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Abstract

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High-Resolution Mass Spectrometric Characterization of Molecules on Biochar from Pyrolysis and Gasification of Switchgrass

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S Supporting Information

ABSTRACT: Organic molecules entrapped in biochar during pyrolysis and gasification of switchgrass have been studied using high-resolution mass spectrometry. Two solvent systems, toluene and a mixture of water/methanol, were used to extract hydrophobic aromatic compounds and hydrophilic polar compounds, respectively. Laser desorption ionization and atmospheric pressure photoionization were used for toluene extracts, while electrospray ionization was used for water/methanol extracts, followed by orbitrap mass spectrometric data acquisition. Molecular compounds previously known in bio-oils were observed for fast pyrolysis biochar, with phenolic and carbohydrate-derived compounds originating from the pyrolysis of lignin and holocellulose, respectively. In contrast, polycyclic aromatic hydrocarbons (PAHs) with various ring sizes were observed for gasification biochar and also for slow pyrolysis biochar in low abundance.

INTRODUCTION

Once thought to be a low-value waste byproduct of biomass pyrolysis, biochar has shown promise as a soil amendment and a carbon sequestration agent.^{1–4} Biochar application can improve soil quality through increased moisture and nutrient retention, increased microbial activity, and decreased bioavailability of organic contaminants.^{5–7} Biochar is produced from various feedstocks (including cornstover, wood, and even municipal waste) via various thermochemical conversion processes, such as pyrolysis and gasification.^{8,9}

Pyrolysis involves heating of organic matter in the absence of oxygen to maximize either bio-oil, as in fast pyrolysis, or biochar, as in slow pyrolysis. The difference between fast and slow pyrolysis involves the heating rate and heating temperature: fast pyrolysis occurs at 400–600 °C with less than 2 s of heating time, and slow pyrolysis occurs at 300–800 °C for at least 1 h. Alternatively, gasification systems rapidly heat biomass in the presence of oxygen to produce syngas (CO and H₂). Gasification generally produces the least amount of biochar (~10% of biomass weight converted to solid char), followed closely by fast pyrolysis (~12%), and surpassed by slow pyrolysis (~35%).⁹

Brown and co-workers have characterized biochars from various thermochemical conversion processes and various feedstocks.^{10,11} Fourier transform infrared (FTIR) spectra showed functional groups unique to the thermochemical conversion method. Oxygen-containing functional groups, specifically hydroxyl stretch at 3400 cm⁻¹ and carboxylic carbon stretch at 1700 cm⁻¹, were dominant in fast pyrolysis spectra, weak in slow pyrolysis, and almost absent in gasification. Additionally, ¹³C direct polarization nuclear magnetic resonance (NMR) spectra showed highly abundant oxygen-containing carbons in fast pyrolysis biochar compared to slow pyrolysis or gasification. Aromatic carbons dominated the NMR spectra for all biochars. The aromatic C–H was most abundant for slow pyrolysis (~30%), slightly lower for fast pyrolysis (~23%), and lowest for gasification (~10%). Similar

results were obtained by Lee and co-workers in their FTIR analysis of fast pyrolysis and gasification chars from corn stover.¹²

FTIR and NMR techniques provide valuable information about chemical bonds and functional groups; however, they cannot separate the information from each individual molecule and only provide the average information of the whole mixture. Volatile organic compounds (VOCs) within biochar were studied by Spokas and co-workers using gas chromatography–mass spectrometry (GC–MS) analysis with headspace desorption at 150 °C for 10 min.¹³ Over 140 unique compounds were identified but limited to volatile gases with molecular weights mostly below 100. A comprehensive understanding of all organic molecules would be very important for soil application of biochar because they might be released to the soil and affect soil microbial systems.^{7,14}

Ultrahigh-resolution mass spectrometry, such as Fourier transform ion cyclotron mass spectrometry (FT-ICR MS), is a major tool for petroleomics, allowing for direct chemical composition analysis of complex crude oils, and was successfully applied to characterize tens of thousands of compounds in petroleum crude oils.^{15–17} Podgorski and co-workers adapted desorption atmospheric pressure photoionization (DAPPI) for direct molecular characterization of intact biochar materials using FT-ICR.¹⁸ DAPPI–FT-ICR analysis on combusted char showed a bimodal distribution of aromatic (low H/C and O/C ratios) and aliphatic (high H/C and O/C ratios) compounds originating from lignin and holocellulose, respectively. Pyrolyzed oak biomass displayed increased aromaticity and lacked the aliphatic distribution. FT-ICR MS was also used in a study by Hockaday and co-workers that examined dissolved organic matter from naturally degraded charcoal particles over a period of 100 years.¹⁹

