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Supplementary Material

2D Solid-State HETCOR ^{1}H-^{13}C NMR Experiments with Variable Cross Polarization Times as a Tool for a Better Understanding of the Chemistry of Cellulose-Based Pyrochars—A Tutorial

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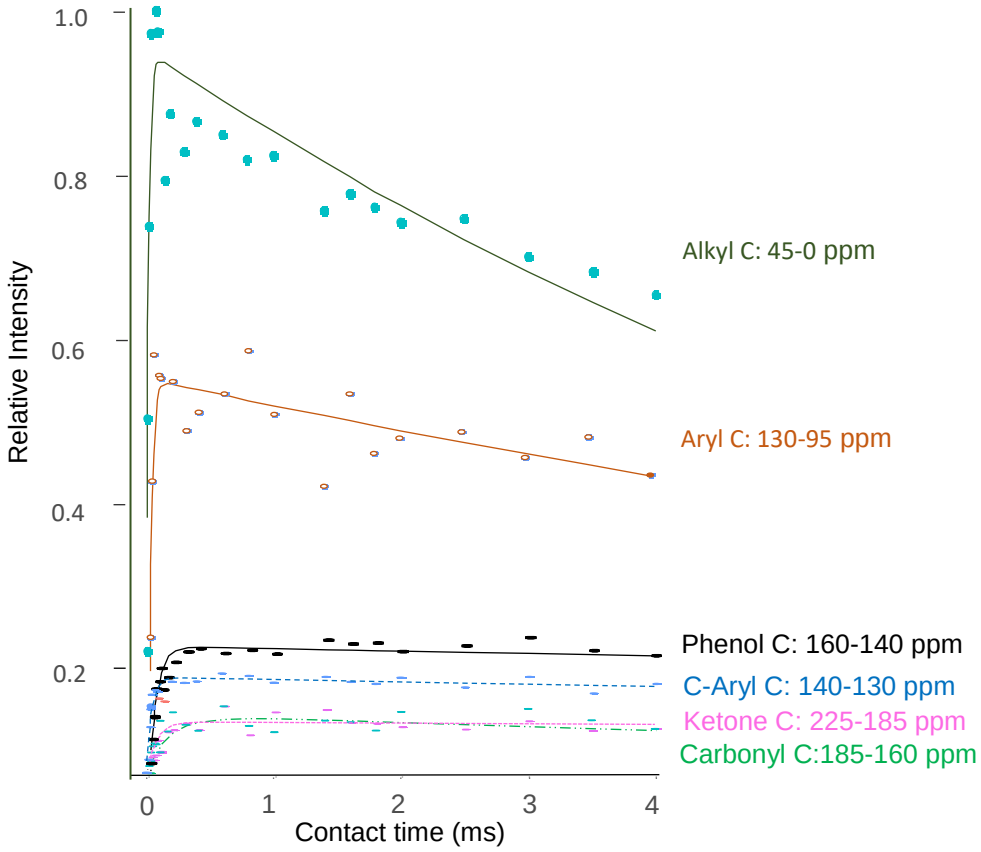

Figure S1: Relative ^{13}C intensity of the different chemical shift regions a functions of the contact time. The intensity is calibrated to the maximal signal intensity detected during the experiment. Note, no indications for a larger fraction of aromatic C with long CP times are indicated.

Table S1: Cross polarization dynamics with cross polarization rate (T_{CH}) and spin-lattice relaxation time in the rotating frame ($T_{1\rho H}$) of a pyrochar derived from cellulose and charred at 350°C for 1 hour. The data were obtained by fitting with a two component model with NMR-Relax provided by CMK (Munich, Germany) and based on Equation 1[1][2].

	Ketone C	Carboxyl C	Phenol C	C-Aryl C	Aryl C	O-Alkyl C	Alkyl C
Ppm	225-185	185-160	160-140	140-130	130-95	80-60	45-0
Fraction 1 fast (%)	59	100	57	100	100	100	100
Fraction 2 slow (%)	41		43				
T_{CH1} fast (μs)	120	75	40	40	26	17	19
T_{CH2} slow (μs)	304		174				
$T_{1\rho H1}$ fast (ms)	11	74	36	44	18	6	9
$T_{1\rho H2}$ slow (ms)	11		36				
Maximum Error	0.028	0.030	0.032	0.029	0.072	0.026	0.192
Rmse	0.011	0.016	0.015	0.011	0.029	0.012	0.080
R^2	0.909	0.808	0.966	0.970	0.938	0.827	0.876

Equation 1:

$$M(t_c) = \sum_i \frac{M_{0i}}{a_{+i} - a_{-i}} \left[exp\left(-\frac{a_{-i} t_c}{T_{CH\,i}} \right) - exp\left(-\frac{a_{+i} t_c}{T_{CHi}} \right) \right]$$

$$a_{+i} = a_{0i} \left(1 + \sqrt{1 - \frac{b_i}{a_{0i}^2}} \right)$$

$$a_{-i} = a_{0i} \left(1 - \sqrt{1 - \frac{b}{a_{0i}^2}} \right)$$

$$b_i = \frac{T_{CHi}}{T_{1\rho Hi}} \left(1 + \frac{T_{CHi}}{T_{1\rho Ci}} \right) + \varepsilon \frac{T_{CHi}}{T_{1\rho Ci}}$$

$$a_0 = \frac{1}{2} \left(1 + \varepsilon + \frac{T_{CHi}}{T_{1\rho Hi}} + \frac{T_{CHi}}{T_{1\rho Ci}} \right)$$

$$\varepsilon = \frac{N_S S(S+1)}{N_I I(I+1)} \quad (1)$$

Here, t_c represents the respective contact time, $M(t_c)$ is the experimental ^{13}C-magnetization at t_c, M_{0i} the equilibrium ^{13}C-magnetization of the component *i*, *S*, *I* the spin quantum numbers of ^{13}C ($S = 1/2$) and ^{1}H ($I = 1/2$). N_S and N_I are the

number of ^{13}C and ^{1}H nuclei, respectively. The nuclei number is taken into account by ε, which approximately becomes zero for a ^{1}H–^{13}C spin system under extreme dilution of ^{13}C ($N_I >> N_S$).

Table S2: Intensity distribution in the 1D solid-state ^{13}C CPMAS NMR spectrum of a cellulose derived pyrochar produced after pyrolysis at 350°C for 1 hour and the respective ^{1}H spin-lattice relaxation times (T_{1H}).

ppm	275-225*	225- 185	185-160	160-140	140- 130	130- 115	115- 95	95-45	45-0	0-50*
% C	1.3	4.1	4.2	13.1	10.1	15.4	6.8	13.0	30.7	1.3
T_{1H} (ms)		271	321	293	292	286	257	330	280	

*chemical shift region assigned to spinning side bands

References

1. Mehring, M. *High Resolution NMR in Solids*; 2nd ed.; Springer: Berlin, 1983;
2. Abelmann, K.; Kleineidam, S.; Knicker, H.; Grathwohl, P.; Kögel-Knabner, I. Sorption of HOC in soils with carbonaceous contamination: Influence of organic-matter composition. *J. Plant Nutr. Soil Sci.* **2005**, *168*, 293–306, doi:10.1002/jpln.200421622.