Improving the Deconvolution and Interpretation of XPS Spectra from Chars by *ab Initio* Calculations

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Abstract: The interpretation of C1s XPS spectra from disordered oxygenated carbons remains uncertain despite a variety of schemes reported in the literature. Here, a thermoseries of cellulose chars was studied to evaluate six published deconvolution schemes; however, none were capable of correctly identifying the oxygen content determined by the O1s spectrum. To improve the self-consistency of the XPS interpretation a method is proposed based on a 7 peak C1s deconvolution, 3 C-C peaks, 3 oxygenated peaks, and pi-pi* transition peak. Deconvolution of the O1s by 4 peaks is used to determine O-C and O=C contributions which provide upper and lower bounds for the related C1s peaks: C-O, C=O and COO. To improve assignments, various functional groups and carbon structures have been examined via DFT using an initial state approximation. DFT calculations of model compounds (pyrene, cellobiose and perylene tetracarboxylic dianhydride (PTCDA)) were compared with experimental results to confirm the validity of the calculation method used. The DFT calculations identified several defect structures that justify the use of 3 peaks for deconvolution of the C-C region of C1s XPS spectra. The deconvolution method proposed provides C:O ratios in good agreement (within 5 %) of those obtained from total C1s and O1s peaks.

1. Introduction

Pyrolysis chars have received increasing attention in the literature for both agricultural and industrial applications. Both the physical and chemical structure of these materials have drastic impacts on critical parameters including reactivity and adsorption capacity, with accurate analysis of the surface being necessary to evaluate these parameters. Despite this, quantitative analysis of the physical structure of chars and other non-graphitizable carbons has proven to be a challenging endeavor [1-5]. Soluble surface compounds confound the titration analyses commonly used for activated carbon analysis [6, 7], while the continued release of volatile vapor phase products from materials produced at temperatures below 1000 K makes analysis by temperature programmed desorption (TPD) questionable [8]. Spectroscopic techniques can be useful in analysis, however techniques such as FT-IR and Raman spectroscopy [3, 9], where good signal dispersion can be obtained for carbons, are not directly quantitative [9].

X-ray photoelectron spectroscopy (XPS) is quantitative in nature, however the core level spectra of carbon tends to become heavily convoluted by multiple oxidation states and often demonstrate non-ideal behavior for both poorly conducting samples [10-12] and highly conductive samples [13, 14], complicating analyses. Despite these challenges, XPS is an exceptionally powerful tool for the characterization of the surface layers, and has been applied to the analysis of every type of carbon, ranging from amorphous and diamond like thin films [15-18], to graphite [14, 19], graphene [13], and carbon nanotubes [20-22]. There are also a number of publications [23-25] on the use of XPS for the study of chars. In these analyses the binding energy shifts associated with various heteroatoms including oxygen, nitrogen and fluorine are used to determine the elemental composition of the materials surface. A relatively simple peak fitting for oxygen containing carbons (referred to here as deconvolution), by far the most common heteroatom studied, sets the primary carbon-carbon peak at 284.4 eV, with hydroxyl/ether, carbonyl and carboxylic groups shifted approximately 1.5, 3, and 4.5 eV higher, respectively [26, 27]. A fundamental problem exists with this analysis; the oxygen concentration determined from the C1s spectra is seldom consistent with the concentration determined by quantifying each elemental peak independently.

To determine oxygen content from the C1s scan several quantification schemes have been

proposed. The first, and simplest, method for the quantification of oxygen is based on the assumption that all C-O bonds are hydroxyl like and all COO bonds are carboxyl like, allowing for oxygen to be calculated as the sum of the C-O, C=O and twice the COO peak intensities [13, 14, 26]. A second quantification method proposed by Smith et al. [2] assumes a 50:50 distribution of C-O bonds in the form of hydroxyl (C-OH, C:O = 1) and ether (C-O-C, C:O = 2) like groups. This is achieved by assigning a multiplication factor of 0.75 to the C-O peak. Carbonyl and COO peaks are treated with the same assumptions as the previous method. A separate quantification method has also been proposed for use when adventitious carbon is the primary contribution to the carbon peak [28].

In attempts to more accurately assign the C1s region, a variety of deconvolution schemes have been proposed including methods that use: two C-C peaks [14, 29], an asymmetric C-C [13, 14, 26], a combination of an asymmetric C-C peak with a second symmetric C-C peak, and most recently utilization of two defective peaks in combination with an asymmetric primary C-C peak [13]. The asymmetry factor often noted in graphitic carbons [14, 30] is attributed to semi-metal effects resulting from conduction band electrons, and has also been identified in polyaromatic compounds larger than 1 nm by Cheung [31]. The secondary C-C peak, commonly shifted by 0.7-1 eV from the first, is variously attributed to defect structures [14, 29] and sp^3 carbon [16, 32]. The defective peak assigned near 284 eV has also been assigned to defective carbon structures [22, 33, 34]. Each of these schemes affects the overall distribution and interpretation of deconvoluted peaks.

To better identify the origins of defect structures in carbon, a recent study by Feng et al. [29] combined XPS analysis and Raman spectrometry to study defects formation in pyrolytic carbon when subjected to different doses of Ar^+ irradiation. This study demonstrated a strong correlation between the formation of Raman intensity near 1150 and 1500 wavenumbers and the formation of an intense peak, shifted to a higher binding energy by approximately 1 eV in the XPS spectrum. Raman intensity near 1150 and 1500 wavenumbers has been linked with out-of-plane distortions resulting from either various point defects [1] or mechanical stress [35]. These proposed defects are in strong agreement with those previously observed by high resolution transmission electron microscopy for activated carbon [36].

While these results have given some clarification on the origins of the defect peaks, the effects of various potential structures on the C1s profile is difficult to determine due to the variety of possible chemical states [37]. To better determine the effects of structure and bonding, density functional theory (DFT) calculations have been used to analyze a wide variety of systems [38-43]. For these calculations binding energies are determined using several possible approximations, including; initial state, final state, and transition state approximations. Initial state approximations are the simplest to implement but least accurate, neglecting core-hole screening effects [44]. The final state approximation is more intensive, isolating the desired core-hole in the structure and determining the full screening effect. The transition state approximation utilizes partial orbital occupations to describe the excitation process [45]. These methods have been applied by several studies to examine the core binding energies associated with a wide variety of carbon containing compounds, including; small molecules [37, 38], graphitic carbons [42, 43] and chars [41]. These studies have used both initial state [37, 41, 43] and final state calculations [38, 42]. The work of Levi et al. [41] and Barinov et al. [42] provide an excellent initial assessment of the effect of defect structures on carbonaceous materials by DFT simulations.

In this paper we will examine the deconvolution of XPS spectra from chars with assignments and positioning supported by molecular simulations. Here, the effects of several defect structures previously proposed for cellulose chars are examined with respect to their role on the core level binding energies relevant to XPS. This information is used in conjunction with a newly proposed combined O1s and C1s deconvolution strategy to better deconvolute and interpret XPS spectra obtained from chars.

2. Materials and Methods

All studies described here have been performed with model compounds or thermally treated model compounds purchased from Sigma Aldrich. Avicel cellulose (product# 11365) is used to evaluate the effect of pyrolysis temperature on the surface chemistry of the resultant chars. Several model compounds have been used to validate DFT simulations, including pyrene

(product# 572145), cellobiose (product# 22150), and anhydrous perylene tetracarboxylic dianhydride (PTCDA) (product# P11255). All compounds have a minimum purity of 95% and have been used as received.

2.1. *Pyrolysis*

A series of five pyrolysis chars have been produced at temperatures between 300 and 700 °C from Avicel cellulose in a spoon pyrolysis reactor following same methods as previously described [1, 5]. Briefly, the furnace is preheated to a desired temperature while a pre-weight sample is stored in a water-jacketed cooling zone. The cooling zone and furnace are purged with a N₂ gas (99%) stream flowing at approximately 300 mL/min for a minimum of 10 minutes prior to treatment. At the start of the experiment the sample is introduced into the furnace and treated for 30 minutes before withdrawal to the cooling zone. A secondary preheated nitrogen sweep gas, flowing at approximately 550 mL/min, is employed in the reactor zone to minimize vapor-char interactions. Samples were allowed to cool to temperatures below 25 °C under N₂ before exposure to air.