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A petroleomic approach was first adapted by our group for the analysis of bio-oils.²⁰ Using laser desorption/ionization (LDI) as an ionization method, we have analyzed over 100 nonvolatile lignin pyrolysis products in bio-oils. Recently, we have further expanded this approach using negative electrospray ionization [(-)ESI] and could characterize over 800 chemical compositions.²¹ (-)ESI could analyze most volatile compounds with $m/z > 100$, including pyrolysis products of not only lignin but also cellulose and hemicellulose. In the current study, we adapt this high-resolution mass spectrometry approach to characterize molecular components in the biochar produced by three different thermochemical processes.

EXPERIMENTAL SECTION

Materials. Switchgrass biochar samples were obtained from Robert Brown at Iowa State University. The fast pyrolysis biochar was produced on a fluidized-bed reactor at 450 °C.¹⁰ Gasification char was produced on a bubbling fluidized-bed reactor at 824 °C under steam/oxygen-blown conditions. Slow pyrolysis biochar was generated in a paint can heated at a rate of 15 °C min⁻¹ up to 500 °C and held for 30 min. The three biochars are the same material as biochars 7, 10, and 13 in the report by Brown's group,¹¹ corresponding to fast pyrolysis, gasification, and slow pyrolysis chars, respectively. Elemental analysis of fast pyrolysis switchgrass biochar showed carbon, hydrogen, nitrogen, and oxygen percent contents at 37.5, 2.2, 0.5, and 8.9, respectively; 25.4, 0.4, 0.3, and 4.5 for gasification, respectively; 39.4, 1.3, 0.7, and 5.6 for slow pyrolysis, respectively.¹¹ Water and methanol were purchased at the highest available purity from Fisher Scientific (Fair Lawn, NJ). High-performance liquid chromatography (HPLC)-grade toluene ($\geq 99.9\%$) was purchased from Sigma-Aldrich (St. Louis, MO).

Mass Spectrometry. A linear ion trap-orbitrap mass spectrometer (LTQ-Orbitrap Discovery, Thermo Scientific, San Jose, CA) was used for the current study. For the LDI-MS study, the instrument was configured with a matrix-assisted laser desorption/ionization (MALDI) system operating at intermediate vacuum pressure (75–80 mTorr). A nitrogen laser (MNL 100, Lasertechnik Berlin, Berlin, Germany) was used to vaporize and ionize samples spotted on a MALDI plate. MALDI plates were deep-cleaned prior to analysis according to the instruction manual. A total of 5 mL of toluene was added to 50 mg of biochar samples and sonicated for 10 min. An 1 mL aliquot of the liquid fraction was centrifuged to separate unsettled char, and 500 μ L of the supernatant was taken for the analysis. Extraction efficiency using toluene was ~ 5 mg/g for fast pyrolysis and gasification chars and < 0.5 mg/g for slow pyrolysis char. The extracts were spotted in three increments of 0.5 μ L on the MALDI plate, allowing each drop to air-dry between spotting. The laser power was carefully adjusted, and 15–35 μ J per pulse of laser power was used with two neutral density filters, reducing the actual laser power to 25%. A tandem mass spectrometry (MS/MS) study was performed for a few major compounds in the linear ion trap of the mass spectrometer at a collision energy of 35% and with an isolation width of 1.8 Da.

For ESI and atmospheric pressure photoionization (APPI), the MALDI source was removed from the mass spectrometer and the atmospheric pressure ionization chamber was reconfigured. A vacuum ultraviolet (UV) lamp (PhotoMate, 10.0/10.2 eV, Syagen, Tustin, CA) was used for APPI-MS analysis of toluene extracts with IonMax source (Thermo) and API probe. The API probe vaporization temperature ranged from 380 to 400 °C with the MS inlet capillary held at 275 °C and the tube lens voltage set at 70 V. A 50:50 mixture of water and methanol (v/v) was used to extract polar compounds entrapped in biochar with a similar sampling process as toluene extraction. Extraction efficiency using the water/methanol solvent system is ~ 48 mg/g for fast pyrolysis char, ~ 19 mg/g for gasification char, and < 0.2 mg/g for slow pyrolysis char. ESI in negative-ion mode was used for the water/methanol extracts. All of the experiments were performed in three replicates.

