Effect of Pyrolysis Temperature on Aromatic Cluster Size of Cellulose Char by Quantitative Multi Cross-Polarization ^{13}C NMR with Long Range Dipolar Dephasing

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Abstract:

Recent results obtained by Raman spectroscopy as well as Transmission Electron Microscopy highlight the importance of irregular structures within amorphous chars. Results from DFT simulations, reported here, suggest that irregular ring systems contribute strongly to the asymmetry often observed in the aromatic peak near 140 ppm. By combining a recently developed cross-polarization pulse sequence designed for quantitative analysis of even low hydrogen containing materials with long range dipolar dephasing, we examine the structure of a thermoseries of chars produced from cellulose. These results demonstrate the consistent growth of cluster size with pyrolysis temperature, and examine for the first time the distribution of ether groups and defects within the cluster. These results highlight the contribution of defects to the structure and show localization of ether groups toward the periphery of the clusters. Only minor ether contributions were associated carbon sites most distant from hydrogens, suggesting that cluster growth occurs largely by reaction at these sites. The prevalence of oxygenated and defect carbon sites throughout the aromatic clusters highlights the need for additional characterization of these materials as these sites are likely to offer substantially different reactivity and adsorption behavior compared to regular aromatic structures.

1. Introduction

Carbonaceous materials formed from the pyrolysis of lignocellulosic materials are complex polyaromatic systems decorated with oxygenated functionalities [1-4]. A growing body of research has examined the reaction pathways associated with char formation from biomass [5-8] and purified constituents, such as cellulose [3, 9-13]. These results indicate that the initial stages of pyrolysis, temperatures up to approximately 330 °C for cellulose, consist almost entirely of dehydration and depolymerization of the feedstock [2, 9, 11, 14-17]. As the temperature increases a range of additional depolymerization, dehydration and crosslinking reactions occur leading to substantial mass loss from the solids and the initial formation of a range of aromatic ring systems [5-9]. At higher temperatures (over 500 °C) polycondensation becomes prevalent [2, 18-22] leading to aromatic systems with a higher degree of aromaticity [23, 24], though once crosslinked these structures typically resist the formation of crystalline regions [25]. While these results are critical to our understanding of how chars form, the underlying chemical structure remains poorly explored and is very often modeled using idealized systems [23, 24].

Combustion and thermogravimetric analysis of chars have been used to detail critical compositional information, including elemental and proximate composition. While these results provide little structural detail, such bulk properties are relatively simple to collect and essential to understanding the basic chemistry of chars. Additional structural information can be determined by spectroscopic techniques such as FT-IR [3, 26, 27] and X-ray Photoelectron spectroscopy (XPS) [28-30], which can identify a wide range of elements and bonding patterns. Raman spectroscopy [31-35] and X-ray diffraction (XRD) [16, 36, 37] techniques also provide excellent tools for the analysis of graphitic materials. However, the analysis of the size of small aromatic clusters found in pyrolysis chars by these spectroscopic methods is uncertain. Several challenges arise due to the amorphous structure of the material that precludes clear crystallite peaks from XRD [38, 39]. These same structures, identified as a series of defects, result in a diffuse defect region in the Raman signal between 1200 and 1400 cm^{-1} [4]. Defects have also been more directly observed by transmission electron microscopy (TEM) [40, 41]. While these methods do provide sound tools for qualitative analysis, quantification by methods such as Raman are difficult due to varying vibrational response intensities [42]. Nuclear magnetic

resonance (NMR), by contrast offers a potentially quantitative method of analysis, since signal intensity from well-designed experiments are proportional to the distribution of spin states within the compound.

NMR spectroscopy offers a unique method of analyzing these materials via rotational-echo, double resonance (REDOR) type experiments. This method relies on a series of pi-pulses spaced at 1 rotor period over the dephasing period to ensure decoupling of heteronuclear interactions [43], and was successfully applied by Mao and Schmidt Rohr to selectively assess the aromatic region of humic material and chars [44]. This series is required, because at dephasing times greater than one rotor period magic angle spinning (MAS) can partially refocus heteronuclear interactions, confounding dephasing results. This technique was successfully applied by Brewer et al. [23] to estimate average aromatic structures of slow pyrolysis, fast pyrolysis and gasification chars. The results of this study indicated a cluster size of approximately 7 rings for fast pyrolysis chars produced 500°C and 17 rings for gasification chars produced near 750 °C. These results are in good agreement with those of McBeath et al. [24] who predicted ring clusters of up to 13 rings with pyrolysis temperatures of 500-700 °C, by analyzing the up field shift of sorbed ^{13}C labeled benzene [45].

A fundamental limitation of the direct quantitative analysis of aromatic carbons has been the need to use direct polarization to provide equivalent polarization to all carbons within the aromatic systems. This polarization method requires substantial recycle delays, on the order of one to several minutes per scan to allow complete longitudinal relaxation (T_1) of the polarized carbon [44]. While a reasonable signal can still be obtained via cross-polarization (CP), which requires substantially shorter recycle delays due to the more rapid relaxation of hydrogen, tertiary and quaternary carbons do not achieve the same degree of polarization as primary or secondary carbons, eliminating this method as a quantitative tool [44]. A recent method published by Johnson and Schmidt-Rohr [46] overcomes this limitation through the use of multiple CP passes which successively build the polarization within the internal aromatic structure. The optimized contact time and CP passes is determined by comparison to direct polarization, and once determined allows for the collection of high resolution spectra in a

fraction of the time required for DP experiments. This method was successfully demonstrated for the analysis of humic acid, switch grass and low temperature pyrolysis char [46].

Though several studies have examined the average chemical structure of char by various NMR techniques, each assessment assumes a regular aromatic structure to interpret the results [23, 24]. Defects such as those identified by TEM and Raman studies have not yet been incorporated in the analysis of these spectra. These defects affect both the overall structure of the char by precluding the formation of planar regions, and the reactivity of the char though increased reactive defect and edge sites. Because of these effects, developing a clearer understanding of these materials is critical to understanding the behavior of chars in real systems. The literature on how the aromatic ring structure grows as a function of pyrolysis conditions is also very limited. Thus, the main goal of this paper is to study the effect of pyrolysis temperature on cellulose char aromatic cluster size by quantitative ^{13}C NMR spectroscopy using a multi cross-polarization (multi-CP) pulse sequence with long range dipolar dephasing.

