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Research Article

Supercritical Extraction of Biomass—A Green and Sustainable Method to Control the Pyrolysis Product Distribution

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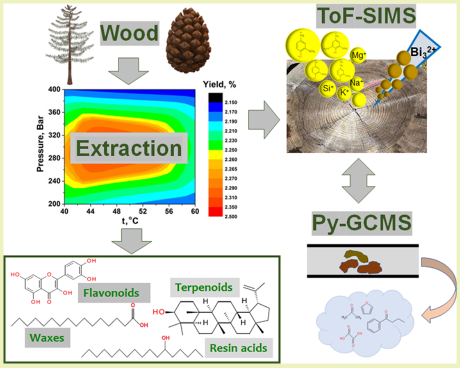
ABSTRACT: This research demonstrates that supercritical extraction of the biomass has a remarkable and complex influence on Scots pine tree fractions changing the surface concentration of water, lipids, and metals simultaneously. Surprisingly, this surface composition modification makes a considerable impact on the pyrolysis of the bulk biomass mechanism, leading to the alternation of the volatile and inorganic matter composition. The unique combination of time-of-flight secondary-ion mass spectrometry analysis and utilization of pyrolysis gas chromatography-mass spectrometry data on the thermal behavior of woody biomass demonstrates, for the first time, the extraordinary influence of surface adsorbed metals on the composition of pyrolysis products. ScCO$_2$ could extract the surface metals in the form of fatty acid salts, demonstrating a sustainable and environmentally friendly pretreatment method for controlling the pyrolysis products.



KEYWORDS: *supercritical extraction, surface, metal cations, Scots pine, Py-GC/MS, ToF-SIMS*

INTRODUCTION

For our society to be sustainable, it must rely on the concept of a circular economy. The creation of resource loops which close the flow of materials in manufacturing chains, thereby stimulating reuse and waste minimization, is a key aspect of a circular economy.[1] The integration of the circular economy concept can promote economic growth by creating new enterprises, boosting the labor market, saving the cost of the raw materials, improving security and stability of material resources, and, in doing so, also reducing environmental impacts.[2] The circular economy strategy supports the holistic utilization of biomass and bio-based wastes.[3] In holistic multiprocess biorefinery systems, the wood can be converted into value-added chemicals, while residues can be exploited as fuels for energy production.[4] Based on circular economy principles, low-quality waste wood from forestry and biomass appears to be a promising resource for exploitation and the creation of closed product loops.[5] A promising valorization route of low-quality wood refers to various biorefinery processes developed to produce chemicals. Wood bark is an excellent potential source of bio-based aromatics due to the high concentrations of lignin; however, the presence of such components limits bark application for sugar production, compared to stumps which are considered to be a very promising source of polyphenols and syngas.[6] Therefore, new concepts for low-quality wood processing within the circular economy are required to meet the guidelines as described in the EU green deal.[7] Extraction and pyrolysis are two biomass processing technologies that can be utilized for the conversion of low-quality wood into value-added products.

Pretreatment of biomass is a potential way to tune the selectivity of the pyrolysis and gasification processes to individual products. The main purpose in pretreating biomass is to decrease the solid yields and enhance the formation of value-added volatile compounds during pyrolysis. Considering that pyrolysis vapor is composed of many highly valuable chemicals in low concentrations, the high yield of specific species is the key incentive to combine the biomass thermochemical processes with the extraction methods. Extraction can support the establishment of sustainable methods to control the distribution of products in pyrolysis. Conventional extraction methods of solid matrices typically suffer from several disadvantages including low applicability, complexity, and the use of environmental-hazardous solvents.[8] Consequently, in recent years, the development of clean chemical technologies such as microwave-assisted extraction and supercritical fluid extraction may overcome such disadvantages.[9] Supercritical carbon dioxide (scCO$_2$) extrac-

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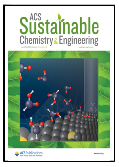


tion is a sustainable process with the potential to have low environmental impacts due to the minimized operational time, excellent solvent recyclability, and the overall reduced use of chemicals with greater lipid yields compared to conventional extraction methods.[10] Lignocellulosic biomass can have a variety of physical and chemical properties depending on environmental influences during growth and the resulting structure of the wood.[11]