Data Analysis. Composer (Sierra Analytics, Modesto, CA) was used for spectra calibration, chemical composition assignment, and molecular visualization of the data sets acquired from the extracts of fast pyrolysis chars. The data obtained from the orbitrap was exported in a text file using QualBrowser (Thermo Scientific) for the peaks above 0.5% relative abundance; they are all above 6 times the baseline noise. The orbitrap was calibrated externally according to the procedure provided by the manufacturer, and its mass accuracy is confirmed with previously characterized bio-oil samples obtained at the same condition: < 3 ppm for (+)LDI and < 5 ppm for (-)ESI. Mass errors in positive-ion mode are consistent within the same spectrum, further confirming its reliability in mass measurement; e.g., all major peaks in Figure 1 have a mass error from -1 to -3 ppm. Mass calibration in negative-ion mode had more errors (up to 5 ppm); nonetheless, most peaks show at low mass ($< m/z$ 200), where misassignment of the chemical composition is not likely. Peak assignment was further confirmed through the Kendrick mass chart. The chemical composition analysis was performed with Composer for extracted compounds, and the chemical compositions were limited to 30 carbons, 60 hydrogens, 15 oxygens, and 5 nitrogens, with a mass accuracy tolerance of 5 ppm. No ³⁴S isotope was observed, and sulfur was not included as a possible element.

RESULTS AND DISCUSSION

Overall Strategy. We first attempted direct LDI-MS analysis of biochars by attaching the biochar particles to the MALDI plate using double-sided tape (Supplemental Figure 1 of the Supporting Information). This approach generated large distributions of fullerene-like compounds produced in the high-energy, high-density laser plume, which is consistent with the initial discovery of fullerenes by laser vaporization of graphite.²² Hence, the subsequent studies focused on the solvent extracts of biochar to separate and enrich the small molecules from solid char materials. We used two different solvent systems, toluene and a mixture of water and methanol. Toluene was chosen to extract lignin-derived aromatic compounds that might have been adsorbed on the surface of polyaromatic biochar. Water/methanol was chosen to extract hydrophilic polar compounds, particularly originating from cellulose or hemicellulose. Toluene extracts were investigated by LDI and APPI, because of their efficient ionization of aromatic compounds. ESI was used for water/methanol extracts because of its efficient ionization of polar compounds. A LTQ-Orbitrap high-resolution mass spectrometer was used for accurate mass measurement and direct determination of their chemical compositions. The lower version of orbitrap used in the current study (Orbitrap Discovery) has limited mass resolving power ($m/\Delta m \sim 30\,000$ at m/z 400) compared to FT-ICR MS or a higher version of orbitrap. However, the biochar extract is much less complex than bio-oils or petroleum oils, with little or no overlapping peaks, and its mass resolving power was sufficient for the current study. For example, the complexity of biochar extract in the current study is less than that of our previous LDI-Orbitrap analysis of bio-oils, which is confirmed to have sufficient mass resolution in comparison to FT-ICR.²⁰

Toluene Extracts of Biochar. LDI experiments on toluene extracts of biochar were performed in a similar fashion to the recent LDI-MS analysis of bio-oils.²⁰ Careful attention was made to avoid any possible aggregation reactions in the laser plume. Specifically, the spotted sample concentration and laser power were minimized to the lowest possible value. Unlike direct biochar analysis, extracts spotted in low concentration do not produce high-density laser plume and accompanying aggregation reactions. Figure 1 compares LDI-MS spectra of toluene extracts from three biochars produced from fast

pyrolysis, slow pyrolysis, and gasification. Marked differences can be found among the three spectra: mostly O4 and O5 compounds in fast pyrolysis (Figure 1A), polycyclic aromatic hydrocarbons (PAHs) in gasification (Figure 1B), and lack of peaks except for a few PAHs in slow pyrolysis (Figure 1C).