2.1.1 *General Characterization*

The bulk carbon to oxygen ratio of the cellulose chars was determined in triplicate using a LECO elemental analysis system. All measurements utilized approximately 150 mg of samples per trial. The calibration was checked by analysis of a cellulose standard (deviations of less than 1%). FT-IR spectra were obtained using a ThermoFisher Nicolet IS10 spectrometer. Final spectra are the average of 64 scans collected between 600 and 4000 cm⁻¹. Surface area was determined based on the Dubinin-Radushkevich (DR) equation [46, 47] for CO₂ adsorption isotherms collected at 273K as described previously [2].

2.2. *Computational*

Pyrene, cellobiose, and PTCDA have been analyzed via density functional theory (DFT) to confirm the validity of the computational methods presented here. Defect based daughter

compounds of polyaromatic parents have been used to evaluate the effects of various carbon bonding structures proposed to be prevalent in the chars [1] and activated carbons [36]. Several oxygenated defects have also been included to determine likely shifts associated with both the C1s and O1s spectra. All calculations have been performed using the Gaussian 09 rev. B.01 software package [48], and evaluated using most abundant isotopes. Geometry optimizations is performed using the Becke three-parameter Lee-Yang-Parr (B3LYP) hybrid functional [49], and a Pople type split valence 6-311G(d,p) basis set [50], following the results presented previously by Giesbers [37]. A singlet state was previously confirmed to be the ground state configuration for each daughter compound examined in this study [1]. The individual electron energies for each atom were determined using the NBO 3.0 package available within Gaussian 09. Koopmans' theorem [44] has been applied, in which the core-binding energy is estimated as the negative of the electron energy in the initial state. This estimate does not take into account electron rearrangement, but has been found to provide a reasonable estimate for binding energies using a simple linear correction factor [37], given in Eq. 1a. This equation was established using a reference binding energy of 285.0 eV for alkene carbons, to accurately reflect the reference energy used here of 284.4 eV the offset was reduced by 0.6 eV to 19.74 eV, Eq. 1b. Because of its simplicity, this method allows for rapid screening of multiple compounds without the need to calculate additional electronic configurations for each molecule of interest, as required for difference or final state approximations.

$$BE_{corrected} (eV) = BE_{B3LYP}(eV) * .9678 + 20.34(eV) \quad \text{Eq. 1a}$$

$$BE_{corrected} (eV) = BE_{B3LYP}(eV) * .9678 + 19.74(eV) \quad \text{Eq. 1b}$$

The linear fit presented in Eq. 1a is based on the best fit results obtained by comparing experimental and simulated C1s binding energies from 9 organic compounds comprising a total of more than 20 unique carbons sites. The resulting mean deviation was 0.29 eV from experimental results with a maximum deviation of 0.72 eV. From this, a variance of more than 0.4 eV ($0.29 \text{ eV} * 2^{0.5}$) from the average calculated binding energy of a coronene structure is considered significant for the results of the current study.

2.3. XPS

The X-ray photoemission spectra of each char in the thermoseries, as well as all reference compounds, were evaluated using an AXIS-165 manufactured by Kratos Analytical Inc. (Spring Valley, NY, USA). Scans are conducted following the same method previously employed [2]. Briefly, an achromatic X-ray radiation of 1253.6 eV ($\text{MgK}\alpha$) was used for each material. All spectra were recorded using a pass energy of 40 eV and spot size of approximately 120 μm . The spectrometer was calibrated against both the Au $4f_{7/2}$ peak at 84.0 eV and the Ag $3d_{5/2}$ peak at 368.3 eV. The minimum full width at half maximum (FWHM) for the Au $4f_{7/2}$ peak is approximately 0.85 eV, representing the absolute minimum possible broadness achievable for this configuration. Survey scans have been obtained using step sizes of 1 eV to determine overall chemical composition. To determine the speciation of carbon-oxygen groups high resolution scans of the C1s and O1s regions have been collected for each material using 0.15 eV step sizes. All XPS spectra were analyzed using the XPSpeak4.1 software. Baseline corrections were made using a Shirley type background correction [51]. Static charging was detected in raw cellulose and chars produced at temperatures of 500 °C or less. This charging was corrected with a neutralizer (flood gun) by centering the dominate C-C peak near 284.4 eV (filament current set to 1.8 A, charge balance varied between 2.4-3.0V). This procedure introduced varying degrees of shift in the baseline, which have been corrected by applying an offset of 1.0-2.0 eV.

2.3.1 XPS Deconvolution

Existing XPS deconvolution schemes: Examples of several deconvolution schemes proposed in the literature are given in supplement Figure S1 (see supplement section S1) and have been applied to the thermoseries of cellulose chars using the XPSpeak4.1 software. These schemes are broken down into two broad classes: three schemes using only symmetric line shapes, denoted Sm1-3 (Supplemental Figures S1A-C) [20, 27], and three schemes using an asymmetric C-C peak at approximately 284.4, denoted ASm1-3 (Supplemental figures S1D-F) [13, 14, 26]. The supplemental section S2 details the use of this asymmetric peak shape. Each of these classes utilize one [26, 27], two [2, 14, 15, 52], and three [13] C-C peaks. The primary C-C peak is that

typically assigned at 284.4 eV for aromatic C-C/C-H bonds. The second peak, near 285 eV is variously assigned to sp^3 [15] carbons and defective carbon structures [14, 52]. The third and most recently implemented peak is situated near 284 eV and has been assigned to a second class of defective carbons [13, 21, 22]. The sets of binding energy positions used for each scheme are given in Table 1.

Table 1.

Deconvolution of the O1s spectrum is performed based on the assignments given by Beamson and Briggs [53] for oxygenated polymers. These positions are also summarized in Table 1. This strategy places a C=O peak at 531.2-531.6 eV with an aliphatic C-O group positioned at 532.5-532.9 eV and aromatic C=O positioned near 533.0-533.4 eV. These positions are consistent with those reported by other groups [54]. The assignment of adsorbed moisture and oxygen is variously assigned between 533 and 535 eV. Work by Herman et al. [55], demonstrated that the binding energy of water was sensitive to total surface coverage on anatase. At coverage less than 1 monolayer, binding energies of approximately 535 eV are observed. The apparent binding energy decreases toward 534 eV as the surface coverage exceeds 1 monolayer. Because sub monolayer adsorption is anticipated on chars only exposed to atmospheric conditions and then degassed, the moisture peak is assigned here at 534.8-535.2 eV.

Three oxygen quantification schemes have been evaluated; see equations 2a-2c. These methods are referred to as schemes a-c. The first (scheme a), given by equation 2a, is the most commonly utilized method for the quantification of oxygen. Here, the described oxygenated species are taken as isolated systems and the sum of peak intensities of the C-O, C=O and twice the COO peaks gives the total oxygen intensity [13, 14, 26]. The second (scheme b), proposed by Smith et al. [2] and shown in equation 2b, assumes that C-O bonds are evenly distributed between carbon bound hydroxyl groups and ethers by assigning a sensitive factor of 0.75 to the C-O peak. The third quantification method (scheme c) given in equation 2c, assumes that the entirety of the C-O signal results from ether bonds and lactones, while the COO peak results entirely from lactones. These assumptions yield the minimum possible oxygen content for the deconvoluted C1s spectra.

$$O_{C1s} = A_{C-O} + A_{C=O} + 2 * A_{COO} \quad \text{Eq. 2a}$$

$$O_{C1s} = A_{C-O} * 0.75 + A_{C=O} + 2 * A_{COO} \quad \text{Eq. 2b}$$

$$O_{C1s} = \frac{A_{C-O} - A_{COO}}{2} + A_{C=O} + 2 * A_{COO} \quad \text{Eq. 2c}$$

Where:

A_x = the total integrated intensity of the specified deconvolution peak (C-O, C=O, and COO)