Understanding inorganic matter distribution on the surface of the raw wood is of significant importance because metal concentrations have a strong impact on the gas-surface reactions at high temperatures.[12,13] These reactions affect the formation of soot and tar products and thus appear to control the gasification efficiency during pyrolysis.[14] A recent study postulated that extractives within the biomass may have a catalytic effect on both the composition and yield of products.[15] Extractives may enhance gas and char formation due to vapors being retained for longer periods with the solid matrices.[16] Such interactions would be at the expense of forming liquid products or bio-oil. However, it has been demonstrated that alkali metals have a predominating effect on both pyrolysis yields and composition.[17] Selection of an appropriate analytical method for the analysis of ash composition is also key in the determination of the element concentration.[18] The quantification of ash composition and content is typically determined using atomic adsorption spectroscopy or more communally inductively coupled plasma coupled with optical emission spectrometry (ICP-OES).[19] ICP-OES requires dissolution procedures that can include dangerous hydrofluoric acid (HF) with the microwave digestion.[20] Moreover, the ICP-OES methods are expensive and lengthy and can lead to the loss of volatile elements.[20] X-ray fluorescence is a fast and non-destructive method for the simultaneous quantitative analysis of elements.[21] In contrast, alternative techniques such as neutron activation analysis have limited availability and are costly. Common analytical techniques including microscopy (scanning electron microscopy, transmission electron microscopy, and atomic force microscopy) in addition to infrared and Raman spectroscopy are utilized for biomass analysis.[22] The main function of these techniques is related to the visualization of surface features, whereas the chemical compositional analysis is expected to be less accurate than that from time-of-flight secondary-ion mass spectrometry (ToF-SIMS).[23] X-ray photoelectron spectroscopy (XPS) is a highly informative surface analysis technique, which is also highly complementary to ToF-SIMS. Analysis of trace elements on 10 nm or smaller wood particles is challenging for XPS as its typical detection limit is $\approx$0.1% and the lateral resolution is several micrometers.[22] An advantage of the ToF-SIMS application in the raw wood characterization is related to the significant amounts of information generated on inorganics and organic species which typically cannot be identified in the entire variety of biological samples by XPS.[24] ToF-SIMS can have a depth resolution as low as nanometers,[25] and it is an extremely versatile and sensitive analysis technique for surface characterization, where the detection of reactive intermediates is vital for understanding reaction mechanisms in catalytic systems. The ToF-SIMS analysis determines the available alkali metals on the fuel surface and can be further used as a platform to calculate the additional amount of alkali metals required in the reactor to minimize the formation of undesired soot and tar. Therefore, the ToF-SIMS characterization of the biomass surface examines compositional differences which are a crucial factor for the modeling of pyrolysis and gasification reactions. Few studies have investigated the influence of $scCO_2$ extraction on the dispersal of inorganic species on the surface of wood using the ToF-SIMS technique and correlations with reactions during pyrolysis.

The aim of this investigation is to gain a fundamental understanding of surface properties of both virgin and $scCO_2$-extracted wood fractions (cones, branches, stumps, needles, and bark from small- or large-diameter pines), thereby understanding how the surface composition of wood fractions controls the production of certain groups of compounds during pyrolysis. The effect of $scCO_2$ extraction on the extractive and inorganic matter composition remaining on the biomass surface was investigated by the ToF-SIMS technique. Initial investigations were focused on the volatile yields using pyrolysis gas chromatography−mass spectrometry (Py-GC/MS). The results were found to be sample-specific, as were the ToF-SIMS data.

■ MATERIALS AND METHODS

Sample Preparation. Scots pine tree fractions were harvested and characterized in accordance with previously published methods. Trees were on average 147 years old. The fractions utilized for pyrolysis and valorization included needles, branches, cones, heartwood, bark from a 210 mm basal log, and bark from a 100 mm log. Fractions were milled to generate particles of sizes of 0.05-0.2 mm using a MAFA EU-4B hammer mill, followed by sieving.

Proximate Analysis. ASTM standards were used to measure the moisture (ASTM D2216-19), ash (ASTM D1102-84), volatiles (ASTM D3175-11), and fixed carbon content (ASTM D3172-13) for all samples. The calorific value was measured using an IKA C-200 bomb calorimeter in accordance with ASTM D2015-95.

Ash Compositional Analysis. Original and $scCO_2$-extracted samples were heated in an oven at a rate of 5 °C min^{-1} to 550 °C and then maintained at this temperature for 7 h. Microwave heating was used to digest the resulting ash materials with nitric acid, hydrogen peroxide, and HF ($HNO_3-H_2O_2-HF$), as reported in BS EN 15290:2011. Before ICP, the digested samples were neutralized with boric acid and filtered, and 1 mL was transferred to a volumetric flask, which was then made up to 10 mL with 1% HNO_3. In the ash analysis, the plastic-based laboratory dish was used to avoid any addition of silicon compounds from glass.

Lignocellulosic Analysis. Structural carbohydrates and lignin contents of tar samples were determined using previously published methods.[26] $ScCO_2$ extractions were carried out using published methods by Attard and Hunt.[27] Typical extraction conditions are 180 g of biomass in a 500 mL vessel at 300 bar, 50 °C, and 40 g min^{-1} CO_2.[28]

Pyrolysis Gas Chromatography−Mass Spectrometry. Py-GC/MS analysis and quantification were carried out according to previously published methods by Trubetskaya et al.[28]

ToF-SIMS Analysis. ToF-SIMS pelletized samples were analyzed with an ION-TOF secondary-ion mass spectrometer with a 25 kV pulsed Bi_3^+ primary-ion gun in the static mode. The intensity of ions corresponding to the inorganic contaminants was normalized using the total number of counts, as reported previously.[29]

■ RESULTS AND DISCUSSION

Biomass Characterization. A recent study demonstrated the compositional analysis of original and $scCO_2$-extracted Scots pine fractions utilized in this current study. The ash content and minerals therein and also the proliferation of lignocellulosic components demonstrated substantial differences between tree parts (the needle, stem, cone, bark, and branch), as previously reported.[30] Pine needles have significant