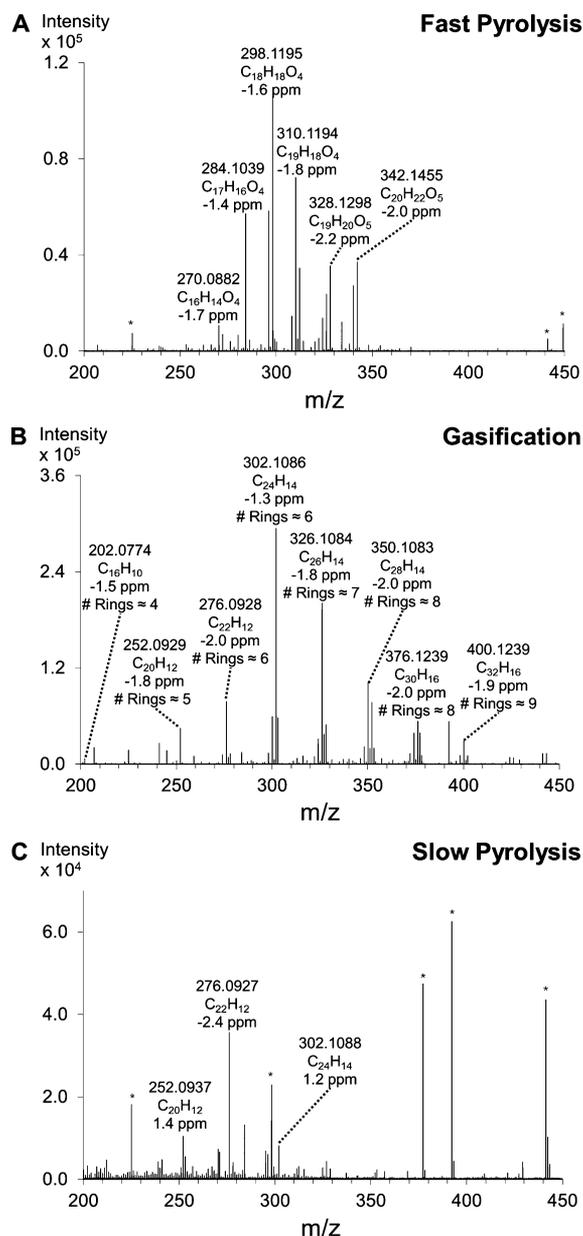


Figure 1. (+)LDI-MS spectra for toluene extracts of biochar from (A) fast pyrolysis, (B) gasification, and (C) slow pyrolysis. The number of rings is estimated for the polycyclic aromatic hydrocarbons in Figure 2B. (*) Contamination.

The MS spectrum of toluene extracts of fast pyrolysis biochar (Figure 1A) is very similar to that of the fast pyrolysis bio-oils previously reported (Figure 2A in ref 20), specifically the major compounds of m/z 270 (C₁₆H₁₄O₄), 284 (C₁₇H₁₆O₄), 298 (C₁₈H₁₈O₄), 328 (C₁₉H₂₀O₅), and 342 (C₂₀H₂₂O₅). The MS/MS spectra of a few major compounds are consistent with those of bio-oil compounds, further confirming their structural similarity (Supplemental Figure 2 of the Supporting Information).²⁰ It is not surprising to find bio-oil-like components in

fast pyrolysis biochar. The fast pyrolysis biochar is a side product of bio-oil production in the fast pyrolysis process. Specifically, the pyrolysis reactor used in the current study is designed to filter out char materials by having pyrolysis vapors pass through the Cyclone.²³ Some bio-oil vapors might not have escaped from the char particles and left behind as condensate.

There are a few differences between the MS spectrum for biochar extracts and previous bio-oil data. The previous LDI-MS spectrum of bio-oils was composed of two distinguished groups of peaks: lignin dimers at m/z 250–400 and lignin trimers at m/z 400–550.²⁰ Lignin trimer compounds are roughly about ~15% of dimers in the previous bio-oil spectrum, but they are present in very low abundance in biochar extracts with roughly 1% (Figure 1A). One possible explanation is that the lignin dimers and trimers are mostly produced from secondary reactions between monomers. If we assume the pyrolyzates are mostly monomeric initially and oligomerized through reaction with each other, the oligomerization reaction would be much less favored in biochar-entrapped molecules because of the competition with absorption to the char surface. Dimerization may still happen, but the reaction probability for trimerization would be very low.

