

## **Which kind of aromatic structures are produced during biomass charring? New insights provided by modern solid-state NMR spectroscopy**

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Intense research on biochar and charcoal of the last years has revealed that depending on the production conditions, the chemical and physical characteristics of their aromatic network can greatly vary. Since such variations are determining the behavior and stability of charred material in soils, a better understanding of the structural changes occurring during their heating and the impact of those changes on their function is needed. One method to characterize pyrogenic organic matter (PyOM) represents solid-state  $^{13}\text{C}$  NMR spectroscopy applying the cross polarization (CP) magic angle spinning technique (MAS). A drawback of this technique is that the quantification of NMR spectra of samples with highly condensed and proton-depleted structures is assumed to be bias. Typical samples with such attributes are charcoals produced at temperatures above  $700^{\circ}\text{C}$  under pyrolytic conditions. Commonly their high condensation degree leads to graphenic structures that are not only reducing the CP efficiency but create also a conductive lattice which acts as a shield and prevents the entering of the excitation pulse into the sample during the NMR experiments. Since the latter can damage the NMR probe and in the most cases the obtained NMR spectra show only one broad signal assignable to aromatic C, this technique is rarely applied for characterizing high temperature chars or soot. As a consequence, a more detailed knowledge of the nature of the aromatic ring systems is still missing. The latter is also true for the aromatic domains of PyOM produced at lower temperatures, since older NMR instruments operating at low magnetic fields deliver solid-state  $^{13}\text{C}$  NMR spectra with low resolution which turns a more detailed analysis of the aromatic chemical shift region into a challenging task.

In order to overcome this disadvantages, modern NMR spectroscopy offers not only instruments with greatly improved resolution but also special pulse sequences for NMR experiments which allow a more detailed chemical shift assignment. Applying the latter to various charcoals and biochars, we intended to test their usefulness for a better characterization of PyOM and elucidation how specific aromatic features can affect their behavior in soils. We could demonstrate that furans represent the major compound class of low temperature chars produced from woody material. As indicated by 2D techniques, residual alkyl C in such chars has minor covalent binding to the aromatic network. Reducing the electrical conductivity of high-temperature chars by addition of aluminum oxide permitted the application of the cross CP technique. Determination of the relaxation and CP dynamics confirmed high rigidity of their aromatic domains which were dominated by coronene-type moieties. In contrast to common view, we could demonstrate that quantifiable CP NMR spectra can be obtained from high temperature chars with contact times of 3 to 5 ms and pulse delays  $> 3$  s.