Characterization of Pyrogenic Black Carbon by Desorption Atmospheric Pressure Photoionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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Results and Discussion

We present a new method for molecular characterization of intact biochar directly, without sample preparation or pretreatment, based on desorption atmospheric pressure photoionization (DAPPI) coupled to Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. Conventional ionization methods (e.g., electrospray or atmospheric pressure photoionization) for characterization of natural organic matter have limited utility for the characterization of chars due to incomplete solubility in common solvents. Therefore, direct ionization techniques that do not require sample dissolution prior to analysis are ideal. Here, we apply DAPPI FT-ICR mass spectrometry to enable the first molecular characterization of uncharred parent oak biomass, and after combustion (250 °C), or pyrolysis (400 °C) (see **Figure 1**). Parent oak is primarily composed of cellulose-, lignin-, and resin-like compounds. Oak combusted at 250 °C contains condensed aromatic compounds with low H:C and O:C ratios while retaining compounds with of high H:C and O:C ratios. The bimodal distribution of aromatic and aliphatic compounds observed in the combusted oak sample is attributed to incomplete thermal degradation of lignin and hemicellulose. Pyrolyzed oak constituents exhibit lower H:C and O:C ratios: approximately three-quarters of the identified species are aromatic. DAPPI FT-ICR MS results agree with bulk elemental composition as well as functional group distributions determined by elemental analysis and solid state ^{13}C NMR spectroscopy.[1] Complete molecular characterization of biomass upon thermal transformation may provide insight into the biogeochemical cycles of biochar and future renewable energy sources, particularly for samples currently limited by solubility, separation, and sample preparation.

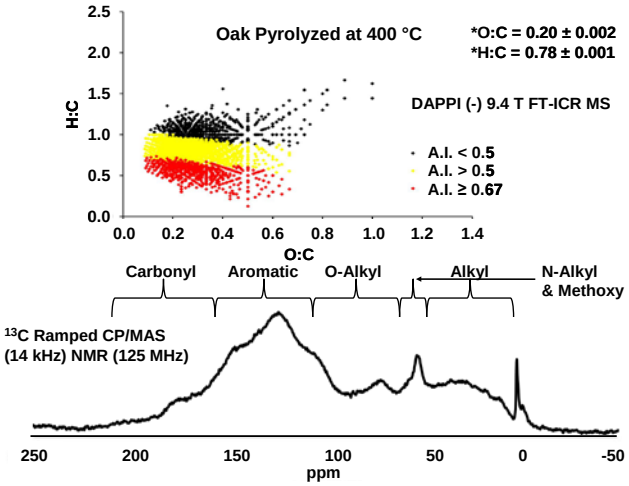

Figure 1. (Top) van Krevelen diagram of the molecular formulas assigned to oak pyrolyzed at 400 °C. Molecular formulas exhibit lower O:C and H:C ratios relative to parent oak and oak 250 due to depolymeriztion of cellulose and dehydration and deacetylation of lignin and cellulose. (Bottom) NMR spectrum of oak 400. The spectrum is dominated by the aromatics, with almost no O-alkyl contribution relative to the parent oak and oak 250. (* bulk O:C and H:C ratios determined by elemental analysis).

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References

[1] Podgorski, D. C., *et al.*, Anal. Chem., **84**, 1281-1287 (2012).