Another major difference between bio-oil and biochar extract is the fact that the most abundant peak in the previous bio-oil spectrum, m/z 272 (C₁₆H₁₆O₄), is very low in Figure 1A (~7% of the base peak). We attribute this to the difference between the biomass materials: loblolly pine (previous study) versus switchgrass (current study). We have previously noted the structural uniqueness of m/z 272 in its MS/MS spectrum compared to others. This ion at m/z 272 has been found in pyrolysis–field ionization and pyrolysis–molecular beam mass spectrometric studies by several research groups, particularly for hardwood biomass materials.^{24–28} Its abundance might be related to the biomass materials, presumably hardwood. A further study is needed to understand the structural nature of this particular compound.

LDI-MS spectra of toluene extracts of biochar materials produced from gasification and slow pyrolysis (panels B and C of Figure 1) give some insights about the associated thermochemical processes. First of all, unlike fast pyrolysis, oxygen compounds do not exist in both spectra, suggesting that the feed of oxygen fuels in gasification or long reaction time in slow pyrolysis could successfully remove most of the oxygen compounds in biomass materials and convert them into CO or CO₂. Previous NMR and FTIR studies suggest that there still are some oxygen-containing functional groups on these biochars,¹⁰ but they must be from solid biochar materials and not from small molecules adsorbed on the surface. Toluene extracts of gasification biochar (Figure 1B) are all PAHs with various ring sizes. It is consistent with a molecular beam mass spectrometry study on the syngas derived from gasification of corn stover.²⁸ They found up to five-ring PAHs, with one or two aromatic ring compounds most abundant (c.f., toluene, phenol, styrene, and naphthalene). Very large PAHs with the number of rings of 6–8 are most dominant in our study, and small ring compounds are absent. This is mostly because LDI-MS analysis was performed in intermediate vacuum (~75 mTorr) and volatile molecular compounds are all vaporized before the analysis. The removal of these compounds is important in the gasification process, and their detection adsorbed on the biochar might indicate their efficient removal in the current thermochemical process. Slow pyrolysis shown in

Figure 1C, on the other hand, has almost no peaks other than a few PAHs, suggesting that complete reactions occur in the slow pyrolysis process.

Photoionization at atmospheric pressure, APPI, was also used for the analysis of three biochar extracts. APPI allows for the direct analysis of liquid samples with photoionization using vacuum UV photons (10/10.2 eV). One critical limitation in APPI of the biochar extracts is that the spectra are dominated by contaminations from various sources. APPI is subject to contamination in general because it has the ability to ionize most organic compounds, but it was especially significant in biochar extracts because of plasticizers accrued in the extraction procedure, despite of the use of Nalgene tubes to minimize contamination. Despite the significant contaminations, we could confirm the existence of major compounds in panels A and B of Figure 1, ensuring LDI–MS results (see Supplement Figure 3 of the Supporting Information).

Chemical composition analysis was performed for the LDI–MS spectrum of toluene extracts of fast pyrolysis biochar (Figure 1A) and reliably identified 32 chemical compositions. Heteroatom class distribution shown in Figure 2A is very

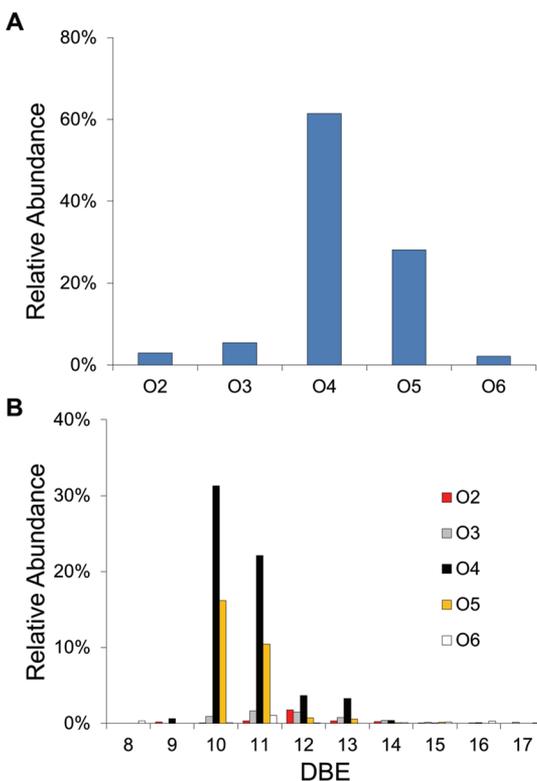


Figure 2. Chemical composition analysis of the (+)LDI–MS spectrum of toluene extracts of fast pyrolysis char shown in Figure 1A: (A) heteroatom class distribution and (B) DBE distribution for each heteroatom class.

similar to that of bio-oils (Figure 4A in ref 20), except for much less abundant O6 compounds, which is attributed to the lack of lignin trimers in biochar extracts. In bio-oils, O6 compounds represent most of the lignin trimers [double bond equivalent (DBE) of 14–17], while the lignin trimer compounds are almost negligible in the DBE distribution of biochar extracts shown in Figure 2B.