O_{C1s} = equivalent oxygen content determined from C1s scan

New C1s Deconvolution: The most detailed of the previously discussed schemes (ASm3, see Figure S1F) is used as the basis for a more constrained fitting procedure. Several modifications have been made to this procedure to improve the estimation of the C/O ratio and ensure a self-consistent evaluation, these include; utilization of sequential deconvolution of the O1s and C1s spectra, fixed asymmetric tail length (TL) and a freely variable asymmetry contribution (TS), as well as inclusion of a variable oxygen quantification scheme, Eq. 3, that allows for shifting distributions of hydroxyl and ether like groups, D_{HE} (0 for all hydroxyl and 1 for all ether), as well as carboxyl and lactone/ester groups, D_{CL} (0 for all carboxyl, 1 for all lactone). This method also estimates the distribution of carbons bonded to two ether/hydroxyl groups and carbonyl groups. In this assessment, carbons bonded to two oxygens by single bonds are evaluated as part of the A_{C-O} peak. Details of the oxygen constraints are given in Supplemental section S3.

$$O_{C1s} = (A_{C-O} - D_{CL} * A_{COO}) * \left(1 - \frac{D_{HE}}{2}\right) + A_{C=O} + 2 * A_{COO} \quad \text{Eq. 3}$$

All deconvolutions utilizing this method have been performed using an in-house excel based routine. A Shirley type background correction is used; calculated based off of 10 iterations. Deconvolution is conducted using a sum based asymmetric pseudo Voigt function, as implemented in XPSpeak 4.1 and shown in Eq. 4, for the primary C-C. A symmetric pseudo Voigt function ($A(x,p,w,m) = 0$ in Eq. 4) is used for all other peaks. Optimization is performed by minimization of the sum of the square errors between the deconvolution curve and real spectrum

using the built in GRG2 solver in excel. A convergence criterion of 10^{-7} over 5 iterations was used to determine convergence.

$$AGLsum(x, p, w, m, h) = h[G(x, p, w, m) + L(x, p, w, m) + A(x, p, w, m)] \quad \text{Eq. 4}$$

$$G(x, p, w, m) = (1 - m) * e^{-\ln(2) * \left[\frac{2 * (x - p)}{w} \right]^2}$$

$$L(x, p, w, m) = \frac{m}{1 + \left(2 * \frac{x - p}{w} \right)^2}$$

$$A(x, p, w, m) = TS \left[1 - e^{-\ln(2) * \left[\frac{2 * (x - p)}{w} \right]^2} \right] * e^{-\frac{6.9}{TL} * \left(2 * \frac{(x - p)}{w} \right)^2}$$

Where:

G = Gaussian contribution; L = Lorentzian contribution; A = Asymmetric contribution

x = binding energy (eV), p = peak center (eV), w = FWHM (eV), m = Gaussian-Lorentzian mixing (0 Gaussian: 1 Lorentzian), h = peak height (counts/sec) TS = asymmetry parameter, and TL = asymmetry tailing parameter

Deconvolution of the C1s spectra utilizes 7 peaks (3 C-C peaks, 3 C-O peaks and a pi-pi* shake-up peak) as discussed by Blume et al. [13], see the Asm3 scheme in supplemental Figure S1F. The full width half-maximum (FWHM) of each C-C peak is set to 1.2-2 eV while the oxygenated peaks are set to 1.8-2.2 eV, this variance is allowed due to the narrower expected chemical state distribution for each C-C region compared to the oxygenated species.. This discrepancy is due to the larger distribution of possible oxygen binding states for each group as compared to the C-C region. A minimum broadening of approximately 1 eV is expected due to the X-ray source. The pi-pi* transition peak, is assumed to be a broad feature and is allowed to vary between 2 and 3 eV. The primary C-C (peak II) is assigned to aromatic carbons, and is allowed a variable asymmetry factor based on the empirical equation utilized by Kwok in XPSpeak 4.1, given by $A(x, p, w, m)$ in equation 1, with the TL value fixed at 200 (see supplemental S2 for further discussion regarding this selection). The remaining two C-C peaks, centered near 283.8 eV (peak I) and 285 eV (peak III), are assigned to assorted defects and evaluated as symmetric peaks. The oxygenated region consists of three curves centered at approximately 286.2 eV (C-O, curve IV) 287.5 eV (C=O or O-C-O, curve V) and 289 eV (O-C=O, curve VI). These peaks are evaluated as symmetric peaks and are constrained by information from prior deconvolution of the O1s spectrum.

3. Results

Cellulose chars have been produced at temperatures from 300 to 700 °C using the spoon pyrolysis reactor at [Washington State University](#). The apparent surface area (SA) and elemental composition are presented in Table 2, here chars are denoted as CX, where X is the pyrolysis temperature. [The char yield drops](#) off significantly as temperature is increased to 500 °C. At higher temperatures the total yield decreases only slightly suggesting that the primary loss of carbon and oxygen occurs by 500 °C with subsequent mass loss a result of poly-condensation reactions [5, 56, 57]. Both surface area and total carbon content were found to increase continuously as pyrolysis temperature was increased (see Table 2). A small contamination of nitrogen was found to exist in each char, increasing with pyrolysis temperature, however did not exceed 0.4% for any material. The content of H was found to decrease as a function of temperature, from approximately 6 wt% to 1.5 wt% (see Table 2). Increasing pyrolysis temperatures resulted in substantial increases in surface area. Despite the increased surface area, higher treatment temperatures also resulted in a more hydrophobic surface, resulting in reduced adsorption of moisture from the atmosphere following production. These results clearly indicate that the structural composition of chars can vary widely over the pyrolysis temperature range studied here, and interpretation via XPS must be robust to account for the varying forms of the material.

Table 2.

A preliminary assessment of bulk oxygenated groups has been performed by FT-IR analysis, given in Figure 1. These results indicate a sharp reduction in in O-H stretching modes near 3300 cm^{-1} when pyrolysis temperatures are increased from 300 °C and 400 °C with nearly complete loss of these groups by 500 °C. Despite the loss of hydroxyl groups, aromatic C-O stretches, which present near 1200 cm^{-1} , are identified at all treatment temperatures at or above 400 °C, indicating the formation of ether or ester like groups within the aromatic structures. Acid or ester groups can also be identified by a relatively sharp peak near 1700 cm^{-1} that persists on chars produced at 300-600 °C. Because little OH stretching is observed at temperatures above 400 °C

these vibrations are most likely related to esters and lactones. The IR results demonstrate a consistent decrease in C-H modes near 2900 cm^{-1} , as well as rapid development of C=C stretching modes near 1600 cm^{-1} at treatment temperatures of $400\text{ }^{\circ}\text{C}$ consistent with increasing aromatic condensation. It is important to note that in comparison to XPS, FT-IR has a greater sampling depth, resulting in greater signal contributions from the bulk. Still, these results provide useful insights into the changes in composition of the char with temperature. The change in hydroxyl and ether group distribution identified must be considered in any oxygen quantification scheme based on the C1s spectra since the C:O ratios for these groups differ (1:1 for carbon bound to hydroxyls and 2:1 for ethers). The same is also true for potential shifts in carboxylic acid and lactone/ester distributions (2:1 and 1:1).

Figure 1.

3.1 XPS analysis of thermoseries

Survey scans have been collected for each char in the thermoseries. These results are displayed in Figure 2A. A small peak is also identified at $\sim 52\text{ eV}$, however the location, and lack of additional peaks throughout the spectra indicate that this is a carbon ghost peak resulting from Al $K\alpha$ x-ray contamination [58]. This result is supported by a minor peak near 300 eV identified in the cellulose and C300 spectra which decreases proportionally with the primary oxygen peak. The results demonstrate that only C and O contribute significantly to the surface chemistry. Quantification of the C1s and O1s region has been achieved by applying a Shirley type background correction [51] to each peak and applying the pertinent relative sensitivity factors (RSF) to **standardize** the reported counts. The RSF for oxygen compared to carbon is 2.31 for the AXIS 165 instrument used based on the **factory tuning**. This value is considerably lower than the commonly used Scofield RSF of 2.93 [59], highlighting the importance of accurate tuning parameters when quantification is required. The resulting C:O atomic ratios determined by XPS using this value compare exceptionally well to the bulk elemental ratios for materials treated at temperatures below $400\text{ }^{\circ}\text{C}$, as shown in the parity plot, Figure 2B. Comparison of more heavily surface weighted results determined by XPS and bulk C:O ratios determined by combustion analysis demonstrate increasing divergence of the bulk and surface properties as pyrolysis temperature is increased above $500\text{ }^{\circ}\text{C}$. This effect is attributed to rapid chemisorption of oxygenated species at active sites [27, 60] and has been previously observed for a thermoseries

of cellulose chars [61]. Similarly, dissociative adsorption of CO₂ at carbene like sites has also been proposed [62]. Previous studies have established that only a small fraction of the char surface contains these free radicals, however they tend to form more readily at temperatures above 400 °C during pyrolysis [63, 64]. Combined with the low oxygen content of chars produced at these elevated temperatures, dramatic offsets, as seen in the parity plot, are not unexpected.

