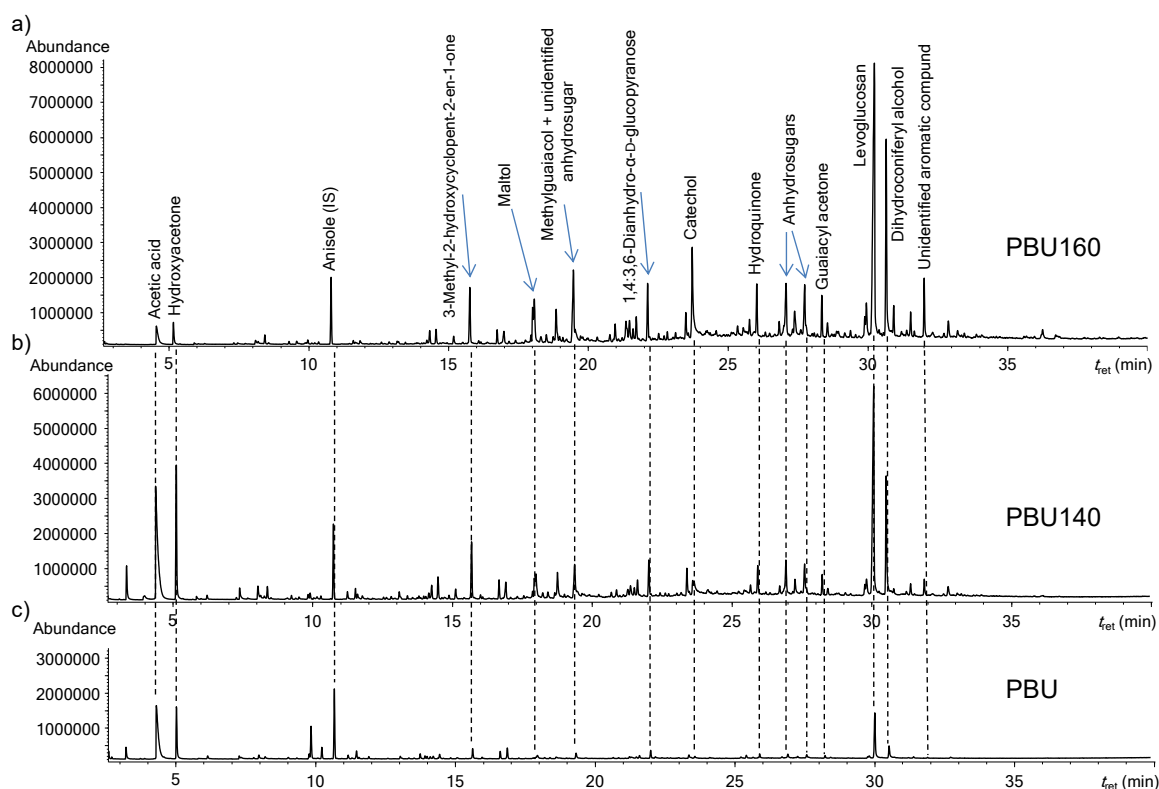


Figure 2: GC/MS chromatograms of (a) PBU160, (b) PBU140 and (c) PBU sample solutions indicated with the main identified components.

A group of volatile oxo compounds with smaller molecular weight, including both open-chain and cyclic ketones, aldehydes, and carboxylic acids, showed a distinct tendency. As an example, the relative intensities of acetic acid, hydroxyacetone, and hydroxyacetaldehyde are presented in Figures 3a–c. In comparison to relative intensities measured in the raw condensates, the concentration of these compounds was higher in the samples treated at 140 °C. However, some of these molecules were devolatilized during the thermal treatment performed at 140 °C as their relative increase was proportionally smaller than it could be simply due to volume reduction based on the yield of posttreatment. Therefore, the devolatilization of these compounds was relatively low during a posttreatment performed at 140 °C. On the other hand, thermal treatments performed at 160 °C resulted in a considerably more intense removal of these compounds as their concentration was measured much lower or similar than in raw condensates. Note that the removal of acetic acid is beneficial for bio-binder applications by mitigating its inherent corrosivity. In the next specific group of compounds are furfural (Figure 3d) and 5-methylfurfural (Figure 3e). The relative intensity of these compounds was measured much lower in posttreated samples than in raw condensates, which indicates the advanced decomposition of these compounds during posttreatment instead of evaporation. Despite acid-catalyzed decomposition reactions, polymerization and condensation processes of furfurals (Almhofer et al., 2023) could contribute to the increase of the higher

molecular weight fraction, which is not amenable by GC/MS, but it was detected by TGA. It should be noted that the PBL had a higher concentration of furfurals (Babinszki et al., 2026), which difference was retained in each thermally treated sample.