Water/Methanol Extracts of Biochar. To study polar compounds in biochar, a 50:50 mixture of water and methanol

was used as an extraction solvent and the extracts were subjected to high-resolution mass spectrometry using ESI. Mass spectral acquisition in positive-ion mode suffered from contaminations, particularly from K and Na metal ions present in high abundance in switchgrass, which significantly suppressed ion signals. Therefore, we focused on negative-ion mode, where alkaline metal ions and plasticizers are all suppressed. We could not obtain meaningful mass spectra for biochar extracts from slow pyrolysis and gasification, suggesting that there is almost no polar compounds adsorbed on biochars (for slow pyrolysis) or inefficient deprotonation because of high Na/K contents (for gasification). For fast pyrolysis biochar, however, we could obtain a nice clean spectrum, as shown in Figure 3. The spectrum is dominated by low-molecular-weight

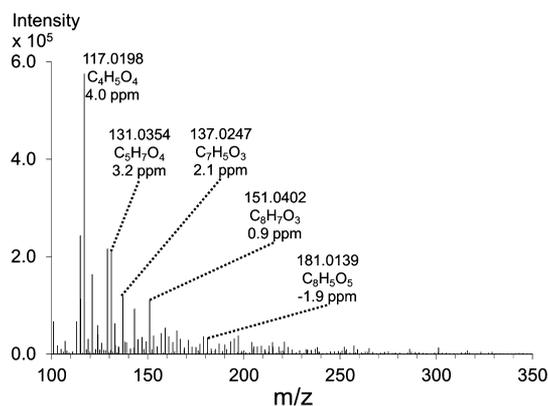


Figure 3. (–)ESI–MS spectrum of the water/methanol extract from fast pyrolysis char.

components in the m/z range of 100–200 and mostly composed of O2–O5 compounds, which is similar to our recent study on fast pyrolysis bio-oils in (–)ESI.²¹ Some of the major compounds are also present in the previous study, such as m/z 131 and 181, but some are different, such as m/z 117, 137, and 151.

A few differences should be noted in understanding the ESI–MS spectra in negative-ion mode (Figure 3) compared to LDI–MS spectra in positive-ion mode (Figure 1). First, aromatic ring compounds are efficiently ionized in LDI through multiphoton absorption by aromatic rings.²⁹ In contrast, polar compounds with deprotonatable hydrogen are ionized in (–)ESI. Second, LDI produces molecular radical ions (M^{\bullet}) with the same chemical composition as the original compounds, whereas the (–)ESI produces deprotonated ions ($[M - H]^-$) with one less hydrogen than its original molecule.³⁰ All ions in Figure 1 are even mass ions, and those in Figure 3 are odd mass ions, following the nitrogen rule. Third, LDI is operating at moderate vacuum conditions (~ 80 mTorr), while ESI is in atmospheric pressure. ESI–MS can effectively ionize volatile compounds, such as those at m/z 100–200 in Figure 3, which are not observed in LDI–MS.

Chemical composition analysis was performed for the spectrum shown in Figure 3, and 25 chemical compositions were confidently assigned. Figure 4A shows the relative abundance of each heteroatom class compound. The O4 compounds are most dominant, which is similar to LDI–MS analysis in Figure 2A. However, the DBE distribution of each heteroatom class shown in Figure 4B is completely different from that of LDI–MS (Figure 2B). Most of all, the aliphatic compounds (DBE < 4) are most abundant, followed by single-