Figure 2.

The C:O ratio determined by the wide scan comparison of carbon and oxygen represents, in theory, the maximum quantity of oxygen that can be bound to carbon. In materials such as chars or activated carbons from biomass the quantity of oxygen that can be bound to carbon will be lower (larger C:O ratio) due to oxygen associated with inorganic moieties (such as CaO or SiO₂) in these complex materials and must be considered in any quantification. In the case of cellulose chars presented here this effect is of only nominal importance because of the very low mineral content of the original Avicel cellulose. Therefore the oxygen content determined for the O1s peak area and deconvolution of the C1s peak should be in strong agreement. In more complex biomass systems containing quantifiable mineral matter, it will be necessary to determine the oxygen associated with the mineral content first to accurately quantify the oxygen associated with carbon.

3.1.1 Deconvolution of XPS curves by published methods

High resolution scans of C1s and O1s for a thermoseries of cellulose chars is given in Figure 3. The C 1s spectrum recorded for cellulose is in good agreement with previously published spectra [65]. A strong reduction in intensity of peaks near 286-287 eV is noted with increasing pyrolysis temperature, a product of the loss of hydroxyl and ether groups. These results are qualitatively in agreement with both the wide scan data and the bulk elemental analysis data.

Figure 3.

Total peak areas for the C1s and O1s spectra of each material are given in Table 3. The O1s deconvolution results are also given for each material. From these results, the development of the O=C peak is apparent at pyrolysis temperatures of 400 °C or greater. The content of this group increases from negligible in the raw material and the material produced at 300 °C to approximately 35% at 600 °C and 700 °C.

Table 3.

Each of the deconvolution schemes derived from the literature has been used to analyze the C1s char spectrum for each material. Table 4 details the results obtained by the totally symmetric deconvolution methods Sm1-3. Also included in table 4 are comparisons of 3 oxygen quantifications schemes (as given in equations 2a-c) and the associated deviation from the C 1s/O 1s ratio obtained from the fine scan totals. For this analysis deviation from the measured C 1s/ O 1s ration of 10% is considered a good fit and 20% is acceptable. These results highlight the wide ranging variability of chars as a function of temperature, as well as the difficulty associated with accurate deconvolution. Each symmetric deconvolution procedure produced good results when comparing the estimated and measured oxygen content for cellulose and C300, while only scheme Sm2 and Sm3 provided acceptable results for C500. This improved fit is most strongly correlated to the shift of the C-O peak by +1.8 eV. Addition of secondary and tertiary C-C peaks without shifting this position did not result in substantial changes to the results (data not shown). Deconvolution using these methods substantially overestimates the oxygen content of C400. Based on the strong signal intensity near 285.5 eV, it is probable that much of the intensity attributed to C-O bonds can instead be attributed to the secondary C-C defect peak and that the C-O position may need to be shifted to higher binding energies. The symmetric peak analysis failed to reasonably quantify the oxygen content of chars produced above 500 °C, revealing substantial overestimations of oxygen, even when considering the least oxygen intensive quantification, scheme c. The inclusion of secondary and tertiary C-C peaks (Sm2 and Sm3) did improve oxygen quantification somewhat for both C600 and C700 samples, however not substantially. The poor fitting here suggests that secondary emission effects are occurring that distort the C1s spectrum for each of these materials.

Table 4.

The results for asymmetric deconvolution of the C1s spectra are presented in Table 5. The calculated C 1s/O 1s ratios are also presented for each quantification scheme as before. Because the symmetric deconvolution was found to acceptably fit the results for material treated at temperatures at or below 500 °C, analysis of the use of asymmetric peak shapes is limited only to materials treated at 500 °C and higher. In this analysis the asymmetry factor is varied manually in 0.01 step increments until reasonable agreement with total oxygen is obtained and fit error is minimized. An error in the quantification of the asymmetric peak within XPSpeak4.1 is noted, where the total area of the asymmetric peak can, under moderate asymmetry, exceed the total signal substantially. To minimize this challenge the total peak area is assumed to be the total background-corrected area. The symmetric peak areas of the defect and oxidation peaks are subtracted from this value, and the asymmetric peak fraction reported here is the calculated difference.

Table 5.

The results for the asymmetric deconvolution of C500-C700 show substantially better agreement with the oxygen content predicted by comparison of the C1s and O1s scans, particularly when considering quantification scheme b, providing a good fit for the C600 and C700 data. The optimized peak asymmetry was found to vary slightly depending on the defect peaks used, however a consistent trend of increasing asymmetry was observed with temperature. The TS parameter was found to increase from approximately 0.05 to 0.15 as pyrolysis temperature increased.

The wide variety of fitting methods proposed for XPS spectra in the literature, and the relatively poor internal consistency obtained when applied to chars, clearly demonstrate the need for a defined and consistent methodology in fitting the C 1s region of many char spectra. While at least one combination of peaks (Sm1-3 or ASm1-3) and oxygen quantification schemes (a-c) did provide an internally consistent result for most chars, no single method was effective for the deconvolution of all materials. The results demonstrate that while simple fitting procedures may

be valid for material produced at temperatures at or below 300 °C, additional C-C peaks and asymmetry are often needed for chars produced at higher temperatures.

To improve on the results of the initial deconvolution trials a new procedure is needed. To ensure reasonable peak assignment and constraints for each deconvolution parameter, ab initio DFT calculations have been performed to evaluate the contributions of a variety of carbon-carbon and carbon-oxygen bonding conditions. These results are combined to propose an improved deconvolution scheme in section 3.3.

3.2. Computational analysis of strained and oxygenated systems

To establish the validity of the computational models used in this study, several reference model compounds (pyrene, cellobiose, and PTCDA) were evaluated experimentally and by DFT analysis. The results of these studies are compared in Figure 4. The black line represents the calculated spectrum for the listed compounds, while the red line gives the corresponding experimental spectrum. The calculated positions were corrected based on the empirical linear correction factor (Eq. 1b) based on the results published by Giesbers et al. [37]. Charging effects required baseline correction of 1.0-2.0 eV for the experimental spectra. This equation has tentatively been extended to the O1s spectra with the offset increased to 33.49 eV to fit the O1s peak position of cellobiose.

Figure 4.

The computational and experimental fitting parameters used for each reference compound are listed in Table 6. To match the shapes of the experimental spectra, a Gaussian:Lorentzian sum (G:Lsum) function was used to broaden the calculated binding energy identified for the core electrons of each carbon in the model system. To optimize this parameter, the G:L distribution and the full width at half maximum (FWHM) were allowed to vary as a single parameter for all atoms within each individual compound. A single G:L ratio and FWHM was not universally calculated because of varying effects such as charging, which can cause minor variations in the recorded line-shape of each spectrum [11]. These parameters are compared to those obtained by

fitting a single deconvolution peak to the primary C-C peak of each experimental spectrum. Here, the optimized FWHM parameters compare well to the single peak analysis, while the Lorentzian contribution is significantly higher for the simulation fit parameters. This behavior is expected as the convolution of several overlapping Lorentzian signals will tend to produce a curve with far more Gaussian character. While neither the FWHM nor the distribution of G:L shapes was consistent between samples, an average FWHM of approximately 1.56 eV with a 55% Lorentzian profile is estimated based on the results. This averaged broadening factor is used to produce theoretical line shapes for all simulated spectra. These results indicate that any deconvolution peak should have a minimum G:L ratio of no more than 0.3 and a minimum FWHM of approximately 1.4 to 1.5 eV for non-conductive samples. Materials with multiple atoms with similar peak positions will show substantially lower G:L ratios.

Table 6.