2. Materials and Methods

Avicel Cellulose purchased from Sigma Aldrich (LOT# BCBG9043V) was used for the production of a thermoseries of chars. Douglas fir (*Pseudotsuga menziessii*) wood (DFW) was provided by Herman Brothers Logging & Construction (Port Angeles, WA) from standard mill operations. A torrefied sample (DFW300) was utilized for method tuning and a high temperature char (C700) to confirm stability with low hydrogen samples. Perylene tetracarboxylic dianhydride (PTCDA) (product# P11255) has been used as a reference compound to assess the NMR pulse sequences used here.

Cellulose and Douglas fir wood (DFW) chars have been produced following the same methods previously described using a spoon reactor at WSU [3, 4]. Treatment time was 30 minutes at a specified fixed temperature (300, 400, 500, 600 and 700 °C for cellulose and 300 °C for DFW) with a constant nitrogen sweep of 300 ml/min. These samples are denoted as CX00 or DFWX00 respectively where X00 represents the treatment temperature. A preheated nitrogen sweep of 550 ml/min was employed in the reaction zone to minimize vapor residence time. The test chamber

was purged for 10 minutes prior to pyrolysis to ensure an oxygen free environment. Samples were allowed to cool under nitrogen in a water-jacketed region of the reactor for 20 minutes to ensure sample temperatures of less than 25 °C were obtained prior to exposure to air. All samples were weighed immediately and stored in glass vials until testing.

2.1 X-ray Diffraction

X-ray diffraction patterns have been collected using a Rikagu MiniFlex 600 benchtop X-ray diffractometer. Diffraction spectra were collected between 2 θ of 5 to 50 degrees at constant scan rate of 1 degree per minute. To ensure representative samples the sampling pan was rotated during acquisition.

2.2 NMR Spectroscopy

Solid-state NMR data was collected at ambient temperature on a Bruker Avance DRX 400 spectrometer at 100.61 MHz for ^{13}C using Chemagnetics 5 mm and 3.2 mm probes. Rotors were filled completely and either Teflon or boron nitride spacers were used to constrict the sample to just the region of the coil. Samples were spun at 7 KHz for the 5 mm rotor and at 10 KHz for the 3.2 mm rotor. To ensure flat baselines acquisition of all data was done using a Hahn-echo applied for 1 rotor period directly following the last cross polarization period or directly following the direct polarization pulse. For the 5 mm probe the $\pi/2$ pulse widths were 4.0 and 4.7 μs for ^1H and ^{13}C respectively while for the 3.2 mm probe the $\pi/2$ pulse widths were 4.7 and 4.6 μs for ^1H and ^{13}C respectively. Decoupling during acquisition and during the Hahn-echo was accomplished using TPPM modulation and RF fields ($\gamma B_1/2 \pi$) of 62.5 KHz and 60 KHz for the 5 mm and 3.2 mm probes respectively. Cross polarization periods for ^1H were constructed using a 64 step linear ramp from 50 to 100% of amplitude. Recycle delays for cross polarization experiments were 4 s, whereas for direct polarization recycle delays were either 90 s or 135 s. Durations for the repolarization delay (Z) in the multi-CP sequences were either 500 ms or 1 s depending on the sample. Acquisition time for all experiments was 7.8 ms with a spectral width of 50,000 Hz. Data were apodized with 50 Hz of exponential line broadening and zero filled to 2

K points prior to Fourier Transform. For multi-CP based sequences a total of 2048 scans were acquired. For direct polarization sequences a total of 256 scans were acquired.

2.2.1 Direct Polarization Scheme

Quantitative reference spectra for DFW chars and select cellulose chars have been collected. Direct polarization spectra were collected using pulse sequence B in Figure 1 with a 90 degree excitation pulse on ^{13}C with acquisition following a Hahn-echo and TPPM decoupling used throughout. Recycle delays of 90 seconds are used for all samples except C700 for which a recycle delay of 135 seconds was required. Recycle delays of 90, 180 and 420 s were also performed during the analysis of PTCDA. Spectra from the DFW300 sample were collected using a 5 mm rotor with a spin rate of 7 KHz. A very broad peak was observed within the aromatic region in the direct polarization spectra, which was attributed to Teflon components used in the construction of stator. This background persisted even when using boron nitride spacers and was corrected for by collecting a background signal using the same rotor packed with silica gel under identical pulse and acquisition parameters. To lessen background contamination during dephasing trials and to mitigate potential arcing in conductive samples (higher temperature chars) a smaller 3.2 mm rotor was used. A spin rate of 10 KHz was employed for the 3.2 mm rotor to reduce side band contributions relative to the 7 KHz spin rate used initially.

2.2.2 MultiCP scheme

The multiple cross polarization scheme (MultiCP) introduced by Johnson and Schmidt-Rohr [46] has been employed in this work to produce quantitative spectra approaching direct polarization results while significantly reducing the total time required for data collection. Data was collected using pulse sequence A in Figure 1 wherein a series of ramped cross polarization periods is employed to successively build polarization at carbon sites distant from any proton spin until a quantitative spectrum can be obtained. Contact times of 0.5 or 1.0 ms were used employing a 50

to 100% linear ramp of 64 steps on the ^1H channel. Both ^1H and ^{13}C magnetization is then stored on the Z axis which is followed by a delay Z that allows for restoration of ^1H magnetization from T_1 relaxation processes while storing the ^{13}C enhanced polarization. The process is repeated n times after which a final CP “read” period is used to produce transverse ^{13}C magnetization that is detected following the Hahn-echo. Further details can be found in the [supplemental material section S1](#).

2.2.3 Standard short-range dipolar dephasing

To gauge the effect of strong dipolar interactions the cross polarization, multi-cross polarization and direct polarization sequences were modified with the introduction of a period during the Hahn-echo whereby the ^1H decoupling was omitted allowing the strong dipolar coupling between close ^1H and ^{13}C spins to dephase the ^{13}C transverse magnetization prior to acquisition (Figure 1 C, D). For dipolar dephasing time less than 1 rotor period the ^1H spins were decoupled using continuous wave ^1H decoupling on either side of the ^{13}C π pulse.

2.2.4 Long range dephasing

To probe the effects of longer range dipolar interactions between ^1H and ^{13}C spins the pulse sequence in Figure 1 E was used. For dephasing times longer than 1 rotor period the C-H dipolar interaction can be refocused under MAS conditions necessitating the use of a REDOR style recoupling of the interaction using π pulses on the ^1H channel [every half](#) rotor period flanking the ^{13}C π pulse to refocus chemical shift [44].

Figure 1.

2.3 Density Functional Theory Calculations

Density functional theory calculations have been performed using the Gaussian 09 computational software suite [47]. All calculations have been run using a Beck three parameter functional with a Lee Yang Parr correlation (B3LYP) [48]. A triple zeta Pople type basis set with d and p shell

augmentation (6-311G (d,p)) [49] was used to optimize the geometry of each compound except the clustered PTCDA which used a smaller double zeta, d shell augmented 6-31G (d) basis set to **reduce calculation time**. NMR spectra are calculated from the optimized geometry using the Gauge Independent Atomic Orbital method [50, 51]. All spectra have been corrected based on the theoretical shielding of tetramethylsilane (TMS), equal to 184.67 ppm and 189.78 for the triple zeta and double zeta basis sets respectively. For comparison to experimental spectra, calculated signals have been broadened using a Lorentzian curve structure with a full width at half maximum of 2 ppm.

3. Results

The bulk properties for the cellulose chars examined here, including elemental analysis and surface area, have been previously reported [52]. A Van Krevelen plot of the **H:C** and **O:C** ratios of each materials is given in Figure 2. Vectors associated with CO and methane loss are given by solid black lines for various initial compositions, while the dehydration line is highlighted with a dashed arrow below. H:C ratios are found to decrease sharply from 1.8 for the native cellulose (close to the theoretical value of 1.67) to 0.26 after treatment at 700°C. Likewise the O:C ratio decreases from 0.89 (theoretically 0.83) to 0.06 at 700°C. During the first stages of pyrolysis, up to 300°C, dehydration of the **feedstock** is clearly the dominating pathway. Other oxygen decomposition processes and polycondensation reactions, which proceed through the removal of hydrogen (C_xH_y , and $C_xH_yO_z$) compounds, become increasingly prominent at temperatures of 400°C and higher. Previous analysis by XPS and FT-IR has indicated that much of the remaining oxygen content after treatment at 400 °C and higher is confined to ether and lactone groups with substantial loss of both hydroxyl and carboxylic charter at these temperatures [52]. Much of the oxygen loss has been accomplished by 600°C, **heating further to 700°C results in a sharp drop in the H:C ratio with** relatively little change in O:C, consistent with continued polycondensation. The progression of polycondensation reactions, mixed with continued oxygenated group removal, result in increasingly condensed aromatic systems with a strong reduction, though not elimination, of oxygen content as the treatment temperature increases to 700 °C.

Figure 2.

Though the elemental analysis provides strong support for the increasing aromaticity of the char with pyrolysis temperature, little information can be determined regarding the degree of aromaticity. Previous work using XPS and Raman spectroscopy [4, 52] have also revealed significant structural information regarding the chemical state of cellulose pyrolysis chars, however the overall cluster size and distribution also cannot be directly determined by these methods.

Analysis by X-ray diffraction, shown in figure 3, reveals only mild destruction of the original cellulose crystalline structure when treatment of 300 °C are used, consistent with the hypothesis that at low treatment temperatures degradation primarily proceeds through intramolecular dehydration of the material. This is supported by the amorphous signal, present between 2θ of approximately 15 and 25 degrees, which increases moderately during treatment, and suggests some loss of crystallinity. At higher temperatures of 400°C and above, the crystalline cellulose peaks are replaced by a very broad amorphous carbon signal centered near 22 degrees. Interpretation by the Scherrer equation for both cellulose and cellulose chars has been performed for qualitative reference, with the results displayed in Figure 3. The defective, crosslinked surface causes sufficient broadening to make quantitative analysis by this equation impossible [25, 53]. The results do not show any significant deviation for chars produced between 500 and 700°C. They do however indicate that any crystallites that do form are likely to be small, on the order 2 nm or less even for chars produced at high temperatures.

Figure 3.

3.1 Tuning and Method Validation

Because of the small cluster sizes suggested by XRD, more accurate analysis methods are needed. To achieve these measurements NMR spectroscopy with long range dipolar dephasing has been examined. In order to achieve this in a reasonable amount of time, a recently proposed quantitative cross polarization (CP) method is employed [46]. Here multiple CP periods are used to ensure full polarization of all carbons, even when those several bond distances from the

nearest hydrogen. To ensure adequate polarization, a series of tests have been performed in large 5 mm rotors using an increasing number of CP periods with varying contact time. DFW processed at 300 °C has been chosen for this analysis rather than any cellulose char because it contains strong aromatic and aliphatic signals, allowing for the comparison of relative intensities. These results are presented in figure 4A and 4B. Using contact times of both 0.5 and 1.0 ms spectra equivalent to those obtained from direct polarization could be obtained given a sufficient number of passes, 7 for 1.0 ms contact time and 11 for 0.5 ms contact time. Additional passes do not improve the signal intensity for any carbons present in the system. The maximized signals obtained compare well to a corrected DP spectrum collected using the same rotor and pack (see figure 4C and 4D). These signals originally contained a significant Teflon background peak. This peak was removed by subtraction of a spectrum collected using the same rotor and caps packed with silica gel.

Figure 4.

Because of the residual Teflon signal in the available 5 mm stator, and to avoid potential arcing with chars produced at high temperatures [23] a smaller 3.2 mm rotor **has been** used for the remainder of the tests. A higher spin rate of 10K is also employed to **reduce the intensity and improve the separation of side bands**. To confirm that tuning parameters established for the 5 mm rotor remain valid, initial and dephased DP and multiCP spectra for the C700 char are compared in Figure 5. The direct polarization spectra are the result of 256 scans compared to 2048 for the multiCP and so have been scaled using the same factor for direct comparison. The sensitivity obtained by multiCP was found to be higher than for DP, requiring a correction of 11X rather than the expected 8X to obtain a reasonable match between the initial spectra. While significantly noisier, the results for both polarization methods are extremely consistent, and show the same dephasing behavior, indicative of equivalent polarization of even distant carbons by each method.

Figure 5

3.1.1. Analysis of reference compound (PTCDA)

To confirm the efficacy of the multiCP approach with dipolar dephasing for both accurate quantification and accurate determination of equivalent bond distances (r_{C-H}), perylene tetracarboxylic dianhydride (PTCDA) has been evaluated, the resulting spectrum as well as two spectra for simulated conformations are presented in figures 6A-D. Because of the ridged, in-plane bonding **patterns** of this compound, relaxation times are excessively long, in excess of 7 minutes, when attempting direct polarization (See figure 6B). Because of this no comparable scan has been produced to compare the multiCP scans. Instead, a series of experiments was conducted with an increasing number of CP passes to confirm maximum signal intensity (not shown). As before, 7 passes with a contact time of 1.0 ms was found to produce the maximum **intensity**.