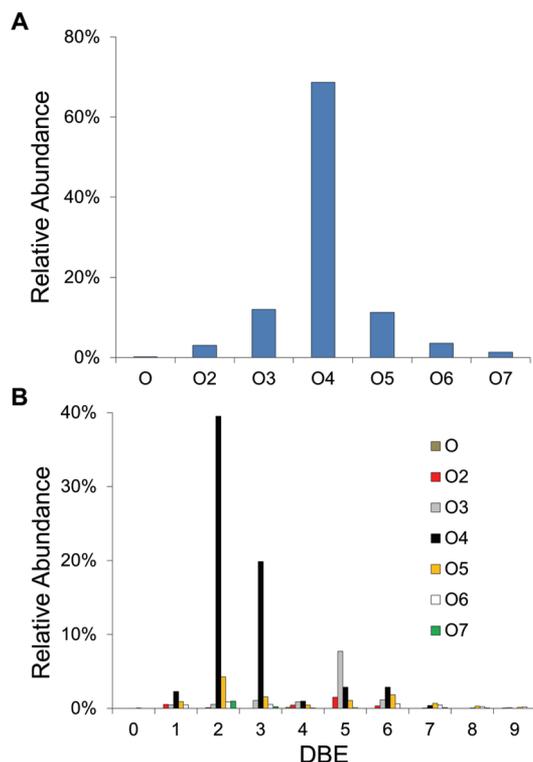


Figure 4. Chemical composition analysis of the (–)ESI–MS spectrum of water/methanol extracts of fast pyrolysis char shown in Figure 3: (A) heteroatom class distribution and (B) DBE distribution for each heteroatom class.

ring aromatic compounds with DBE of 4–7, while those in LDI–MS are mostly double-ring aromatic compounds with DBE of 9–13.

The O4 and O5 aliphatic compounds are extensively examined in our recent study of bio-oils in (–)ESI.²¹ In short, they are mostly pyrolysis products of cellulose and hemicellulose. We call these polyhydroxycyclic hydrocarbons “sugarc compounds” in the previous paper opposed to “phenolic compounds” from lignin pyrolysis. Levoglucosan, a well-known cellulose pyrolysis product, is present in Figure 3 at m/z 161 (deprotonated $C_6H_{10}O_5$; DBE = 2) but in much less amount than other major compounds. However, the relative ion abundances in (–)ESI are easily affected by pH or organic modifiers, and a further study is needed for the quantitative understanding.²¹ The contour maps for the number of carbon versus DBE of O4 and O5 compounds are shown in Figure 5, and the phenolic (DBE \geq 4) and carbohydrate-derived (DBE < 4) compounds are clearly distinguished on these plots. The O5 DBE of 2 compound with six carbons corresponds to levoglucosan ($C_6H_{10}O_5$), and the O4 DBE of 2 compound with five carbons corresponds to anhydropentose (either anhydroxylypyranose or anhydroarabinofuranose). However, other carbohydrate-derived compounds were not previously reported in any GC–MS or LC–MS studies of bio-oils. Overall, polar compounds from fast pyrolysis biochar are also similar to those of bio-oils.²¹ Minor differences are suspected to have come from the difference in biomass.

CONCLUSION

High-resolution mass spectrometry was successfully adapted for molecular characterization of the organic compounds entrapped in biochar during pyrolysis and gasification of switchgrass.

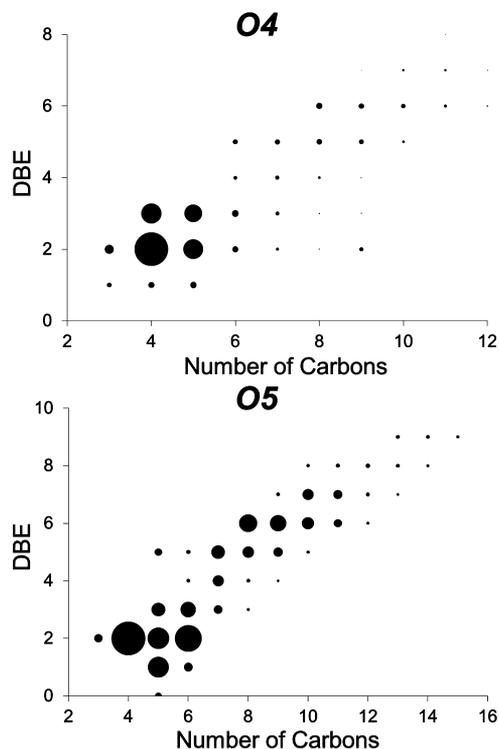


Figure 5. Contour maps of the number of carbons versus DBE for O₄ and O₅ compounds in the (–)ESI–MS spectrum of water/methanol extracts of fast pyrolysis biochar shown in Figure 3. The size of circles represents the intensity of corresponding ions.