Overall, the computational models identified shifts in the C1s binding energies exceptionally well and the use of a GLsum function was found to provide a good approximation of the shapes of the experimental peaks, see Figures 4A-C. The excess tailing observed in the experimental C1s scan of PTCDA (Figure 1C) near 292 eV is attributed to a shake-up peak [66, 67]. An important effect is noted for the cellobiose sample, Figure 4B, where a shoulder, shifted approximately 1.5 eV from the primary C-O peak is observed. This peak results from carbons at the C1 position in each monomer. These carbons are linked to both the internal ether and the 1-4 β glycosidic linkage, resulting in two C-O bonds for each carbon atom. This causes a shift comparable to that reported for carbonyl groups and must be considered in the analysis of chars produced at low temperatures, where portions of the original biomass structure may not be fully degraded.

O1s fine spectra were also collected and calculated for each compounds. The calculated results for cellobiose, show good agreement when an offset of 33.49 eV is employed, Figure 4D, though total FWHM is somewhat larger than the experimental results. These results demonstrate a relatively wide dispersion for O-C, roughly 1.8 eV within cellobiose alone. This high dispersion would account for the relative insensitivity of peak broadness to X-ray source observed in

previous studies [13]. The results for PTCDA do show strong shifts between the C-O and C=O positions for the cyclic anhydride groups, however the predicted shift between the C-O and C=O are calculated to be 3.8 eV, more than 1 eV greater than the experimental shift. Similar exaggerations in O1s binding energies were also observed for simulated compounds presented in 3.1.4. In addition to positional offsets, the experimental intensity of the peak associated with the bridging ether oxygen is substantially greater than expected. This effect has been observed previously and is linked to a shake-up peak associated with the carbonyl that presents near the ether bonded oxygen [66, 67]. Based on these results it is concluded that to properly simulate the O1s spectrum of aromatics, final state effects must be considered. This is beyond the scope of this work, and so O1s deconvolution parameters have been taken from experimental literature results, and have been found to agree with the limited reference peaks obtained here. While this may somewhat limit interpretation of results, this also limits the possibility that peak positions are erroneously assigned.

3.2.1 *Effect of hybridization and hydrogenation*

To confirm that the calculated spectra of aromatic systems of varying sizes do not show substantial binding energy variations, three polyaromatic systems of increasing size were adopted as parent structures. These include coronene, circumpyrene, and circumcoronene. Figure 5 shows the normalized calculated XPS spectra for each of the parent molecules used. As with pyrene, each displays a sharp symmetric peak centered near 284.6 eV. Only a very mild shift in the central binding energy is observed as ring size increases. This is attributed to the reduction of C-H and C-C which presents slightly shifted positions.

Figure 5.

The effect of sp^3 carbons was tested by incorporating alkane side chains to the periphery of a coronene molecule with the results shown in Figure 6A and 6B. The addition of these carbons had an unexpected effect; a general reduction in binding energy identified for the overall molecule of 0.1-0.25 eV. This downshift is outside of the quantifiable limits of the experiments performed here, but is surprising as sp^3 carbons are commonly assigned near 285.0 eV. This

effect is attributed to the high degree of hydrogenation associated with these chains. In contrast to the deviations that result from sp^3 carbons, alkene chains, shown in Figure 6C and 6D, do not have any appreciable effect on the resulting XPS signal. Though minor shifts in binding energy are associated with hybridization and hydrogenation, they are not sufficient to explain the substantial defect peaks observed previously. To explain these peaks defect structures must be considered.

Figure 6.

3.2.2 Effect of Defects on C-C core electron binding energies

The effect of an internal cyclopentane ring within a polyaromatic structure is shown in Figure 7A. In this structure three distinct carbons are present and labeled A, B and C. These carbons are repeated in each section around the structure. The central location of the cyclopentane results in a circular out of plane bending for the adjacent benzene rings. Examining the core binding energies for carbons atom in the cyclopentane systems reveals a downshift of 0.57 eV compared to the average C1s binding energy of coronene, and 0.84 – 0.90 eV when compared to carbon atoms contained only in the adjacent rings. This shift is considered significant based on the average error previously reported for this correction factor. As a result of this downshift a distinct asymmetry is observed on the low binding energy side of the carbon peak. When compared to an unmodified coronene system (dashed red line) it is apparent that, while the binding energy of the core electrons in the cyclopentane system does decrease, an increase in binding energy occurs within the surrounding benzene rings. The greater distribution of carbons within these rings results in an overall increase in apparent binding energy, with only very mild increase on the low binding energy side. Despite this, these shifts are not considered significant based on the errors associated with this analysis.

Figure 7.

In contrast to the effect of cyclopentane, inclusion of larger rings such as cycloheptane, see Figure 7B, results in a significant increase of 0.57 eV in binding energy for carbon core electrons

associated with the large ring system. Similar to the cyclopentane results, a contrasting, but not significant, decrease is observed for those carbons in the adjacent benzene-like rings, and because of the greater density of these carbons, the defect results in an apparent binding energy reduction compared to unmodified coronene (dashed red line).

A summation of these effects can be seen in the Stone-Wales defects introduced into polyaromatic parent structures. Figure 8A details the structure and binding energy shifts associated with circumpyrene, while the simulated spectra for this defect in coronene, circumpyrene and circumcoronene are detailed in Figure 8B. Detailed figures for coronene and circumcoronene are provided in the supplement section S4, Figure S5. The results indicate that ring structures containing more than 6 carbons result in mild to moderate increases in the associated binding energies, while carbons present in cyclopentane rings experience a moderate reduction in binding energy. The defect introduced into coronene resulted in a portion of the cyclooctane ring system as well as much of the cyclopentane rings to exist as edge sites in the polyatomic structure. Under these conditions the binding energy shift associated with each defect was substantially reduced. This resulted in less severe tailing at low binding energies than was observed for defects in either circumpyrene or circumcoronene. While changes to the spectra are apparent when using the averaged parameters obtained from the model compound analysis, pertinent to the XPS system used for this study, the impact of defects is far more evident when the FWHM is reduced to 0.5 (Figure 8C). This resolution is not possible on the equipment used here, as the line broadening from the achromatic Mg x-ray source alone exceeds 0.7 eV; however, these substantially improved resolutions are possible with a synchrotron X-ray source as shown by Blume et al. [13]. Using this source the authors identified the formation of two additional C-C peaks shifted +0.4 and -0.4 eV from the primary peak. These peaks were approximately equal in nature and agree very well with the position and behavior noted here for a 5-8-5 Stone-Wales defect in circumcoronene, which have been postulated to form as a result of argon bombardment [29]. Though these structures are likely not the exact form to be found in amorphous chars, the nature of the defects presented in Figures 6-8 are informative regarding potential structures.

Figure 8.

3.2.3 *Effect of oxygen on C1s binding energies for bound and nearest neighbor carbons*

The effect of oxygen on the binding energy of adjacent carbons is well known throughout the literature. However the long range effects of oxygen is not typically considered. The examination of heavily oxygenated carbon species, such as PTCDA demonstrates that the presence of oxygen can have significant effects even on non-adjacent carbons (see Figure 6C). In this case, long range effects resulted in a calculated binding energy shift of approximately 1.2 eV for all non-adjacent carbons. Without accounting for this effect, a preliminary analysis of the spectrum would suggest that the system was composed entirely of carboxyl and hydroxyl or ether bonded carbons.

To determine the effects of individual functional groups on the binding energy distribution of small aromatic compounds, the effects of various oxygen groups, shown in Figure 9 for coronene, were examined. Analysis of the effects of oxidation on a variety of carbon sites, Table 7, yields results consistent with those obtained for the coronene. From these results, the position of the hydroxyl bonded carbon is estimated to be shifted +1.8-2.2 eV from the primary carbon peak. Carbonyl groups are estimated to cause shifts of +2.6-3.0 eV while carboxyl and lactone groups resulted in shifts of 4.2 to 4.5 eV. All results are within the parameters published for such groups[53]. Lactone groups, being directly bonded to two carbons, show equal signal intensity in the same region as carboxyl groups and near hydroxyl groups. Because of this care must be taken in quantification when lactones or esters are present, or the oxygen content will be overestimated. Carboxylic groups were also found to have a moderate effect on the next nearest carbon, resulting in a positive binding energy shift of 0.6-1.0 eV relative to the unmodified parent. Each functional group, aside from hydroxyls, in each configuration, was found to shift the overall binding energy of the rest of the cluster by an average of 0.2 – 0.5 eV. Though mild, these shifts are strong enough to account for at least some of the defect peak considered near 284.8-285.4 eV.