Figure 6

Table 1

Relative peak areas and positions are given in Table 1. The sum total peak area divided by 24 is used as the quantification reference. These results indicate **reasonable** signal reproduction for all peaks, though intensity between 130 and 125 ppm appears to be slightly under represented. On the other hand, the peaks for sites adjacent to the carboxyl groups are slightly overrepresented, even when corrected for side band intensity. This effect is attributed to convolution of slightly different signals from PTCDA molecules within the crystals structure and along the edge. The result of this effect is a percentage of signal from carbon site F being shifted toward 118 ppm. This effect can be seen by examining the shielding parameters of the F site carbons in the peripheral molecules included in supplementary material Figure S1 in section S2. The total shifts are mild, approximately 10-15%, and are not expected to greatly influence the dephasing behavior after the first 0.074 ms.

Figure 7

The dephasing results for PTCDA are presented in Figure 7. These results demonstrate near total signal suppression within 1 ms (10 rotor periods), with total signals only just detectable above the background noise. The initial 74 μ s dephasing period is sufficient to eliminate the majority (>95%) of the C-H signal while leaving the remaining signal largely intact. Still, approximately 10-25% of each remaining peak was attenuated even after this short time period. Signal attenuation after 400 μ s was sufficient to reduce side band intensity to near background levels. By 800 μ s the signal from internal carbons, 3 bond length's removed for hydrogen, are the **most intense** remaining signals. To analyze these dephasing results the total reduction in signal intensity as dephasing is increased from 74 μ s to 600 μ s is analyzed via a first order kinetic model, equation 1, as discussed by Mao and Schmidt-Rohr [44]. 74 μ s was chosen as the initial point to obtain clear separation of the C and D carbon peaks as well as to avoid contamination for the C-H peaks. The dephasing rate, K_{C-H} , was calculated here by the following equation:

$$K_{C-H} = -\frac{\ln(S_{0.60}) - \ln(S_{0.074})}{0.6 \text{ ms} - 0.074 \text{ ms}} \quad \text{Eq. 1}$$

where S_t is the signal intensity at time t .

This kinetic rate was compared to the distance between various carbon and hydrogens (r_{C-H}) by use of an F factor, equation 2

$$F = \frac{1}{(r_{C-H})^3} \text{ or, when more than 1 H is present } F = \sqrt{\sum_1^i 1/(r_{C-Hi})^6} \quad \text{Eq. 2}$$

Figure 8.

The dephasing results (Figure 8B) **compare** the reduction of intensity over long range dephasing with the signal intensity found after 74 μ s dephasing. This point was chosen over the initial spectrum to obtain better separation of the internal carbon peaks at 125 and 130 ppm. The rate of T_1 dephasing is estimated by simple first order kinetics, as shown in equation 1. Plotting these results for each of the 5 unique carbons in tetracarboxylic perylene against the F factor yields results that agree exceptionally well with the empirical equation previously published by Mao

and Schmidt-Rohr [44] based on several different reference standards. The only outlier to this plot is the carboxylic carbon. These have been found to dephase much more rapidly than would be expected when considering only intramolecular carbon spacing. When the lower intermolecular spacing due to **in-plane** hydrogen bonding present in the crystalline structure shown in figure 4C is considered, much shorter r_{C-H} are found. Properly accounting for this spacing results in considerably **better agreement with the observed** dephasing kinetics. In figure 8B first order kinetics using the empirical rate constant **are shown to** accurately predict the dephasing behavior for each carbon site in PTCDA. The relative intensity, given as S/S_0 defines S as the signal intensity at the given relaxation time and S_0 as the signal intensity after 74 μs of standard gated decoupling.

3.2 Effect of cluster size, shape and defects on NMR spectra (DFT studies)

To determine the influence of cluster size and irregular structures within aromatic systems on the chemical shifts observed via NMR, a series of simulated compounds have been evaluated via DFT. The results of these simulations are presented in Figure 9 and demonstrate that carbons within ring systems larger than 6 carbons show chemical shifts between 140-150 ppm for approximately half of the carbons in the system (see Figures 9D and 9E), though this is not universal and can break down with complex defects near edge sites (see figure 9F). 5 carbon ring defects alone do not present substantial shifts **when** compared to more familiar aromatic sites, both presenting between 120 and 140 ppm (see figure 9A-C). The results also demonstrate that carbons near oxygen defects **present** somewhat lower chemical shifts, between 100 and 120 ppm (Figures 9H and 9I). The position of ether, carboxyl, lactone and carbonyl groups are within the range typically reported (Figure 9G-I). The positions of aliphatic carbons are also well established and are found to be present within the expected range for carbons that lack any double bond. Based on these results, a deconvolution strategy is proposed to more specifically assign the aromatic region to both regular and defective (non-hexagonal) sites. An important ring system not modeled here, but presented elsewhere, is that of furans. The ether-bonded carbons in this ring system have chemical shifts of approximately 142 ppm while the other carbons (2 bonds removed from oxygen) have shifts of approximately 115 ppm. Though the ether shifts are somewhat lower than when typically assigned to the shifts associated with two carbon bonds

removed from oxygen, they are nevertheless consistent with the simulated results of larger ring systems. These results are summarized in Table 2.

Figure 9.

Table 2.

While accurate analysis of the initial peak positions and intensities is essential for proper structural assignment, this data cannot be applied without information regarding position within the structure. To determine the relative number of carbons positioned at various distances from hydrogen, dephasing behavior for a variety of carbon sites has first been estimated using apparent bond distances calculated by equation 2 in conjunction with the first order kinetic model from equation 1 to provide additional reference curves.

Figure 10.

The theoretical dephasing plots are shown in Figure 10A, and have been generated for carbons set at specific distances from a single hydrogen, assuming the first order kinetics remain valid for at least 2.5 ms and that $K_{C-H} = 32F$ is a reasonable approximation of this rate. By assuming additive behavior for each carbon, the dephasing behavior of several aromatic structures are estimated and given in Figure 10B. Here the r_{C-H} value used is the apparent distance, calculated from the nearest two sets of hydrogen (based on bond number separation). The dephasing for C-H groups is markedly faster than predicted by the empirical equation due to direct coupling. To account for this, C-H carbons are considered to have a dephasing rate of $K_{C-H} = 75 \text{ ms}^{-1}$ to achieve 95% signal reduction by 0.04 ms based on previous dephasing results set at this time [44].

Table 3.

Table 3 provides structural information on a range of regular aromatic structures ranging from linear aromatic chains (benzene through hexacene) to circular and oval like structures such as

coronene and circumpyrene. Larger structures are denoted by the number of aromatic rings along the x and y axis (e.g. coronene is 3*3, while circumpyrene is 3*4). The H:C ratio and the distribution of r_{C-H} distances are presented for each material. These compounds can be used to provide initial guesses for the unknown chars, with approximate compounds used to bracket the dephasing behavior and the introduction of oxygenated groups and defects used to interpolate between the idealized structures.

3.4 Application to a series of Cellulose Chars

Cellulose chars produced at 300-700 °C was analyzed using the multiCP technique with a 2048 scan composite. The full series, including unaltered cellulose is presented in Figure 11. These results are consistent with the XRD data and show that relatively little structural change occurs with treatment at 300 °C, though some dehydration is apparent. The lack of peak development between 100 and 150 ppm suggests that dehydration reactions involve the formation of anhydrosugar units such as levoglucosan and cross-linking of glycosidic units rather than formation of alkene bonds or aromatic rings. When pyrolysis temperatures are increased to 400 °C drastic changes are observed in the spectra. The cellulose character has been completely destroyed, replaced by an amorphous aromatic region between 100 and 170 ppm. A residual, amorphous, aliphatic contribution is also observed between 0 and 60 ppm. This contribution is strongly reduced at pyrolysis temperatures of 500°C and eliminated at 600°C. The aromatic region becomes sharper and more clearly defined as the pyrolysis temperature increases revealing a distinct ether bonded region between 150 and 160 ppm and a slightly asymmetric aromatic region between 100 and 147 ppm. This asymmetry is attributed here to contributions from defect carbon as discussed in section 3.3.

Figure 11.

A weakly constrained deconvolution has been performed on the initial spectra for each material. This deconvolution allowed for free floating G:L ratios, full width half maximums (FWHM) as well as intensities. Position was monitored to ensure that only a single curve was used for each position discussed in Table 2. Side band positions were fixed as the position of the aromatic peak

varied by +/- 100 ppm (based on rotor speed of 10 KHz). The results of this deconvolution are presented in Table 4. The aliphatic region is estimated as the total contribution between 0 and 60 ppm minus the aromatic side band contribution as measured between 200 and 250 ppm. This was done assuming symmetric side band contributions to remove the aromatic signal from the aliphatic region. Though this is not exactly accurate, this is expected to give a reasonable estimation of the aliphatic contribution. While these results differ mildly from those obtained by integration of the predefined regions given in Table 2 (not shown), these variances are minor when the defect and aromatic regions are considered a single peak.

Table 4.

Figure 12.

Dephasing for each cellulose char revealed differing behavior for each peak region, an example of this behavior is given in figure 12 for C500. The primary aromatic peak shows strong initial reductions with the initial dephasing, however the ether hydroxyl region shows minimal loss. The signal loss for this region accelerates with longer dephasing times, with signal lost entirely prior to the primary aromatic peak.

Figure 13.

The dephasing results for the combined aromatic and defect region (100-147 ppm) are given in Figure 13. Based on the dephasing results and the cluster size, the structures of C400-C700 are estimated to range between that of coronene and circumpyrene. The theoretical dephasing for each compound was calculated using the C-H bond distances for each carbon obtained from geometry optimization at the B3LYP 6-311g(d,p) level and calculating the dephasing rate based on equation 2. Interestingly, C400 was found to contain relatively few aromatic hydrogens, suggesting that much of the hydrogenated carbons exist as aliphatic sp^3 sites. Both C500 and C600 show similar dephasing after 0.8 ms, however the signal intensity of C600 shows improved stability at longer dephasing times suggesting a higher fraction of carbons are 3 or more bonds away from a hydrogen. In each case, the initial dephasing results at 0.074 ms show lower intensity loss than predicted for the model compounds, indicating substitution and inter-cluster

linkages at the edge sites. These substitutions do not result in any substantial increase in carbons 3 or more bonds removed from hydrogen indicating that the cluster sizes cannot be substantially larger than circumpyrene or that hydrogenated internal defects are present within the cluster.

To estimate the approximate contributions of each site type the dephasing data for the aromatic + defect peak, the ether peak, and the aliphatic peak (C400 only) were fitted by a least squares methods using the estimated dephasing rates for C-H bond distances of 1.9, 2.15, 3.4, 3.9 and 4.9 Å. Directly coupled C-H was assumed to fully dephase by the first data point at 0.074 ms. The results of this procedure are summarized in Table 4. These results indicate an increase in overall C-H contribution to the aromatic cluster with increasing pyrolysis temperature. This effect is hypothesized here to be a result of removal of substituted oxygen from edge sites as well as reduced bonding between clusters. This is coupled with a continuous reduction in carbons 2 bonds removed from a hydrogen (1.9-2.15 Å). Interestingly no significant change is observed at the 3-bond position (3.4-3.9 Å), however an increase in carbons 4 bonds removed is observed. Ether groups are found to have markedly different behavior than aromatic carbons in terms of dephasing. Ether linked carbons directly coupled to H show a sharp decrease at temperatures greater than 500°C with no appreciable content being determined for C600 and C700. Ether linked carbons 2 bonds removed from an H show an initial decline as the temperature increases from 400 to 500 °C, before increasing sharply at higher pyrolysis temperatures. The increase in ether carbons 2 bonds removed at C600 and C700 results in decreasing the total contribution from those at 3 and 4 bond distances as well as those directly coupled to hydrogen. This behavior indicates that ether bonded carbons should be relatively constrained to edge or defect sits at higher temperatures. These groups may provide the necessary reactive sites for cluster growth.

Table 5.

To illustrate the changes in cluster size and composition a graphical representation of the data presented in tables 4 and 5 is given in Figure 14. Because chars are heterogeneous 3-dimensional structures no single planar, or semi-planar structure can adequately depict the complexity of the material. While these clusters are designed to closely mimic the data presented they are not necessarily exact, nor do they depict the only viable solutions. These results do however

illustrate the destruction of the original cellulose structure through crosslinking and polycondensation and the formation of increasingly regular structures within the char as the pyrolysis temperature is increased.

Figure 14.

4. Conclusions

In this work we have successfully applied a quantitative cross-polarization technique for the rapid analysis of aromatic carbons. This technique, combined with long-range dipolar dephasing was successful in estimating apparent C-H bond distances for a range of materials, including PTCDA and cellulose chars produced between 300 and 700 °C. A series of theoretical structures was analyzed via density functional theory to provide shift references for analysis. Dephasing behavior was successfully **estimated based** on first order **kinetics**, where the rate constant was proportional to the inverse of the distance between carbon and hydrogen cubed. These results clearly show an increase in cluster size with heating temperature, but also demonstrate that substantial defect regions are present in each char. Through the use of dipolar dephasing the approximate location of these defects within the cluster was estimated, as was the position of ether groups throughout the material. These results indicate that defects and ethers tend to be located towards the periphery of the cluster, suggesting that cluster growth is likely mediated by reactions at **these sites. The results presented here** demonstrate the complexity of the chemical structure of pyrolysis chars, and highlight that estimation as a regular aromatic system is insufficient in the explanation of char structure.

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References:

- [1] Pastorova I, Botto RE, Arisz PW, Boon JJ. Cellulose char structure: a combined analytical Py-GC-MS, FTIR, and NMR study. *Carbohydrate Research*. 1994;262(1):27-47.
- [2] Wooten JB, Seeman JI, Hajaligol MR. Observation and Characterization of Cellulose Pyrolysis Intermediates by ¹³C CPMAS NMR. A New Mechanistic Model. *Energy & Fuels*. 2004;18(1):1-15.
- [3] Wang Z, Pecha B, Westerhof RJM, Kersten SRA, Li C-Z, McDonald AG, et al. Effect of Cellulose Crystallinity on Solid/Liquid Phase Reactions Responsible for the Formation of Carbonaceous Residues during Pyrolysis. *Industrial & Engineering Chemistry Research*. 2014;53(8):2940-55.
- [4] Smith MW, Dallmeyer I, Johnson TJ, Brauer CS, McEwen J-S, Espinal JF, et al. Structural analysis of char by Raman spectroscopy: Improving band assignments through computational calculations from first principles. *Carbon*. 2016;100:678-92.
- [5] Evans RJ, Milne TA. Molecular characterization of the pyrolysis of biomass. 2. Applications. *Energy & Fuels*. 1987;1(4):311-9.
- [6] Evans RJ, Milne TA. Molecular characterization of the pyrolysis of biomass 1. Fundamentals. *Energy & Fuels*. 1987;1(2):123-37.
- [7] Boroson ML, Howard JB, Longwell JP, Peters WA. Product yields and kinetics from the vapor phase cracking of wood pyrolysis tars. *AIChE Journal*. 1989;35(1):120-8.
- [8] Boroson ML, Howard JB, Longwell JP, Peters WA. Heterogeneous cracking of wood pyrolysis tars over fresh wood char surfaces. *Energy & Fuels*. 1989;3(6):735-40.
- [9] Broido A, Javier-Son AC, Ouano AC, Barrall EM. Molecular weight decrease in the early pyrolysis of crystalline and amorphous cellulose. *Journal of Applied Polymer Science*. 1973;17(12):3627-35.
- [10] Luo, Wang, Liao, Cen. Mechanism Study of Cellulose Rapid Pyrolysis. *Industrial & Engineering Chemistry Research*. 2004;43(18):5605-10.
- [11] Piskorz J, Radlein D, Scott DS. On the mechanism of the rapid pyrolysis of cellulose. *Journal of Analytical and Applied Pyrolysis*. 1986;9(2):121-37.

- [12] Radlein D, Piskorz J, Scott DS. Fast pyrolysis of natural polysaccharides as a potential industrial process. *Journal of Analytical and Applied Pyrolysis*. 1991;19:41-63.
- [13] Piskorz J, Radlein DSAG, Scott DS, Czernik S. Pretreatment of wood and cellulose for production of sugars by fast pyrolysis. *Journal of Analytical and Applied Pyrolysis*. 1989;16(2):127-42.
- [14] Golova OP. Chemical Effects of Heat on Cellulose. *Russian Chemical Reviews*. 1975;44(8):687.
- [15] Piskorz J, Majerski P, Radlein D, Vladars-Usas A, Scott DS. Flash pyrolysis of cellulose for production of anhydro-oligomers. *Journal of Analytical and Applied Pyrolysis*. 2000;56(2):145-66.
- [16] Zickler GA, Wagermaier W, Funari SS, Burghammer M, Paris O. In situ X-ray diffraction investigation of thermal decomposition of wood cellulose. *Journal of Analytical and Applied Pyrolysis*. 2007;80(1):134-40.
- [17] Mamleev V, Bourbigot S, Le Bras M, Yvon J. The facts and hypotheses relating to the phenomenological model of cellulose pyrolysis: Interdependence of the steps. *Journal of Analytical and Applied Pyrolysis*. 2009;84(1):1-17.
- [18] Kawamoto H, Murayama M, Saka S. Pyrolysis behavior of levoglucosan as an intermediate in cellulose pyrolysis: polymerization into polysaccharide as a key reaction to carbonized product formation. *Journal of Wood Science*. 2003;49(5):469-73.
- [19] Hosoya T, Kawamoto H, Saka S. Thermal stabilization of levoglucosan in aromatic substances. *Carbohydrate Research*. 2006;341(13):2293-7.
- [20] Hosoya T, Kawamoto H, Saka S. Cellulose-hemicellulose and cellulose-lignin interactions in wood pyrolysis at gasification temperature. *Journal of Analytical and Applied Pyrolysis*. 2007;80(1):118-25.
- [21] Hosoya T, Kawamoto H, Saka S. Pyrolysis behaviors of wood and its constituent polymers at gasification temperature. *Journal of Analytical and Applied Pyrolysis*. 2007;78(2):328-36.
- [22] Kawamoto H, Saito S, Hatanaka W, Saka S. Catalytic pyrolysis of cellulose in sulfolane with some acidic catalysts. *Journal of Wood Science*. 2007;53(2):127-33.
- [23] Brewer CE, Schmidt-Rohr K, Satrio JA, Brown RC. Characterization of biochar from fast pyrolysis and gasification systems. *Environmental Progress & Sustainable Energy*. 2009;28(3):386-96.

- [24] McBeath AV, Smernik RJ, Schneider MPW, Schmidt MWI, Plant EL. Determination of the aromaticity and the degree of aromatic condensation of a thermosequence of wood charcoal using NMR. *Organic Geochemistry*. 2011;42(10):1194-202.
- [25] Ergun S. X-Ray Scattering by Very Defective Lattices. *Physical Review B*. 1970;1(8):3371-80.
- [26] Wu W, Yang M, Feng Q, McGrouther K, Wang H, Lu H, et al. Chemical characterization of rice straw-derived biochar for soil amendment. *Biomass and Bioenergy*. 2012;47:268-76.
- [27] Novak JM, Busscher WJ, Watts DW, Laird DA, Ahmedna MA, Niandou MAS. Short-term CO₂ mineralization after additions of biochar and switchgrass to a Typic Kandudult. *Geoderma*. 2010;154(3–4):281-8.
- [28] Nishimiya K, Hata T, Imamura Y, Ishihara S. Analysis of chemical structure of wood charcoal by X-ray photoelectron spectroscopy. *Journal of Wood Science*. 44(1):56-61.
- [29] Wang Z-M, Kanoh H, Kaneko K, Lu GQ, Do D. Structural and surface property changes of macadamia nut-shell char upon activation and high temperature treatment. *Carbon*. 2002;40(8):1231-9.
- [30] Suliman W, Harsh JB, Abu-Lail NI, Fortuna A-M, Dallmeyer I, Garcia-Perez M. Modification of biochar surface by air oxidation: Role of pyrolysis temperature. *Biomass and Bioenergy*. 2016;85:1-11.
- [31] Tuinstra F, Koenig JL. Raman Spectrum of Graphite. *The Journal of Chemical Physics*. 1970;53(3):1126-30.
- [32] Vidano RP, Fischbach DB, Willis LJ, Loehr TM. Observation of Raman band shifting with excitation wavelength for carbons and graphites. *Solid State Commun*. 1981;39(2):341-4.
- [33] Ferrari AC, Robertson J. Raman spectroscopy of amorphous, nanostructured, diamond-like carbon, and nanodiamond. *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*. 2004;362(1824):2477-512.
- [34] Hu C, Sedghi S, Silvestre-Albero A, Andersson GG, Sharma A, Pendleton P, et al. Raman spectroscopy study of the transformation of the carbonaceous skeleton of a polymer-based nanoporous carbon along the thermal annealing pathway. *Carbon*. 2015;85:147-58.
- [35] McDonald-Wharry J, Manley-Harris M, Pickering K. Carbonisation of biomass-derived chars and the thermal reduction of a graphene oxide sample studied using Raman spectroscopy. *Carbon*. 2013;59:383-405.

- [36] Kercher AK, Nagle DC. Microstructural evolution during charcoal carbonization by X-ray diffraction analysis. *Carbon*. 2003;41(1):15-27.
- [37] Manoj B, Kunjomana A. Study of stacking structure of amorphous carbon by X-ray diffraction technique. *Int J Electrochem Sci*. 2012;7(4):3127-34.
- [38] Dahn JR, Xing W, Gao Y. The “falling cards model” for the structure of microporous carbons. *Carbon*. 1997;35(6):825-30.
- [39] Babu VS, Seehra MS. Modeling of disorder and X-ray diffraction in coal-based graphitic carbons. *Carbon*. 1996;34(10):1259-65.
- [40] Oschatz M, Pré P, Dörfler S, Nickel W, Beaunier P, Rouzaud J-N, et al. Nanostructure characterization of carbide-derived carbons by morphological analysis of transmission electron microscopy images combined with physisorption and Raman spectroscopy. *Carbon*. 2016;105:314-22.
- [41] Harris PJF, Liu Z, Suenaga K. Imaging the atomic structure of activated carbon. *Journal of Physics: Condensed Matter*. 2008;20(36):362201.
- [42] Ferrari AC, Robertson J. Interpretation of Raman spectra of disordered and amorphous carbon. *Physical Review B*. 2000;61(20):14095-107.
- [43] Gullion T, Schaefer J. Rotational-echo double-resonance NMR. *Journal of Magnetic Resonance* (1969). 1989;81(1):196-200.
- [44] Mao JD, Schmidt-Rohr K. Recoupled long-range C–H dipolar dephasing in solid-state NMR, and its use for spectral selection of fused aromatic rings. *Journal of Magnetic Resonance*. 2003;162(1):217-27.
- [45] Smernik RJ, Kookana RS, Skjemstad JO. NMR Characterization of ¹³C-Benzene Sorbed to Natural and Prepared Charcoals. *Environmental Science & Technology*. 2006;40(6):1764-9.
- [46] Johnson RL, Schmidt-Rohr K. Quantitative solid-state ¹³C NMR with signal enhancement by multiple cross polarization. *Journal of Magnetic Resonance*. 2014;239:44-9.
- [47] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 09, Revision B.01. Wallingford CT2009.
- [48] Becke AD. Density-functional thermochemistry. III. The role of exact exchange. *The Journal of Chemical Physics*. 1993;98(7):5648-52.
- [49] Hariharan PC, Pople JA. The influence of polarization functions on molecular orbital hydrogenation energies. *AcTC*. 1973;28(3):213-22.

- [50] Wolinski K, Hinton JF, Pulay P. Efficient implementation of the gauge-independent atomic orbital method for NMR chemical shift calculations. *Journal of the American Chemical Society*. 1990;112(23):8251-60.
- [51] Cheeseman JR, Trucks GW, Keith TA, Frisch MJ. A comparison of models for calculating nuclear magnetic resonance shielding tensors. *The Journal of Chemical Physics*. 1996;104(14):5497-509.
- [52] Smith MW SL, Espinal JF, McEwen J-S, Garcia-Perez M. Improving the Deconvolution and Interpretation of XPS Spectra from Chars by ab Initio Calculations. *Carbon*. 2016;110:155-171.
- [53] Ergun S. Structure of carbon. *Carbon*. 1968;6(2):141-59.

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Table 1. Integrated intensities for PTCDA peaks, see figure 6A for corresponding assignments, and quantification of C associated with each peak compared to the theoretical values.

Table 2. Peak assignment table

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Table 1. Integrated intensities for PTCDA peaks, see figure 6A for corresponding assignments, and quantification of C associated with each peak compared to the theoretical values.