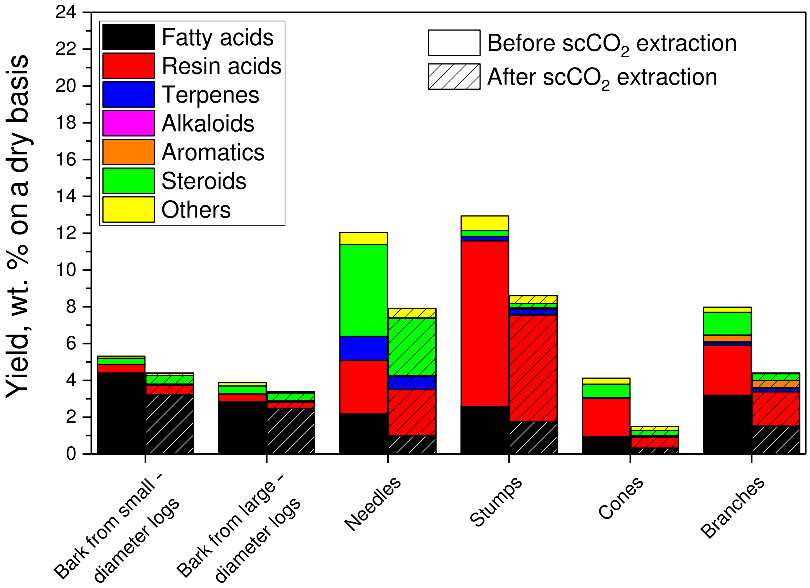


Figure 1. Yields (wt %) of extractives by Soxhlet extraction of original wood fractions and after $scCO_2$ extraction.

quantities of phosphor (1500 mg kg^{-1} for original needles and 1400 mg kg^{-1} after $scCO_2$ extraction), sulfur (0.1% of original and extracted biomass), potassium (5600 mg kg^{-1} for original needles and 5800 mg kg^{-1} after $scCO_2$ extraction), and calcium contents (2450 mg kg^{-1} for original needles and 2600 mg kg^{-1} after $scCO_2$ extraction); in contrast, bark contains significant proportions of calcium (4700 mg kg^{-1} for original needles and 4800 mg kg^{-1} after $scCO_2$ extraction) and magnesium (900 mg kg^{-1} for original needles and 800 mg kg^{-1} after $scCO_2$ extraction), as previously discussed for the spruce wood fractions.[31] The ash content was found to be higher in needles and bark than in other wood fractions.[32] The ash composition of bark from smaller- and larger-diameter logs varied, which emphasized the impact of tree age on the chemistry and structure of pyrolysis products.[33,34] Overall, the variations in ash composition of the original wood and the $scCO_2$-extracted sample were observed. The main differences were observed in the concentration of Ca, K, Mg, and Al.

Lignocellulosic analysis of original wood fractions demonstrated that branches and stumps had a greater proportion of galactan, xylan, and lignin compared to glucomannan-rich stemwood, as previously reported.[35] The extractive content is higher in stumps (13.0 wt %) compared to bark (5.3 wt %), confirming the previous results.[36] Stumps and needles contain significant proportions of lipids, particularly waxes, as illustrated in Figure 1.[37] Therefore, the present study showed that stumps and needles contained significantly higher amounts of extractives in comparison to other fractions. $ScCO_2$ treatment of needles and stumps removed higher fractions of extractives than during the processing of other wood fractions, 8.6 and 7.9 wt % after $scCO_2$ extraction, respectively. The major drawback of $scCO_2$ extraction is its suitability to remove small non-polar molecules due to the non-polar nature of the CO_2 solvent.[38] The polar extracts include phenolics, tannin, and flavonoids, which were more difficult to completely remove in comparison to the non-polar extractives using $scCO_2$ treatment.

Yields of Extractives. The percentages of extractives are shown in Figure 1. The greatest yield of extractives (13 wt %, db) was found in stumps; in contrast, cones demonstrated a significantly lower yield (about 4.1 wt %, db) and bark from pinewood (about 5.3 small diameter and 3.9 wt % large diameter, db) also showed moderate yields. Both stumps and needles demonstrated the greatest proportion of extractives compared to other fractions. The high terpene content of needles (including monoterpenes, sesquiterpenes, diterpenoids, and their derivatives) singles this wood fraction out compared and is consistent with previous studies.[39] Needles gave a great variety of extractives due to their maturity. Needles from the old trees are known to contain a significant range of natural products compared to younger trees.[40] In addition, the stumps contained significant yields of lipids (including resins or fatty acids) due to the greater proportion of heartwood than bark in the stump fraction. The bark gave a large fraction of fatty acids. This is because fatty acids form a tree's protective barrier that protects the tree from the external environment.[41] Bark from small-diameter bark demonstrated the greater fatty acid content compared to large-diameter pinewood. Again, this was due to the proportion of heartwood resulting from age and therefore a greater number of annual rings.[42]

Time-of-Flight Secondary-Ion Mass Spectrometry. Solvent extraction may contribute to the complexity observed in the ToF-SIMS data; this is likely to be a result of lignin-like ions which lead to mass interferences. ToF-SIMS sensitivity is typically in the ppm to ppb levels. Figure 2a demonstrates the signals corresponding to CH-, C_2H-, and O-ions which have been normalized on the intensity of the C-ion, which represents a general composition of the wood fractions. The obtained results demonstrated a rise in the contribution of oxygen and a reduction in the hydrogen content after $scCO_2$ extraction of all wood fractions except the bark fraction from large-diameter pinewood. Prior literature studies indicated that the removal of non-polar extractives such as wax and fatty acids could reduce the hydrogen content and therefore increase the oxygen concentration due to the accumulation of polar components left on the wood surface.[43] In the case of bark obtained from large-diameter wood, $scCO_2$ extracts compounds that have more oxygen than the remaining material. To better understand the surface composition of the wood parts,

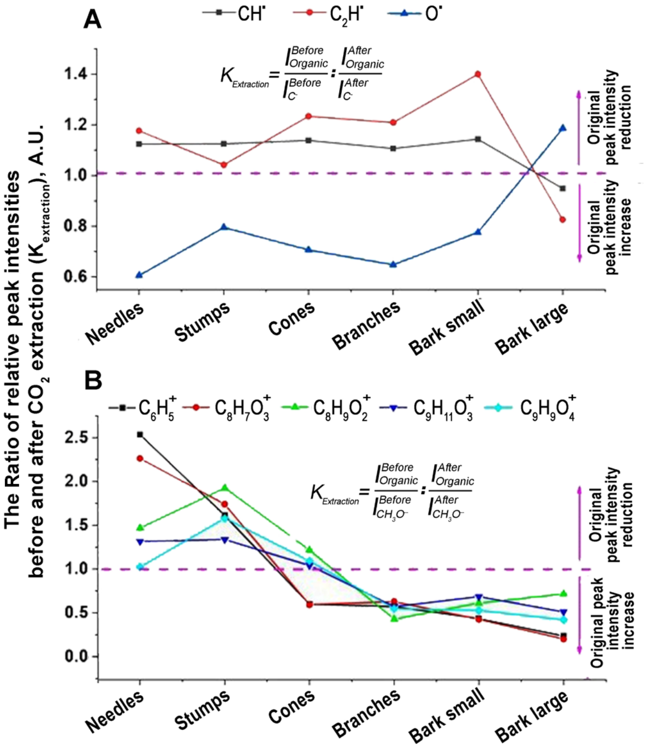


Figure 2. Normalized intensity of selected (a) negative and (b) positive ions as calculated using the mass spectrometry data of the original wood fractions and scCO$_2$-extracted samples.

the influence of scCO$_2$ extraction on the intensities of ions originating from aromatic compounds ($C_6H_5^+$, $C_8H_9O^+$, $C_8H_7O^+$, $C_9H_{11}O^+$, and $C_9H_9O^+$ ions) has been investigated, as shown in Figure 2b. For a valid comparison, these intensities were normalized on the intensity of the ion ascribed to cellulose (CH_3O^+).

ScCO$_2$ extraction of needles and stumps led to a decrease in the aromatic-ion relative intensity, while the extraction of branches and both bark samples resulted in a significant increase in the intensity of ions coming from lignin. The scCO$_2$ extraction of cones does not significantly change its surface composition. These results could be explained based on the diverse nature of the different source of aromatic ions. The aromatic ions could be derived both from small extractable phenol molecules and from insoluble phenolates and lignin. Therefore, it could be proposed that the scCO$_2$ treatment of the parts reached with extractable aromatic compounds (needles and stumps) substantially reduced the intensity of aromatic ions. In contrast, the treatment of the relatively poor extractive phenol wood parts such as barks and branches removes wax and exposes lignin and metal phenolates, increasing the aromatic compound impact. The intensity of ion peaks corresponding to alkaline earth metals (including Na^+, K^+, Mg^+, and Ca^+), Al, and Si obtained from different wood parts before scCO$_2$ extraction are demonstrated in Figure 3a. The surface concentration of the metals varied from one part of the wood to another. For example, the potassium concentration on the surface of a bark fraction from large-diameter pinewood is nearly 10 times higher than that on the surface of the stump. However, the surface concentration of elements is affected more by the nature of the specific element.

The surface concentration of different metals varies by hundreds and thousands of times dependent on their nature.

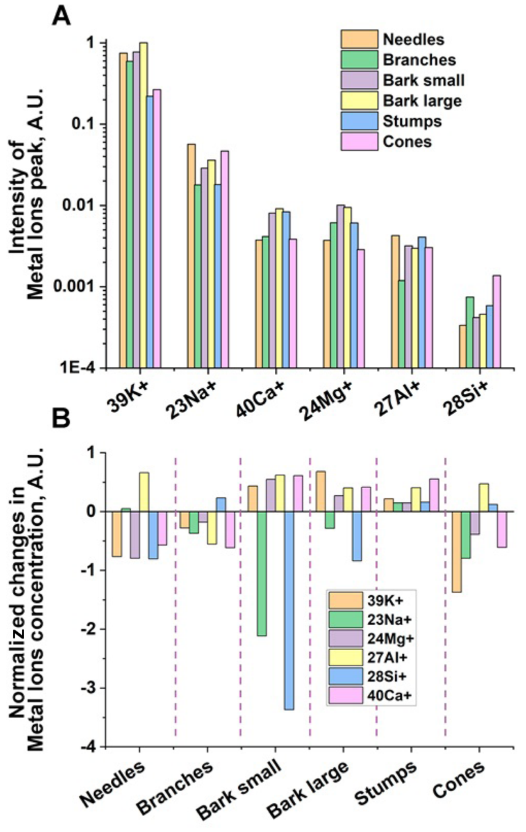


Figure 3. (A) Intensity of the metal ion peak from different fractions of the wood; (B) normalized change in metal concentration after scCO$_2$ adsorption. The changes were found according to the equation $(I^{\text{before}}_{\text{Me}^+} - I^{\text{after}}_{\text{Me}^+})/I^{\text{before}}_{\text{Me}^+}$.

The K^+ surface concentration is 100 times higher than the rest of the metals in all wood fractions. Sodium is the second most significant element in the wood parts. Multivalent elements (Ca^+, Mg^+, Al^+, and Si^+) are represented in much smaller quantities than monovalent metals.

The influence of the nature of both wood fractions and metals is even more significant in the results of the scCO$_2$ extraction. The concentration of metals on the surface of such wood parts as needles, branches, and cones is increased after extraction. In addition, the concentration of aluminum on the surface of cones and needles decreased. However, the scCO$_2$ extraction resulted in a greater aluminum content on the branch surfaces. As it can be seen from Figure 3b, scCO$_2$ treatment of these fractions significantly alters the relative surface concentration of metal ions. As it was previously indicated, scCO$_2$ extraction can lead to relative intensity changes of aromatic ions coming from lignin. The removal of surface phenols could further expose the solid lignin-polysaccharide surface, making metal ions connected to this surface available and thus raising their surface concentration.

Py-GC/MS Analysis. The major pyrolysis products of wood fractions were investigated using Py-GC/MS. The chromatograms demonstrate the presence of more than 130 peaks. The results indicated that the pyrolysis vapor is highly oxygenated, with a significant proportion of oxygen-containing compounds, and is consistent with the pyrolytic decomposition of biomass such as the original pinewood. Figure 4 demonstrates the relative peak areas of 36 identified compounds which have been categorized as acids, ketones,

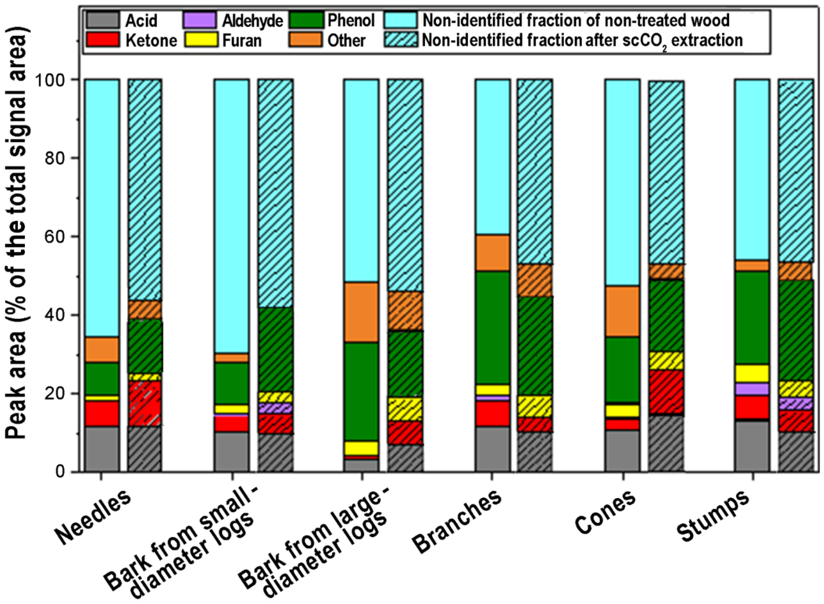


Figure 4. Relative composition of volatiles from pyrolysis at 600 °C shown in % of the total chromatographic peak area.

aldehydes, furans, phenolics, and other products. All these classes are present in both the original and extracted wood fractions. Other identified pyrolysis products include levoglucosan, acetamide, enzacamene, phorbol, retinoyl-glucuronide, and so forth. The high acetic acid concentrations are a result of deacetyl of xylose units.[44] Aldehyde and ketone compounds are derived from monosaccharide breakdown, which are considered as the main products of secondary volatiles during pyrolysis.[45] Levoglucosan is formed at the first step of cellulose pyrolysis and then undergoes dehydration, followed by isomerization to form small volatile molecules such as acids, furans, and aldehydes.[46] For example, cyclohexanone was produced by levoglucosan dehydration in all wood fractions, while 2-furanmethanol was the product of levoglucosan decomposition.[47]

Furfural was a product of either further furfuryl alcohol decomposition or pyrolysis of xylose.[48] Therefore, it is not surprising that furfural is detected in all wood fractions. Furthermore, furan-containing compounds could be produced during the pyrolysis of polysaccharides, carbohydrates, or fatty acids. Significant guaiacyl residues were found in all wood fractions due to the guaiacyl units derived from the monolignol coniferyl alcohol in pinewood lignin. The phenolic compounds were derived from different building units of lignin[49] or tannins.[50] Vinylguaiacol and guaiacol were the dominant pyrolysis compounds derived from guaiacyl lignin.[51] The results showed that extractives can still be found in the $scCO_2$-extracted wood samples.

The α-pinene compounds were identified only in pinewood stumps. The pyrolysis of polymerized coniferyl alcohol and dihydroconiferyl alcohol (G-type lignin) led to the formation of isoeugenol and vanillin.[52−54] The acid fraction includes the long-chain saturated (hexadecanoic and santonical acids) and unsaturated (linoleic and oleic acid) fatty acids, which were likely formed by pyrolysis of triglycerides.[55] The results showed that the different pinewood fractions exhibited a relatively similar composition and yields of identified volatile products.

Figure 5 demonstrates that $scCO_2$ extraction has a significant influence on the distribution of volatile products during wood pyrolysis. The $scCO_2$ treatment of needles leads to the substantial increase of the content of phenols, ketones, and acids. $scCO_2$ extraction of barks from small-diameter logs stimulates the formation of aldehyde and increases the content of phenols, and at the same time, extraction of bark from large-diameter logs boosts ketone production. It is well known that metals crucially influence the biomass pyrolysis pathway. Therefore, it is natural to assume that such a phenomenal influence of $scCO_2$ on the composition of wood pyrolysis products could be as a result of alternation of the surface metal cation distribution within biomass after extraction, as shown in Figure 3. The systematic comparison of the results of ToF-SIMS results and Py-GC/MS was conducted to validate this hypothesis.

Relationship between Py-GC/MS and Analysis of ToF-SIMS Data. Limited information is available about what influence surface chemistry has on biomass pyrolysis. Therefore, the combination of ToF-SIMS with Py-GC/MS must clarify the possibility of the influence of surface metal cations on the pyrolysis of wood and how $scCO_2$ extraction affects this process. This approach examines the influence of six metal cations on the yields of five types of compounds based on data from six wood fractions. This analysis has been carried out on wood fractions before and after $scCO_2$ extraction. This analysis involves a vast number of systems (a minimum of 60 different combinations), which require the application of very efficient analysis methods.

VIA was chosen as a mathematical tool to describe relations between metal surface concentrations and the pyrolysis mechanism. VIA aims at quantifying the effect of each input variable on the uncertainty of the model output, referring to what extent a given model utilizes a variable in order to obtain accurate predictions.[56] If a model depends on a specific variable to accurately predict an outcome, it therefore demonstrates greater importance to the model. VIA generates a descending list of important variables by a mean decrease in contribution to the model. The variables from the bottom of the list could be removed from the model. The results of VIP applications to all experimental systems can be seen in Figure 5.

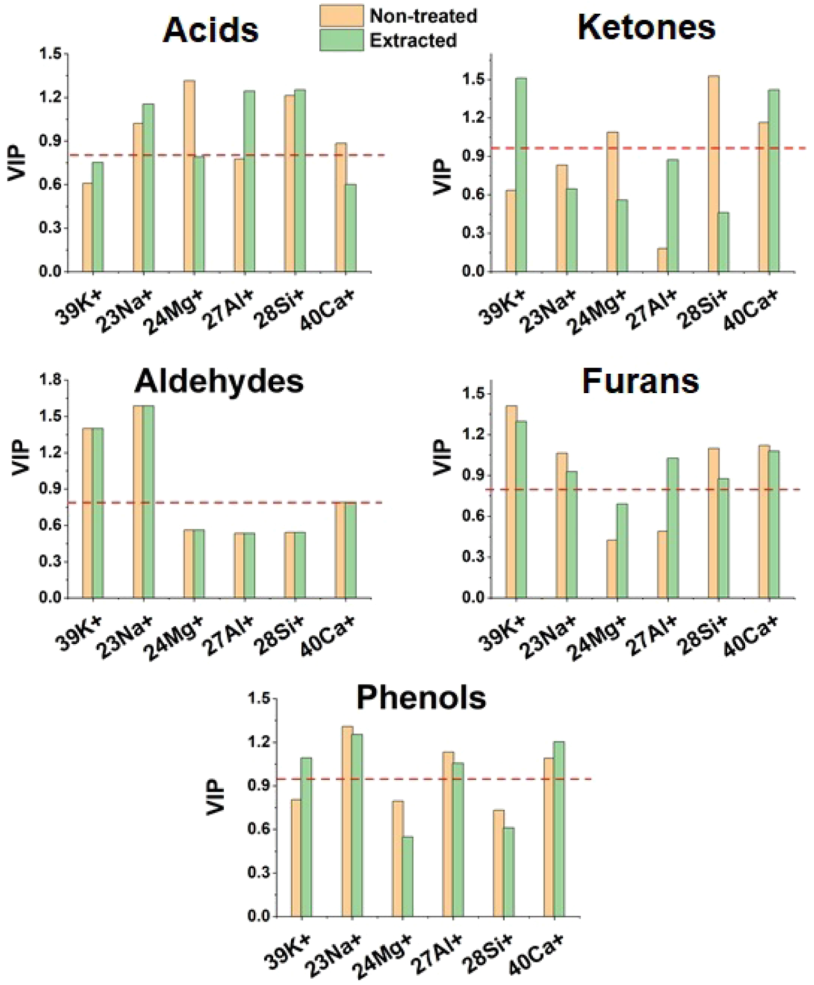


Figure 5. Variable importance analysis (VIA) of the influence of metal cation surface concentration on yield of pyrolysis products utilizing a combined ToF-SIMS and Py-GC/MS approach.

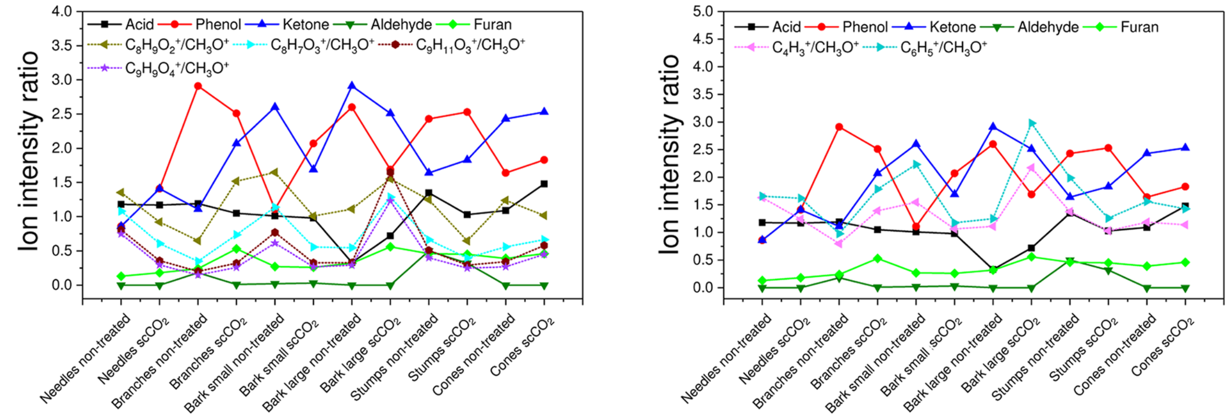
Figure 5 shows the nature of the surface metals and how they influence Py-GC/MS yield of a specific compound. The acid yield is affected by the presence of all elements. Major elements which influence the aldehyde yield are sodium and potassium. There is no influence of $scCO_2$ extraction on the formation of aldehydes. Overall, the differences in yields of aldehydes which were formed during pyrolysis are negligible, leading to the low differences in the composition of both organic matter and metals. Treatment with $scCO_2$ changed the metal composition and concentrations on the surface, which are the most important to produce volatile products. For example, ketones formation from non-treated wood fractions was affected with only Mg^+, Si^+, and Ca^+. In contrast, after $scCO_2$ extraction, the critical metals for ketone production become only K^+ and Ca^+. After extraction, Al^+ demonstrates a key role in furane production, while K^+ becomes crucial to produce phenols.

These results support a hypothesis that the surface chemistry of wood components can play a significant and essential role in their pyrolysis mechanism. This hypothesis could be based on a few pieces of evidence: (i) the concentration of metals measured with such a surface technique as ToF-SIMS is significant for volatile composition; (ii) $scCO_2$ extraction influences only the changes in a surface composition which are vital to produce a certain group of compounds.

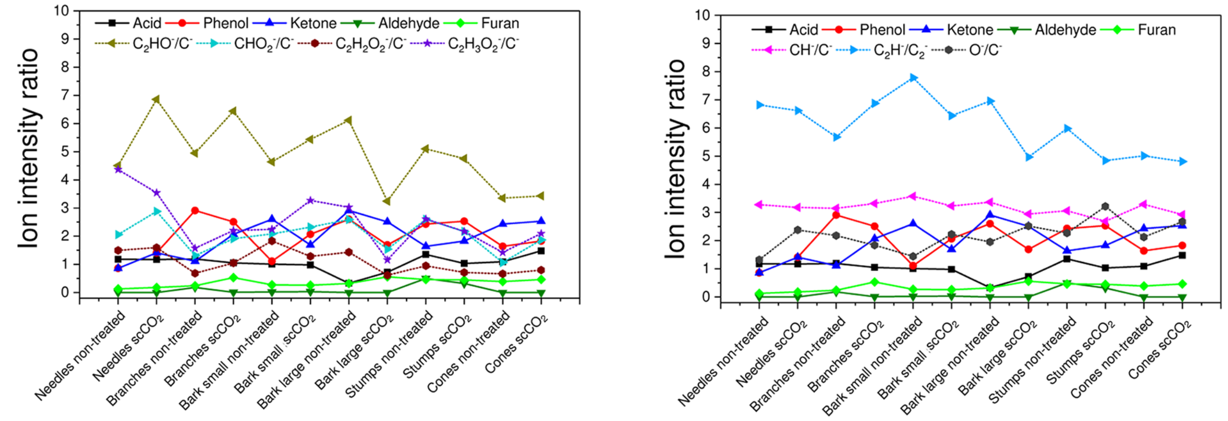
■ DISCUSSION

This study has investigated the release of volatile compounds using Py-GC/MS with the prior characterization of non-treated wood fractions using ToF-SIMS analysis. Figure 6 demonstrates that the composition of volatiles depends on the type of the wood fraction type due to the variation of the ion intensity ratio among samples. However, common trends were observed for all wood fractions when the ion intensity ratio was correlated to the volatile composition. The lowest contribution of acids, aldehyde, and furan and the highest contribution of phenols and ketones correlate with the minimum of the intensity of ions coming from lignin and the maximum intensity of ions originating from aromatics (Figure 6a,b). The low ion intensity coming from lignin could be related to the fact that the ToF-SIMS spectra can overlap with the content peaks originating from extractives. Phenols and ketones in biomass volatiles originate from lignin through aromatization and condensation reactions of slow pyrolysis.[57] In addition, the results concur with previous work that showed that more phenols are formed during wood pyrolysis than in herbaceous biomass heating.[58]

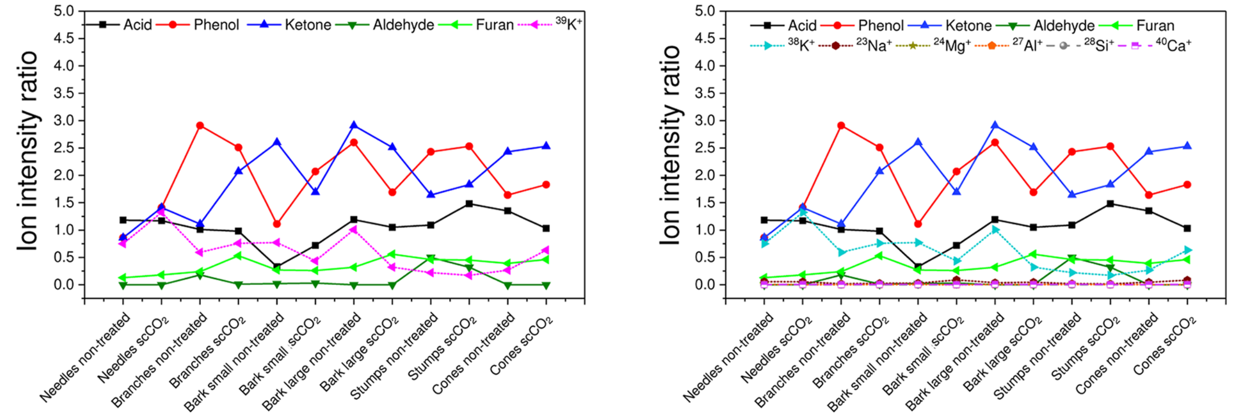
The correlations between the light organic fragments and the total surface concentration on the wood surface with the pyrolysis volatiles highlighted the presence of heavy molecular compounds. The present ToF-SIMS analysis showed that the



6(a): Ion intensity (lignin). 6(b): Ion intensity (aromatics).



6(c): Ion intensity (light organics). 6(d): Ion intensity (CH^-, C_2H^-, O^-).



6(e): Ion intensity ($^{39}K^+$). 6(f): Ion intensity (metals).

Figure 6. (a-f) Correlation of normalized intensity of negative and positive ions determined through mass spectrometry data from the original and $scCO_2$-extracted fractions. The normalized ion intensity was artificially magnified by factor 10.

high intensity of ions coming from light organic fragments and the general organic composition of the wood surface correlate to the low contribution of all detected organic compounds (ketones, aldehydes, phenols, acids, and furans). Small organic fragments can form large molecular compounds with more than five rings in a polyaromatic structure.[13]

Another observed trend is that the highest contribution of phenols and ketones and the lowest contribution of acids, aldehyde, and furan correlate with the minimum metal ion intensity, as shown in Figure 6e,f. The results indicated that metals, especially potassium, migrate across the wood particle surface, leading to the higher quality of volatile vapor during pyrolysis, reducing lignin-type compounds and producing hydrocarbons. Activity of metal ions on the wood surface resulted in phenols, ketones, and high-value hydrocarbons in a pyrolysis vapor through deoxygenation, aromatization, and catalytic cracking reactions.[59] Moreover, acidic metals appeared to deoxygenate the carboxylic acids and carbonyls; therefore, metals present lead to the selective conversion of phenols and methoxy phenols into aromatic compounds.[60]

These results correlate well to the properties of the gas and bio-oil during catalytic pyrolysis.[59]In the present work, the minimum contribution of potassium to furan formation has demonstrated hydrolysis of glycosidic bonds of cellulose and subsequent rearrangement of the monosaccharide monomer, resulting in the production of levoglucosan from cones ($K^+ \approx$ 0.34 wt %) and bark from the large-diameter pinewood ($K^+ \approx$ 0.15 wt %). Thus, it showed that potassium has little influence on levoglucosan production and consequently on the reactions to furans. The formation of levoglucosan during pyrolysis of wood fractions was related to the low acetic acid yields and furans with a concurrent increase in the yield of high-molecular-mass phenols.[61] This is due to the fact that the deoxygenation of organic compounds is likely to take place through a series of decarbonylation or decarboxylation reactions, as suggested in previous work.[62]

■ CONCLUSIONS

A new method using ToF-SIMS was developed to study the catalytic effects of biomass inorganic matter and to predict the differences in ion intensity of both extractives and alkali metals. Py-GC/MS results indicated that volatiles released from non-treated and $scCO_2$-extracted fractions mainly consisted of fatty acids and phenols. It was postulated that the phenomenal influence of $scCO_2$ on the composition of wood pyrolysis products could be a result of changes in the surface metal cation distribution within biomass after extraction. The migration of potassium on the wood surface generated volatiles with the high abundance of phenols and ketones and the low presence of acids, aldehydes, and furans. High concentrations of phenols and ketones in biomass volatiles originated from aromatic compounds of lignin. The composition of residual extractives, the water content, and vitally the surface metal cation distribution within biomass after $scCO_2$ extraction are key factors that influence the product profile. In addition, future work in the application of ToF-SIMS could create opportunities to deepen our understanding of how surface metal cations influence the mechanism of biomass pyrolysis.

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Notes

The authors declare no competing financial interest.

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