Figure 9.

Table 7.

3.2.4 *Summary of peak interpretations and constraints*

From the simulation results reported here, general assignments are proposed for the deconvolution peaks, see Table 8. These interpretations require assessment of treatment temperatures and potential functional group distributions to accurately interpret, as several overlapping features do exist. The FWHM has been set to 1.2 to 2 eV for the C-C peak region based on the results for known compounds discussed previously, and the assumption that binding energy distributions within each peak region will be low. Because of this assumption, a relatively large G:L ratio is allowed for with the bounds set to vary from 0-0.3 based on the pure compound results as well. A larger 1.8 – 2.2 eV FWHM range is given for C:O peaks to allow for broadening due to a distribution of groups. This broadening effect is also associated with increasing Gaussian character and so the range of the G:L ratio here has been reduced to 0 – 0.1.

Table 8.

3.3 *Constrained C1s Deconvolution procedure*

Based on the results of the preliminary fitting given in section 3.1 and the molecular modeling results informing the nature of shifts in C1s peaks shown in section 3.2 a new deconvolution method is proposed for pyrolysis chars. An outline of this procedure is provided in Figure 10. This method employs the full range of C1s curves utilized by Blume et al. [13], as well as the deconvolution peaks from the related O1s spectrum as additional constraints to allow for more consistent assignment of the C-C region as well as defect peaks. For this, the total peak area of each deconvoluted O1s spectrum is used to specify upper and lower constraints for the three oxygenated peaks identified in the C1s spectra as well as their sums.

Figure 10.

The oxygen constraints are estimated based on maximum and minimum distributions for eight potential carbon sites in six oxygenated groups. These sites, highlighted in bold, include: carbon **linked** to a single oxygen, hydroxyl groups (**C-OH**), ether groups (**C-O-C**), and the ether bound carbon in lactone/ester groups (**COOC**); carbons **with** two oxygen bonds, carbonyl groups (**C=O**), and carbon linked to two ether/hydroxyl bonds (**O-C-O**); and carbons **with** three oxygen bonds; carboxyl groups (**COOH**), and the primary carbon in lactone/ester groups (**COOC**). Ether and hydroxyl groups resolve near 286.2 eV and show C:O ratios of 2:1 (maximum) and 1:1 (minimum) respectively, the final distribution of these groups is estimated by the distribution coefficient D_{HE} . Carboxyl and Lactone groups resolve near 289 eV. Carboxyl groups show a C:O ratio of 1:2 while lactone and ester groups result in a 1:1 ratio for the peak at 289 eV and result in a second peak near 286.5 eV, indistinguishable from ether like carbons. The final distribution of carboxyl and lactone groups is given by the distribution coefficient D_{CL} . To estimate the potential contribution of O-C-O to the carbonyl peak region, the probability of 2 C-O bonds forming on the same carbon is estimated. This is done by assuming a random distribution of carbon and oxygen atoms with 3 carbons or oxygens bonded to each carbon. The distribution of O-C-O and C=O groups is uncertain as no distinctive peaks are available from the O1s spectra to guide this deconvolution. To estimate the quantity of carbonyl like groups, the quantity of C=O oxygen associated with the carboxylic/lactone peak from the C1s deconvolution is subtracted from the quantity determined from the O1s C=O peak. The remainder is assumed to be carbonyl carbon. The estimated carbonyl carbon can be subtracted from the C1s C=O peak to give the fraction of O-C-O. These parameters are detailed by equations S2-S12 in the supplemental section S3. Equations S13-S15 detail the estimation of each O1s peak from the C1s deconvolution. Application of this quantification method predicts a D_{HE} value of 0.57, or 4 or 7 oxygen bonds related to ether. This result is highly consistent with the presence of the 2 ether groups and 3 hydroxyl groups within each monomer unit of cellulose.

3.3.1 Application to cellulose char thermoseries

Figure 12A and 12B respectively show the deconvolutions for the C1s and O1s spectra from C600. The defect peak positioned near 284 eV is assigned to both hydrogenated carbons and small rings (C5 or less) within larger aromatic systems. This peak has been found to decrease

consistently with temperature, from 11% to 3.5% as temperature increased from 400 °C to 700 °C. This result suggests that a reduction of total small ring systems occurs with higher treatment temperatures. The fractional distribution of each group obtained from the C1s deconvolution of spectra from cellulose chars are given in Table 9 and show consistent temperature trends. Additional details regarding peak position and peak width are given in Tables S1 and S2 respectively in supplemental section S5.

Figure 11.

The primary C-C peak shows strong development with treatment temperature, and a consistent narrowing of the FWHM as temperature increases from 400 °C to 700 °C, indicating the formation of an increasingly regular aromatic structure. The asymmetry factor has been found to increase with treatment temperature. While an asymmetric C-C peak was not identified for chars produced at or below 500 °C, it quickly develops for materials as treatment temperature is increased above 500 °C. This trend is consistent with the charging effects (or lack of) observed for each sample, and is indicative of the formation of increasing aromatic condensation [31].

Table 9.

The defect peak noted near 285 eV develops rapidly to 27% of the C1s spectrum as treatment temperature increases to 500 °C. This is linked to the formation of relatively large rings (C7+) and may also result from the presence of double bonded oxygen on small ring systems. As temperature increases further, these oxygen groups are reduced and irregular ring systems rearrange to form more stable six carbon rings causing a reduction in this peak to approximately 9% at 700 °C. As with the primary C-C peak, a consistent reduction in peak width is noted as temperature increases, suggestive of an increasingly regular structure.

The peak associated with ether and hydroxyl groups decreases rapidly and consistently with treatment temperature, falling from 66% of peak intensity for cellulose to just 4% for C700. This reduction is associated with a rapid loss of hydroxyl groups as pyrolysis temperature is increased to 400 °C, as demonstrated by the rapid increase in the D_{HE} coefficients in Table 8. This is followed by continued reaction and loss of ether groups. The distribution of hydroxyl groups

begins to increase again at 500 °C and stabilizes near a 1:1 distribution at 600 °C and 700 °C. This result is attributed to the initial chemisorption of oxygen at radical sites immediately following pyrolysis.

The carbonyl peak shows additional signal from carbons bonded to two ether groups. These O-C-O are the primary contributions to this peak for cellulose and C300. The quantity of this contribution is estimated based on the assumption of a randomized distribution of ether/hydroxyl groups, and assumes that the fraction of O-C-O groups is equal to the square of the O-C fraction. This contribution becomes relatively unimportant at treatment temperatures of 400 °C or higher, resulting in contributions of 2.3% or less. The results indicate no significant quantity of carbonyl groups at any temperature, suggesting that these groups tend to form most stably instead as either carboxyl groups or lactone/esters.

Carboxyl/Lactone groups do not form significantly until treatment temperatures of 400 °C or higher are reached. As temperature is increased above 500 °C minor decreases in total contribution are noted. The contribution of lactone groups is highest at 400 °C, however rapidly gives way to carboxyl groups as temperature increases, see the D_{CL} ratio in Table 8. This result is in contrast to the typical stability observed by temperature programmed desorption, which shows carboxyl groups unstable at temperatures above 300 °C, where lactones show stability between 500 °C and 700 °C. The observed increase in carboxyl fractions, as with the increase in hydroxyl content discussed previously, is linked to chemisorption of oxygen at radical sites upon first exposure to air. These strong shifts are consistent with, and required, to explain the large increase in surface oxygen content compared to bulk shown in Figure 2B for chars produced at temperatures of 500 °C and higher.

Overall, the results of deconvolution using this new method are highly internally consistent and was capable of reproducing each of the spectra accurately, without deviation from the stated protocol. A visual comparison of the C:O ratios calculated by this method and for each of original deconvolution and oxygen quantification methods discussed in section 3.1 is provided in the supplemental section S6, Figure S6. These results provide functional group distributions for a range of chars produced between 300 °C and 700 °C that are consistent with expected behaviors.

The current set up was however unable to provide conclusive structural information from the C-C region. Analysis by equipment with increased resolution, such as that afforded by synchrotron x-ray sources, may be able to more conclusively resolve features within this region.