Molecular components extracted from fast pyrolysis biochar are consistent with previously studied bio-oil compounds^{20,21} and further confirmed in Figure 6 by the van Krevelen diagram. In van Krevelen diagrams, elemental H/C and O/C ratios are calculated and plotted against each other (H/C versus O/C ratios). Molecules with similar chemical properties populate certain areas (shaded gray in Figure 6), which allows for visualization of relative changes in chemical composition

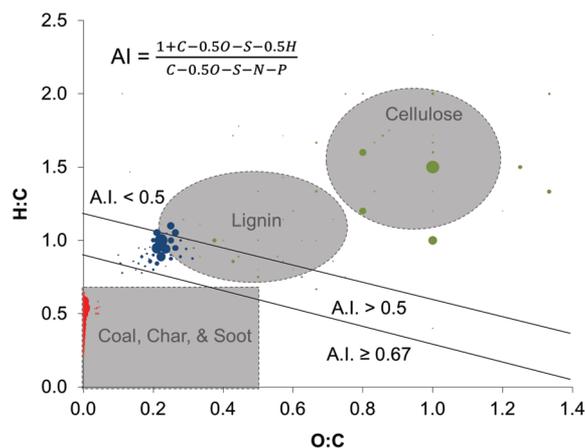


Figure 6. van Krevelen diagram of elemental H/C versus O/C ratios for pyrolysis extracts in water/methanol (green) and toluene (blue), as well as gasification extracts in toluene (red). The modified AI classifies formulas as non-aromatic (AI < 0.5), aromatic (AI > 0.5), and condensed aromatic (AI \geq 0.67, adapted from Podgorski et al.¹⁸). The gray shading represents areas populated by compounds of similar chemical properties (adapted from Kim et al.³²).

resulting from thermochemical processes.^{18,31,32} Furthermore, compounds can be assigned a modified aromaticity index (AI) to further classify formulas as non-aromatic (AI < 0.5), aromatic (AI > 0.5), and condensed aromatic (AI ≥ 0.67).^{18,33} Water/methanol extracts from fast pyrolysis char (green circles) are dominated by non-aromatic, carbohydrate-derived products from holocellulose, with some minor phenolic compounds falling within the lignin group. Toluene extracts of fast pyrolysis char (blue circles) are centered around O/C and H/C ratios of 0.25 and 1.0, respectively, which are aromatic phenolic products from lignin pyrolysis (AI > 0.5). In contrast, the toluene extract of gasification biochar (red circles) is mostly along the y axis (O/C = 0), falling in the category of “coal, char, and soot”. Collectively, Figure 6 suggests some of the bio-oil components are condensed on the surface of biochar during the char-filtering process. These molecules were not observed in gasification or slow pyrolysis biochar; instead, condensed aromatic hydrocarbons (AI ≥ 0.67) were observed, particularly in high abundance for gasification biochar (red circles).

A molecular understanding of organic matters in biochar is often missing in typical biochar analysis. Some NMR or FTIR studies were performed, but most studies are done without separation from the char materials and undistinguishable from the functional groups of char itself. The previous VOC study using headspace GC–MS was limited only to very small organic molecules.¹³ DAPPI–FT–ICR has been successful in directly analyzing biochar materials; however, it has not been adapted to investigate the difference between thermochemical processes.¹⁸ In the current study, we found that significant differences are present depending upon the thermochemical processes. A further study would be needed for a quantitative assay of the detected organic compounds and their chemical toxicity in agricultural field applications. For example, heavy rains might wash off carbohydrate-derived compounds from fast pyrolysis biochar, and the toxicity of entrapped organic molecules to plants or soil microbial systems may need to be evaluated. The petroleomic analysis adapted in the current study is useful in characterizing organic matter in biochar that are otherwise difficult to analyze in GC–MS, such as nonvolatile molecular compounds, thermally unstable compounds, or those not present in the electron impact–mass spectrometry (EI–MS) database.

■ ASSOCIATED CONTENT

📄 Supporting Information

(+)LDI–MS spectra obtained by direct analysis of intact biochar produced from fast pyrolysis of switchgrass and blank spectrum acquired on double-sided tape (Supplement Figure 1), MS/MS spectra of *m/z* 284 and 298 (Supplement Figure 2), and (+)APPI–MS spectra of toluene extracts from fast pyrolysis char and gasification char (Supplement Figure 3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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