Position	Assignment	Primary peak	High side band	Low side band	Total	Equivalent distribution	Theoretical distribution
118.9	B	730933	67523	57306	855763	4.6	4
125-130	C, F, D	1014996	122656	159816	1297467	7.0	8
136.1	E,G	1166080	197944	150929	1514952	8.2	8
161.7	A	638040	74445	62029	774514	4.2	4

Table 2. Peak assignment table

Chemical Shift	Assignment
5-50 ppm	Aliphatic CH _x
20-60 ppm (slow dephasing)	Aliphatic CR ₄
45-90 ppm (110 for double)	Aliphatic ether
100-120 ppm	Aromatic C near Oxygen defects
120-140 ppm	Aromatic 5 and 6 member rings and olefins
140-150 ppm	Contribution for ether bonded carbon in furans and ~ ½ of carbons in larger non oxygenated rings
150-160 ppm	Aromatic linked ethers
160-180 ppm	Carboxylic/Lactone/ester
185-210 ppm	Carbonyl

Table 3. Assorted polyaromatic structures with number of carbons C-(-X)-H bond distances specified

Linear	r _{C-H} (Å)	Benzene	Napthalene	Anthracene	Tetracene	Pentacene	Hexacene
C		6	10	14	18	22	26
H		6	8	10	12	14	16
C:H		1.00	1.25	1.40	1.50	1.57	1.63
C-H	1.08	6	8	10	12	14	16
C-C-H	2.1-2.2	0	2	4	6	8	10
2 Layer			2*2 (Pyrene)	3*2	4*2	5*2	6*2
C			16	22	28	34	40
H			10	12	14	16	18
C:H			1.60	1.83	2.00	2.13	2.22
C-H	1.08		10	12	14	16	18
C-C-H	2.1-2.2		4	6	8	10	12
C(-2)-H	3.3-3.5		2	4	6	8	10
circular and semicircular			3*3 (Coronene)	4*5 Circumpyrene	5*5 (Circumcoronene)	6*7	7*7
C			24	42	54	80	96
H			12	16	18	22	24
C:H			2.00	2.63	3.00	3.64	4.00
C-H	1.08		12	16	18	22	24
C-C-H	2.1-2.2		6	10	12	16	18
C(-2)-H	3.3-3.5		6	10	12	16	18
C(-3)-H	3.9-4.6			4	6	10	12
C(-4)-H	5.1- .5.9			2	6	10	12
C(-5)-H	5.9-6.8					4	6
C(-6)-H	7.2-8.0					2	6

Table 4. Composition of material based on NMR Spectra (%)

Sample	Carbonyl	Carboxyl/lactone	Ether	Defect	Aromatic	Aliphatic
C400	3	5	10	13	51	17
C500	3	4	13	12	68	4
C600	1	3	7	7	82	0
C700	2	2	5	13	78	0

Margin of error is estimated at 2%

Table 5. Estimated contribution of various C-H bond distances for chars produced at 400-700°C based on dephasing results (%)

	Aromatic and defective aromatic carbons				Ether/hydroxyl bonded carbons				Aliphatic	
	C-H	C-X-H	C(-2)-H	C(-3)-H	C-H	C-X-H	C(-2)-H	C(-3)-H	C-H	C-X-H
C400	15	67	17	<1	20	60	20	<1	92	8
C500	31	47	23	<1	37	23	40	<1	100	N/A
C600	37	41	19	2	1	61	38	<1	N/A	N/A
C700	35	35	21	9	0	73	19	8	N/A	N/A

Margin of error is estimated as 5%

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Figure 1. Pulse sequences used for this study, all signal acquisitions were taken on a Han Echo with TPPM decoupling on the ^1H channel. (A) MultiCP with standard acquisition (B) DP with standard acquisition (C) MultiCP with dipolar dephasing and continuous wave decoupling around the dephasing period (D) DP with dipolar dephasing and continuous wave decoupling around the dephasing period (E) drop in long-range dephasing sequence used with both MultiCP and DP experiments. t_r denotes the time required for 1 full rotor period. Time 0 is placed at the initiation of gated decoupling and long range dephasing programs. A detailed explanation of each sequence is given in the supplemental material section S1 with the related code for each method.

Figure 2. Van Krevelen plot of atomic H:C and O:C ratios from combustion analysis. Solid lines represent theoretical vectors for the loss of CO and CH₄ and various initial compositions. The central black line represents the theoretical change associated with dehydration reactions. Data points based on elemental analysis provided by Smith et al. [52].

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Figure 5. C700 with dephasing. Black lines represent multiCP signals from 2048 scan scaled by exactly 1/11. Red lines represent DP signal collected after 256 scans. Total acquisition time for multiCP experiments was 6.5 hrs while DP experiments required 9.6 hrs.

Figure 6. (A) MultiCP spectrum for PTCDA collected from 2048 scans, relative integration areas are provided in Table 1 for the primary signal and each side band. (B) DP spectra for PTCDA using 1.5 (red), 3 (black) and 7 (blue) minute recycle delays, spectra for 1.5 and 7

minutes are a composite of 32 scans while the spectrum for 3 minute delays is a composite of 512 with the background normalized to the other spectra. These scans show no reliable signal acquisition despite extended relaxation delays (C) Comparison of multiCP spectrum (black line) to calculated spectrum for isolated PTCDA (red line) (D) comparison of multiCP spectrum to calculated spectrum for the central molecule of a molecule composed of six PTCDA units.

Figure 7. Dephasing plots for tetracarboxylic perylene

Figure 8. Dephasing results individual carbons in PTCDA (A) comparison of experimental dephasing rate with F value, the solid line denotes empirical equation proposed by Mao and Shmidt-Rohr [44]. (B) dephasing over time for carbons A-E with the theoretical rate for A and C+D given shown as a dashed line.

Figure 9. Theoretical spectra for 9 compounds (A) pentacene (B) coronene (C) circumpyrene (D) cyclopentane centered ring system (E) cycloheptane centered ring system (F) coronene with 5-8-5 Stone-Wales defect (G) conenene with added carboxyl group (H) coronene containing lactone group (I) coronene with single point defect closed by ether group and carbonyl group. All compounds containing carbon at shifts less than 120 ppm and greater than 140 ppm have been assigned alphabetic labels that correspond to each respective figure. New labels are used for peaks separated by more than 3 ppm.

Figure 10. (A) Theoretical dephasing for various carbons within circumpyrene at different apparent distances from hydrogen ($1.9 \text{ \AA} < r_{C-H} < 3.8 \text{ \AA}$) (B) Composite dephasing for various polyaromatic structures of increasing size (squares rylene, diamonds = coronene, triangles = circumpyrene, and circles = circumcoronene). The red line denotes an S/So value of 0.05 as an approximate minimum quantification level.

Figure 11. (A) Changes in Char spectra with temperature. (B) The deconvolution scheme (dashed lines) is shown for C700 where the solid red line represents is the summation of the deconvolutions. The solid black lines in both panels are the phase corrected experimental NMR spectra.

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Cellulose ($C_{12}H_{20}O_{10}$)

C300 ($C_{12}H_{18}O_9$)

C400 ($C_{22}H_{10}O_5$)

C500 ($C_{24}H_9O_4$)

C600 ($C_{32}H_{12}O_3$)

C700 ($C_{37}H_{12}O_3$)