4. Conclusions

A new curve fitting procedure has been proposed for amorphous, oxygen containing carbons that utilizes deconvolution of the O1s peak as a boundary parameters for the interpretation of the C1s peak. The deconvolution of C1s was modified by taking into account the result of molecular modeling studies. Molecular simulations provided insight into the origin of each peak. These results indicate that the peak near 285 eV results from a variety of defects including weak to moderate long range shifts of C-C/C-H binding energies in oxygen containing molecules, aromatic rings larger than benzene, and dehydrogenated sp^3 carbons. The defect peak that is present at lower binding energies has been linked to aromatic regions containing small rings such as cyclopentane. Using this method, C1s deconvolutions were obtained that provide an arcuate fit to the complementary O1s data. A generalized oxygen quantification scheme is given that utilizes two distribution coefficients D_{HE} and D_{CL} for the interpretation of oxidation peaks. This method allowed for reasonable interpretation of the C-C peak asymmetry as well as secondary defect peaks.

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Table 1. Summary of binding energies used for the deconvolution of C1s and O1s spectra (eV)

Method	Peak I	Peak II	Peak III	Peak IV	Peak V	Peak VI	Peak VII
Carbon C1s	C-C low	C-C primary	C-C high	C-O	C=O	COO	Pi-Pi*
1	N/A	284.3 - 284.5	N/A	PII + 1.5	PII + 3.0	PII + 4.5	291 - 293
2	N/A	284.3 - 284.5	PII + 0.4 - 0.8	PII + 1.8	PII + 3.0	PII + 4.5	291 - 293
3	PII - 0.4	284.3 - 284.5	PII + 0.4 - 0.8	PII + 1.8	PII + 3.0	PII + 4.5	291 - 293
Oxygen O1s	C=O	C-O aliphatic	C-O aromatic	O ₂ /H ₂ O			
1	531.2-531.6	532.5-532.9	533.0-533.4	534.8-535.2			
PII: Represents the actual binding energy (eV) determined during deconvolution for peak 2, the primary C-C peak							
The same peak positions are used for both Sm and A deconvolution schemes							

Table 2. Bulk properties associated with cellulose and cellulose chars

	Avicel	c300	c400	c500	c600	c700
Moisture (wt %)	3.6 (0.12)**	2.7 (0.15)	2.6 (0.09)	1.7(0.30)	1.0(0.31)	1.0 (0.21)
SA (CO ₂) (m ² /g)	N/A	21	264	383	485	576
C (wt %)	42.8 (0.14)	44.5 (0.05)	74.5 (0.28)	81.5 (0.17)	87.8 (0.37)	90.2 (0.11)
H (wt %)	6.4 (0.03)	6.1 (0.05)	3.9 (0.02)	3.5 (0.06)	2.7 (0.02)	2.0 (0.02)
N (wt %)	0.06 (0.01)	0.03 (0.01)	0.08 (0.01)	0.11 (0.02)	0.24 (0.01)	0.36 (0.01)
O* (wt %)	50.8 (0.01)	49.4 (0.09)	21.5 (0.28)	15 (0.13)	9.3 (0.4)	7.5 (0.12)
Ash (wt. %)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
C:O (Molar, daf)	1.1	1.2	4.6	7.3	12.6	16.0

*Calculated by difference

** Standard Deviation

daf: dry ash free basis

Table 3. Fine Scan C1s and O1s peak parameters with O1s deconvolution

Fine scan						
Total peak areas	Cellulose	c300	c400	c500	c600	c700
C1s (counts/sec)	12070	11976	12424	13728	13636	18284
O1s (counts/sec)	22048	17952	6205	6209	2763	3889
C:O*	1.26	1.54	4.63	5.11	11.40	10.86
O1s Deconvolution (atomic %)						
O-C (aromatic)	2	3.5	16.6	41.5	51.1	51.6
O-C (aliphatic)	94.3	92.1	55.9	24.9	8.1	5.5
C=O	1.5	2.1	17.9	29.3	38.2	34.4
O ₂ /H ₂ O	2.3	2.3	9.4	4.4	1.6	7.5
*results from comparison of C1s and O1s fine scans						

Table 4. Application of symmetric deconvolution methods utilized within the literature and calculated C:O ratios with deviation from C1s/O1s fine scan ratio given in parentheses. Negative values for the deviation from the C1s:O1s ratio indicates an overestimation of oxygen

XPS Deconvolution Peaks (% of total peak area)									Calculated C:O distribution (deviation from C1s: O1s)		
Sample	Method	C-C low	C-C	C-C high	C-O	C=O	COO	pi-pi*	C:O (a)	C:O (b)	C:O (c)
Cellulose	Sm1		17.8		50.4	28.5	3.3		1.16 (-19.3%)	1.37 (-5.4%)	1.70 (17.5%)
C300			31.4		48.8	16.1	3.7		1.38 (-20.9%)	1.66 (-4.9%)	2.17 (24%)
C400			56.5		28.9	7.7	4.4	2.5	2.14 (-61%)	2.55 (-53.6%)	3.38 (-38.4%)
C500			69.7		18.9	4.6	4.7	2.2	2.97 (-48.7%)	3.47 (-40.1%)	4.64 (-20%)
C600			77.3		12.8	4.3	4.1	1.5	3.89 (-59.5%)	4.46 (-53.6%)	5.85 (-39.2%)
C700			71.5		13.8	5.9	3.6	5.1	3.52 (-72.5%)	4.04 (-68.5%)	5.2 (-59.4%)
Cellulose	Sm2		12.9	5.5	50.4	27.6	3.6		1.17 (-19%)	1.37 (-4.9%)	1.71 (18.5%)
C300			25.6	9.6	41.8	18.7	4.3		1.44 (-17.2%)	1.70 (-2.5%)	2.17 (24.1%)
C400			52.2	12.2	19.9	8.0	5.1	2.6	2.55 (-53.5%)	2.94 (-46.5%)	3.80 (-30.8%)
C500			60.2	18.3	9.8	4.7	4.7	2.3	4.08 (-29.7%)	4.54 (-21.7%)	5.85 (0.7%)
C600			48.7	29.3	12.2	3.5	4.6	1.7	3.94 (-59%)	4.49 (-53.3%)	5.95 (-38.2%)
C700			67.7	8.3	10.0	5.1	3.9	5.1	4.15 (-67.6%)	4.66 (-63.6%)	5.96 (-53.5%)
Cellulose	Sm3	4.7	7.0	6.9	50.1	27.0	4.2		1.16 (-19.4%)	1.36 (-5.6%)	1.71 (17.9%)
C300		4.2	21.2	9.1	42.2	16.8	3.9	2.5	1.45 (-16.6%)	1.73 (-0.9%)	2.22 (27.3%)
C400		1.6	50.2	13.0	20.5	7.9	4.3	2.5	2.63 (-52.1%)	3.05 (-44.5%)	3.96 (-28%)
C500		7.6	60.6	10.4	10.1	4.8	4.3	2.2	4.14 (-28.6%)	4.64 (-20%)	5.98 (2.9%)
C600		2.9	62.4	14.9	10.5	3.4	4.4	1.5	4.33 (-55%)	4.89 (-49.1%)	6.45 (-33%)
C700		10.1	56.6	9.5	10.1	4.8	3.7	5.0	4.22 (-67%)	4.76 (-62.8%)	6.11 (-52.3%)

Table 5. Application of asymmetric deconvolution methods utilized within the literature and calculated C:O ratios with deviation from C1s/O1s fine scan ratio given in parentheses. Negative values for the deviation from the C1s:O1s ratio indicates an overestimation of oxygen