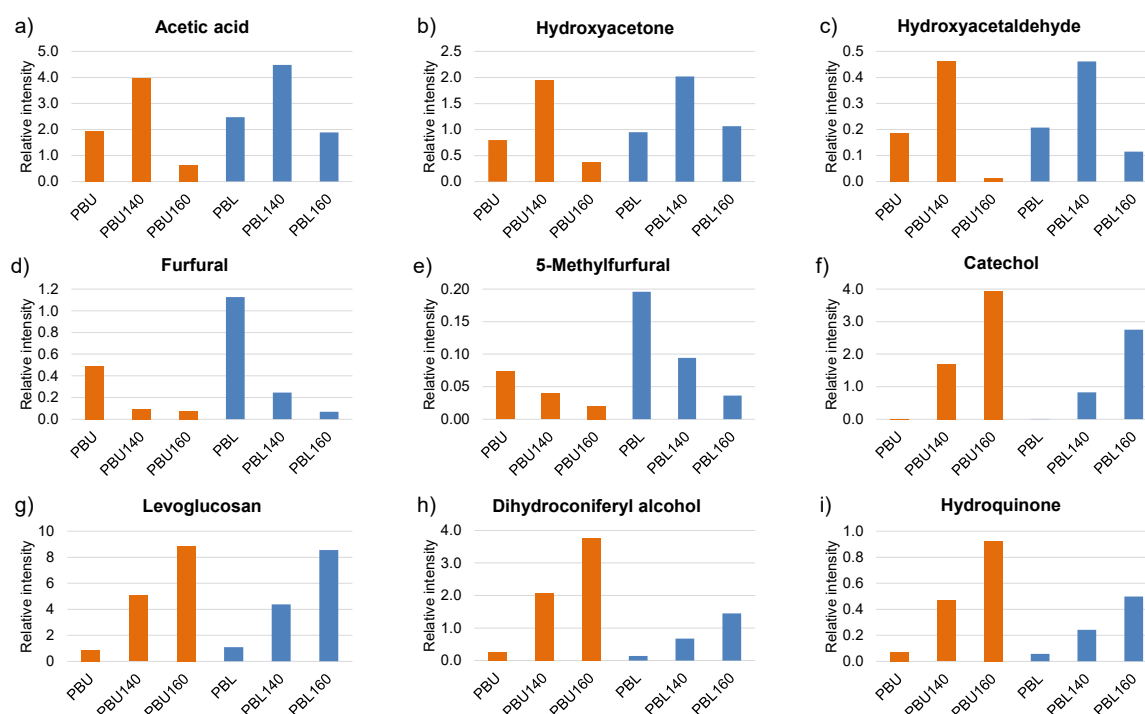


Figure 3: Relative intensity of specific compounds evaluated in the samples.

A group of molecules identified with relatively larger molecular weight showed another distinct tendency as their concentration increased during the thermal posttreatment, proportionally with the final treatment temperature. Anhydrosugars (e.g., levoglucosan in Figure 3g) and phenolics, including lignin decomposition products, (e.g., dihydroconiferyl alcohol in Figure 3h and hydroquinone in Figure 3i) were mainly retained in the samples during posttreatments. As shown in Table 1 by relative intensity ratios, the concentration increase of these compounds in the posttreated samples was proportional to the volume reduction of the samples. However, the concentration increase of a few compounds was also enhanced by formation during the thermal posttreatment performed at both temperatures of 140 and 160 °C (e.g., catechol in Figure 3f, vanillin, acetoguaiacone, furan-2-carboxylic acid). The concentration of these compounds in the raw condensates was below the detection limit (i.e., catechol) or their relative intensity ratios was multiple times higher than expected due to enrichment by volume reduction.

Table 1: Relative intensity (*R*) ratios of specific compounds.

Compound	R_{PBU140}/R_{PBU}	R_{PBU160}/R_{PBU}	R_{PBL140}/R_{PBL}	R_{PBL160}/R_{PBL}
Acetic acid	2.0	0.3	1.8	0.8
Furfural	0.2	0.1	0.2	0.1
Levoglucosan	5.8	10.1	4.0	7.9
Dihydroconiferyl alcohol	8.3	15.0	4.8	10.3
Hydroquinone	6.5	12.9	4.2	8.6
Catechol	very large	very large	very large	very large

These phenolics and furan derivatives are known as potential reactants of polycondensation reactions and increasing fixed carbon content at high carbonization temperatures. Therefore, the enrichment of this type of content in the posttreated condensates is especially useful for applications, e.g., using posttreated condensates in aluminum industry as bio-binder for anode production. As the evaluated data of the presented examples show, thermal posttreatments similarly affected the individual condensate components in both leached and unleached samples.

4. Conclusions

The comparison of GC/MS analysis results showed that thermal posttreatment performed at 140 °C significantly enriched the organic content of both leached and unleached pine bark condensates. While further enrichment of the organic content was achieved by posttreatment performed at a higher temperature of 160 °C, a significant shift in the composition was also observed. These findings are in correlation with the volatilization profiles of the samples. The devolatilization of compounds with lower molecular weight (i.e., open-chain and cyclic ketones, aldehydes, carboxylic acids) became intense at 160 °C than at 140 °C, but molecules of the higher molecular weight fraction (i.e., anhydrosugars, phenolics) were retained during both posttreatments. In addition, some compounds were additionally formed during thermal posttreatments (e.g., catechol, vanillin, acetoguaiacone). A few condensate components (i.e., furfurals) were found to be sensitive to thermal treatment, and they decomposed in a considerable ratio during the posttreatment. At the same time, thermal posttreatments promoted the formation of non-volatile compounds with larger molecular weight through polymerization and condensation. These data and revealed effects of thermal posttreatment of pine condensates provide useful information for the utilization and upgrading of pyrolysis condensates in general, e.g., for the biocarbon industry by producing high-value bio-binders from pyrolysis condensates with a simple thermal posttreatment for metallurgical applications.

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