Sample	Method	XPS Deconvolution Peaks (% of total peak area)							Calculated C:O distribution (deviation from C1s: O1s)		
		C-C low	C-C (asym)	C-C high	C-O	C=O	COO	pi-pi*	C:O (a)	C:O (b)	C:O (c)
C500	ASm1		81.2 (0.04)		12.2	2.4	2.8	1.4	3.58 (-38.3%)	4.22 (-27.3%)	5.69 (-1.9%)
C600			91.6 (0.09)		5.3	0.1	2.0	1.0	7.58 (-21.3%)	8.82 (-8.4%)	12.38 (28.4%)
C700			90.5 (0.14)		3.9	0.0	1.9	3.7	13.1 (2%)	15.03 (17%)	21.07 (64.1%)
C500	ASm2		64.8 (0.04)	20.1	7.7	2.8	3.1	1.6	4.34 (-25.2%)	4.9 (-15.4%)	6.42 (10.5%)
C600			88.7 (0.09)	4.1	3.9	0.1	2.2	1.0	8.44 (-12.3%)	9.56 (-0.8%)	13.28 (37.8%)
C700			87.5 (0.14)	2.4	3.7	0.2	2.4	3.8	11.59 (-9.7%)	12.98 (1.1%)	17.91 (39.4%)
C500	ASm3	5.6	74.7 (0.05)	6.8	6.2	2.7	2.6	1.5	5.15 (-11.3%)	5.79 (-0.2%)	7.5 (29%)
C600		5.0	83.7 (0.11)	4.6	3.4	0.0	2.2	1.0	9.04 (-6.1%)	10.14 (5.2%)	14.09 (46.2%)
C700		6.3	76.8 (0.15)	4.3	4.5	1.1	2.2	4.8	10.03 (-21.8%)	11.32 (-11.8%)	15.08 (17.4%)

Table 6. Fitting parameters used for the analysis of model compounds with a GLsum line shape

Sample	Simulation fit parameters		Experimental fit parameters	
	FWHM (eV)	GL	FWHM (eV)	GL
Pyrene	1.72	0.59	1.78	0.21
Cellobiose	1.40	0.71	1.59	0.06
PTCDA	1.55	0.36	1.51 (1.53)*	0.29 (0.37)*
Average	1.56	0.55	1.63	0.19

* values in parentheses are for a necessary secondary peak and have not been included in the average

Table 7. Calculated binding energies for various oxygenated functional groups positioned on assorted carbons. Lactone and carboxylic group (1) refers to the carbon connected to both oxygens. Lactone (2) refers to the ether bonded carbon, while carboxyl (2) refers to the carbon adjacent to the carboxyl group

Model Compound	Binding energies for carbons associated with listed functional group (eV)					
	Hydroxyl	Carbonyl	Lactone (1)	Lactone (2)	Carboxyl (1)	Carboxyl (2)
Coronene	2.04	2.57	4.12	2.39	4.18	0.91
5-8-5 defect pentane ring	1.9	2.54	4.16	2.28	4.06	0.63
Alkane side chain	1.67	2.86	3.99	1.83	4.20	0.97

Table 8. Peak assignments and parameters for the interpretation of O1s and C1s spectra of chars

Peak	Assignment	BE (eV)	FWHM (eV)	G:L (0-1)
O-C(1)	Ether and hydroxyl groups bonded to aromatics	533.0-533.4	1.8-2.2	0-0.1
O-C(2)	Ether and hydroxyl groups bonded to aliphatics & carbonyl shake-up	532.5-532.9	1.8-2.2	0-0.1
O=C	In carbonyl, lactone and carboxylic groups	531.2-531.6	1.8-2.2	0-0.1
(H₂O)	Absorbed water/oxygen, sub monolayer	534.8535.2	1.8-2.2	0-0.1
C-C low	Cyclopentane ring atoms within cluster	283.4-284	1.2-2	0-0.3
C-C Primary	Primary C-C/C-H peak	284.2-284.6	1.2-2	0-0.3
C-C High	C in cycloheptane or larger rings within clusters, C in small clusters containing C=O bonds, sp ³ bonded carbons	284.8-285.4	1.2-2	0-0.3
C-O	Ether and hydroxyl bonded C, C associated with ether bond in lactone/esters	285.9-286.6	1.8-2.2	0-0.1
C=O	Carbonyl groups and carbons attached to two ether/hydroxyl groups	286.7-287.5	1.8-2.2	0-0.1
COO	Carboxyl, lactone and ester groups	288.3-288.9	1.8-2.2	0-0.1
Pi-Pi*	HOMO-LUMO transition for primary C-C peak	291-292	2-3	0-0.1

Table 9. Peak distribution and C:O ratios determined using proposed deconvolution scheme

Deconvolution peaks	Cellulose	C300	C400	C500	C600	C700
C-C low (%)	4.9	3.5	11.0	5.7	5.0	3.5
C-C Primary (%)	6.0	14.0	35.8	52.0	67.4	75.4
TS (asym. factor)	0.00	0.00	0.00	0.00	0.11	0.16
C-C High (%)	0.8	4.9	26.9	16.0	14.3	9.2
C-O (%)	66.4	59.8	18.1	15.8	5.3	4.3
O-C-O/C=O (%)	20.4	15.4	0.3	2.3	0.3	0.1
O-C-O estimated	20.4	15.4	0.3	0.6	0.2	0.1
COO (%)	0.6	2.4	4.6	4.4	3.4	3.4
Pi-Pi* (%)	1.1	0.0	3.3	3.9	4.4	4.1
D _{HE}	0.57	0.70	0.64	0.84	0.91	0.52
D _{CL}	0.55	0.64	0.64	0.58	0.66	0.42
C:O (C1s)	1.26	1.54	4.63	5.11	11.40	10.86
C:O error (%)	0.1	0.3	1.0	0.2	-0.7	-2.3

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Figure 1. FT-IR transmittance for a thermoseries of cellulose chars produced at temperatures from 300 °C to 700 °C. Dash lines indicate important regions of the various spectra.

Figure 2. (A) Comparison of the wide-scan XPS results for Avicel cellulose and the resultant chars (B) Parity plot of the atomic bulk C:O ratio from elemental analysis with the C:O ratios obtained by XPS using by high resolution C1s and O1s scans.

Figure 3. Development of (A) C1s and (B) O1s XPS spectra with increasing pyrolysis temperature.

Figure 4. Experimental and theoretical binding energy overlays for (A) Pyrene C1s (B) Cellobiose C1s (C) PTCDA C1s (D) cellobiose O1s.

Figure 5. Reference spectra for Coronene, circumpyrene, and circumcoronene.

Figure 6. Reference sp^3 containing carbon structures (A) single pentane chain linked to coronene (B) two pentane chains linked to coronene (C) single buta-di-ene chain linked to coronene (D) two buta-di-ene chains linked to coronene.

Figure 7. Effect of (A) cyclopentane defect and (B) cycloheptane defect on core binding energies. Values A-C give the respective shift of the calculated binding energies for each unique position relative to the average binding energy calculated for coronene (284.63 eV).

Figure 8. (A) Effect of 5-8-5 Stone Wales defect on core binding energies in circumpyrene parent system, values A-J give respective calculated binding energy shifts relative to the average shift of coronene, 284.63 eV, bold denotes significant shifts, values in red are negative shifts (B) Simulated C1s plots for defects in (black lines) and unmodified (dashed red lines) coronene, circumpyrene and circumcoronene parent systems with FWHM of 1.56 and G:L = 0.55 for each atom (C) Spectra from B with FWHM reduced to 0.5. Individual binding energies for coronene and circumcoronene are given in supplemental S5.

Figure 9. Binding energy shifts in adjacent, as well as second nearest neighbors associated with (A) hydroxyl (B) carbonyl (C) carboxylic and (D) lactone groups. Group A represents the average reference shift for C-H atoms, while B is the average shift of C-C in each compound.

Figure 10. Basic algorithm for the combined O1s/C1s deconvolution of XPS spectra of chars and amorphous carbons.

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Figure 5. Reference spectra for Coronene (green), circumpyrene (black), and circumcoronene (red).

Figure 6. Reference sp^3 containing carbon structures (A) single pentane chain linked to coronene (B) two pentane chains linked to coronene (C) single buta-di-ene chain linked to coronene (D) two buta-di-ene chains linked to coronene. The black line in each Figure denotes the modified coronene structure, while the red dashed line gives the parent coronene. Individual binding energies for each C atom are given in supplemental section S4 (Figure S4).

Figure 7. Effect of (A) cyclopentane defect and (B) cycloheptane defect on core binding energies. Values A-C give the respective shift of the calculated binding energies for each unique position relative to the average binding energy calculated for coronene (284.63 eV). The black line denotes the calculated spectrum for the cyclopentane centered ring system shown, while the red dashed line is that of coronene.

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Graphical Abstract: