Appendices A through E of

Schenkel and Shenxue revisited
- implications on char production and biochar properties

Version 1 (June 2010) issued at the
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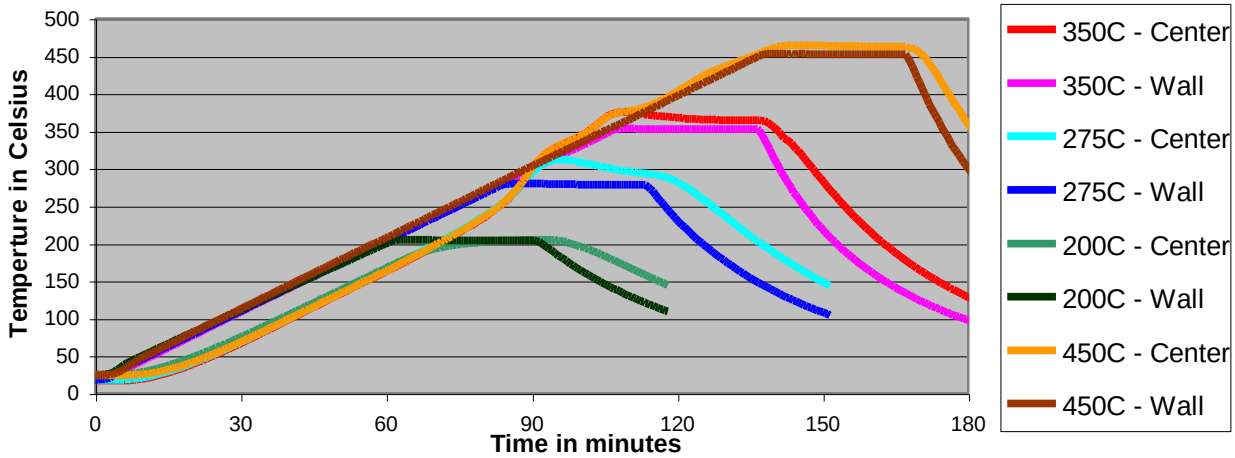
Appendix A: Experimental procedure for carbonizing laboratory chars

The reactors used to prepare the homologous series of laboratory chars are detailed in US Patent #6,982,068 and US Patent #7,199,069 (see http://patft.uspto.gov/ and input patent number to see text and associated images). The key features of the laboratory reactors are the uniform heating of the outer reactor surface with temperature measurement and control of that surface and independent measurement of temperatures at the centerline of the reactor.

The characteristic temperature assigned to any given carbonization was the average of the controlled wall temperature and the peak centerline temperature, which is the correct volume averaged temperature for the limiting case of uniform heating or cooling within the biomass due to chemical reactions (see Section 9.2 of Bird, Stewart and Lightfoot, *Transport Phenomena*, pp. 267-270.)

The chars produced over the range of 200C to 450C were produced directly from dried hardwood pellets in a 1.5 inch NPT Schedule 40 black iron reactor, constructed from a 9 inch pipe nipple and reducing end caps. The reactor had a screen at the bottom to retain the wood pellets. The external wall temperature was measured by a contact thermocouple located on the wall at the midpoint of the reactor. The temperature signal controlled the heat input via a Love Controls Model 16122-992 SELF TUNE plus ¼ DIN temperature controller. The reactor center and wall temperatures were data logged and representative temperature ramps are shown in Figure A-1.

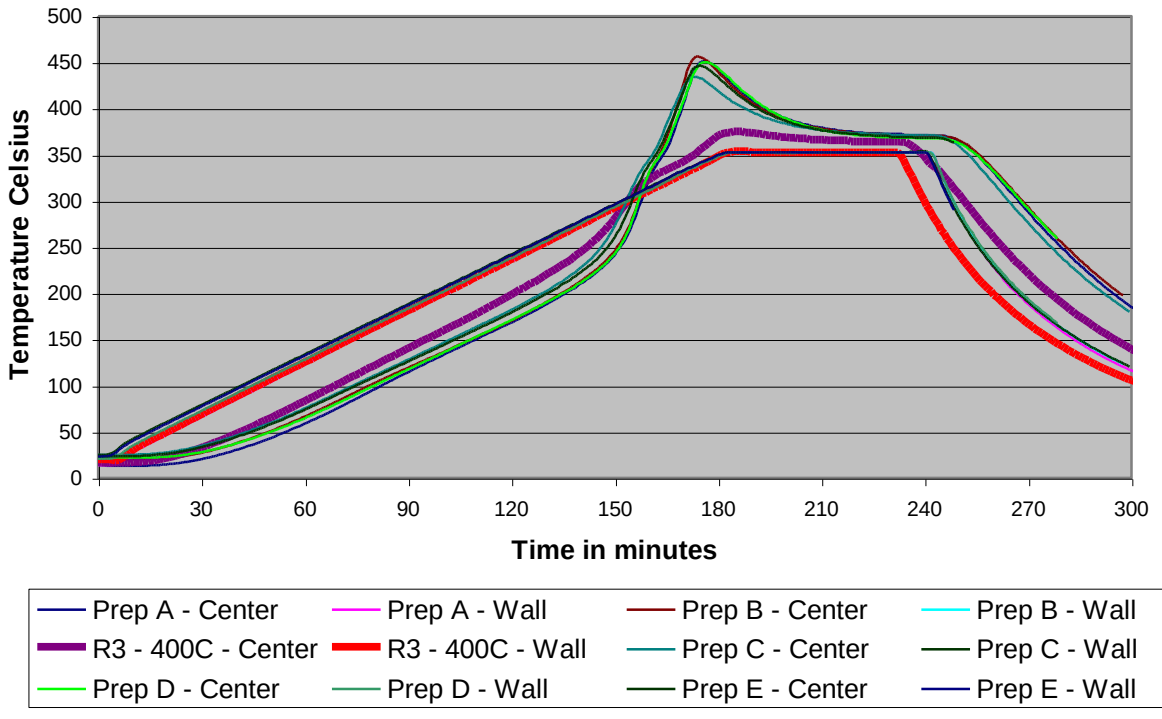
Figure A-1: R-3 Temperature Ramp Data



The chars for the temperature range 500C to 900C were prepared in two steps; where a large amount of char was prepared at a wall temperature of 350C in a larger reactor (Reactor R-1 of the patents, 3 inch NPT pipe). Figure A-2 shows the temperature data for five prep runs, each of which yielded about 175 grams of char at a 35 weight percent yield from dried hardwood pellets. The prep chars were blended and used to prepared the higher temperature chars (500C to 900C). The prep char was carbonized a second time in a 2.375 inch OD thin wall stainless steel reactor capable of higher temperatures by stabilizing the char at 300C in a nitrogen purge (1 bed volume per minute), then ramping at 200 degrees Centigrade per hour to the setpoint temperature and holding for one half hour at the setpoint. The temperature ramp was controlled by a thermocouple located in the wall of the reactor, with the temperature at the middle of the char volume also data-logged.

As can be seen in Figure A-1, there is an exotherm, attributed to the carbonization of the cellulose in the biomass, which initiates around 250C. This exotherm is more pronounced in data shown in Figure A-2, which includes the temperature data from the smaller diameter reactor R-3 at the 350C temperature setpoint. As can be seen, the larger "Prep" reactor has a greater centerline temperature exotherm than the smaller diameter reactor R-3, attributed to the insulting properties of the formed char. In all cases, the HTT experienced by all chars was below the final temperature range of the higher temperature chars, subsequently prepared in the thin wall stainless steel reactor.

Figure A-2: Char preparation runs



Appendix B: GACS assay for measuring Adsorption Capacity

Adsorption capacity is measured by "challenging" the char with a known substance, usually an organic vapor, and measuring the extent of uptake via adsorption of the challenge gas under controlled conditions. The test is not a routine analytical method and the closest historic analytical method is the BET surface area assay. Unfortunately, the BET method is performed under conditions far removed from what occurs in the soil, with the BET method measuring the adsorption of nitrogen vapor in a partial vacuum at liquid nitrogen temperatures (minus 196 degrees Celsius). As such, BET measurements may not accurately predict, or even differentiate, the adsorption capacity of chars in typical biochar applications.

The adsorption capacity test used for this paper is known as "GACS" or Gravimetric Adsorption Capacity Scan. The GACS method is similar to another esoteric method known as the GRPD test for activated carbon, recently renamed GAED, which was developed, in turn, from a test known as TACTIC (developed by Calgon Carbon Corporation to study activated carbons.) The GACS assay is performed on a custom-built modified TGA (Thermo-Gravimetric Analyzer) and measures all the adsorption behavior of chars and activated carbons over a wide range of adsorption conditions. For the purposes of comparing chars, it is sufficient to subject all chars to the same conditions and measure the extent of adsorption, with more adsorption being better and the adsorption capacity being quantified as proportional to the weight gain at a specified temperature..

For this paper, the standard comparison conditions were the weight percent uptake of R134a (1,1,1,2 tetra-fluoro-ethane – the refrigerant used in automobile air conditioners) by a dried sample of char at 100 degrees Celsius. GACS measurements may become a useful standard test for biochar classification, but currently there are fewer than ten such instruments in the world, so it does lack facile accessibility. The actual instrument used by the corresponding author is shown in Figure B-1.

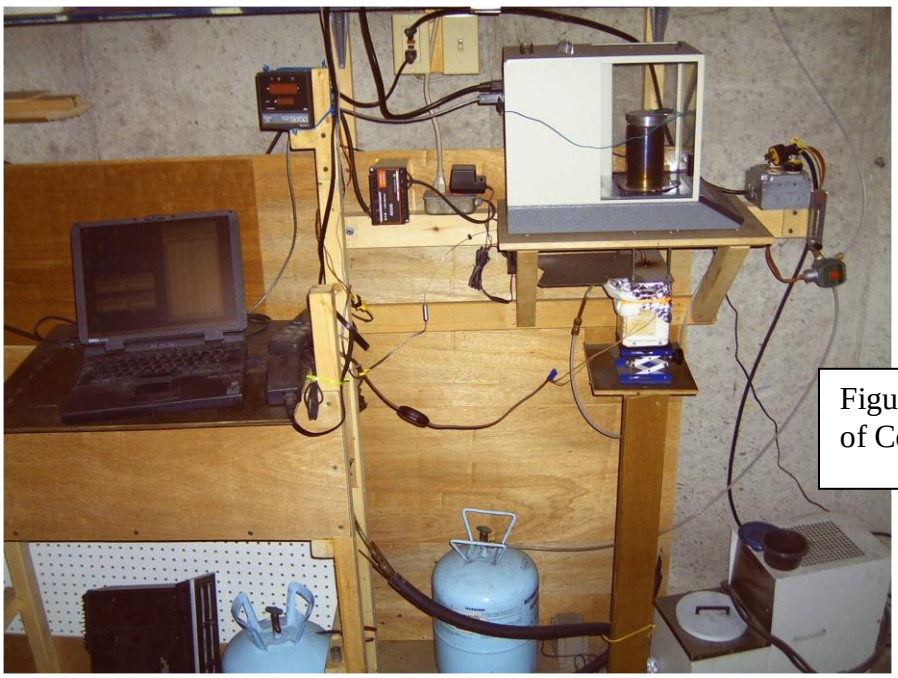


Figure B-1: GACS Instrument of Corresponding Author

The GACS assay measures the adsorption of the challenge gas over a wide range of conditions and generates a significant amount of information about a single char sample in less than 2 hours. The analytical procedure of the GACS assay is as follows: The sample wire basket suspended below an analytical balance in a heated purged chamber, with a thermocouple located just above the sample inside the wire basket.. The empty wire basket is heated in a dry nitrogen purge and the analytical balance tared at 100C. An approximately 1.5 cubic centimeter sample of ground char is placed in a wire basket. The sample is heated to 300C under nitrogen purge, during which the sample is "conditioned" by the removal of any adsorbed moisture and low boiling volatiles. The sample basket and heated purged chamber is shown in Figure B-2.

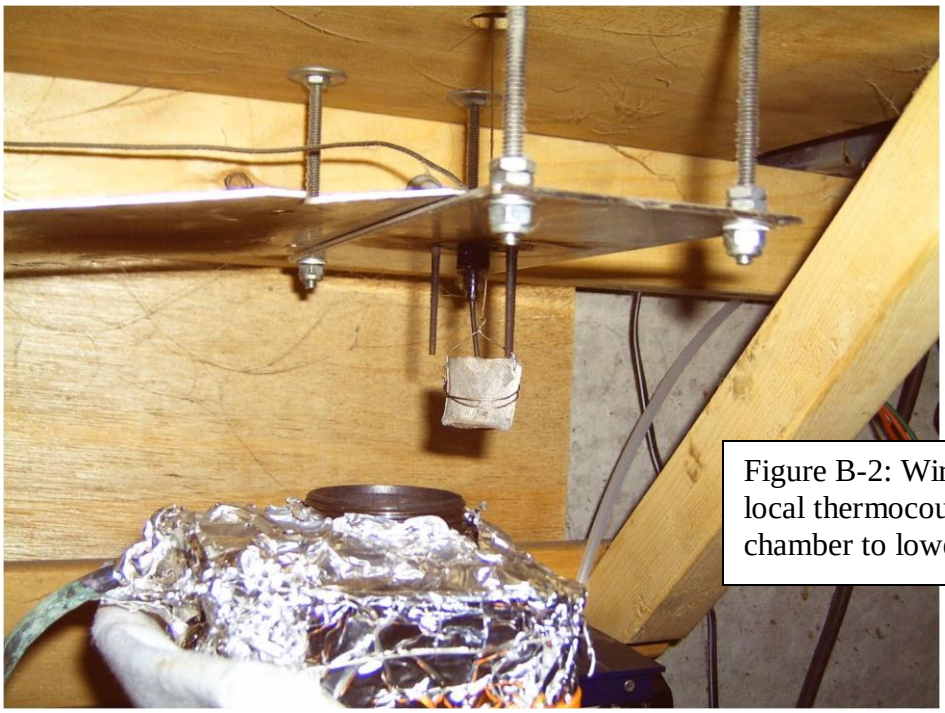


Figure B-2: Wire sample basket with local thermocouple, heated purged chamber to lower left of wire basket.

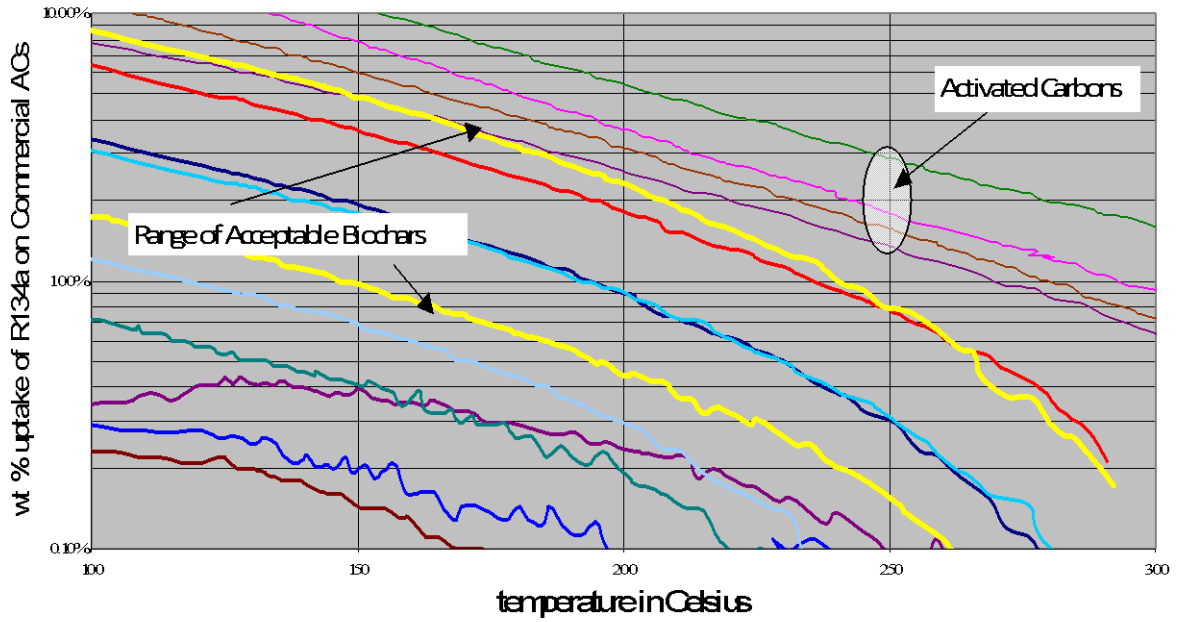
At 300C, the heating supply is turned off and the purge gas surrounding the sample is changed to pure R134a, introduced at the bottom and out of the top of the chamber. The sample and surrounding purged chamber are allowed to cool by passive heat loss to the ambient from 300C to 100C, with the sample temperature and weight being data-logged every thirty seconds.

The complete data set consists of the weight loss data during the heating of the sample in nitrogen from 100C to 300C and the weight gain data as the sample cools in R134a from 300C to 100C. The adsorption data is calculated as the percent weight gain of R134a per minimum weight of the char sample over the entire temperature history.

Figure B-3 shows several sets of GACS data collected for a wide variety of chars and a few activated carbons. The activated carbons are optimized for adsorption and demonstrate higher adsorption capacity across the entire range of temperatures. The two yellow curves shown on Figure B-3 represent one potential range of acceptable biochars. The yellow curves define a relatively wide bracket, where the best biochars have four times the adsorption capacity of the poorest adsorbing. However, it is certainly possible for chars to be below the range of acceptable

biochars, as represented by the curves on the lower left area of Figure B-3. These low adsorbing chars are generally not intentionally manufactured as biochars, but rather are either very dense cooking charcoals, with any adsorption capacity clogged with condensed tars, or byproduct chars from either gasifiers or fast pyrolysis processes.

Figure B-3: Collection of GACS data sets for Chars and Activated Carbons



Other options for measuring adsorption capacity: Adsorption capacity can also be measured in biochars using an analytical procedure known as ASTM D5742: Standard Test Method for Determination of the Butane Activity of Activated Carbon. ASTM D5742 basically measures the weight gain when adsorbing pure butane at 25 Celsius, starting with dried activated carbon. In this test, the biochar is substituted for the activated carbon after drying to 200C. This test has the advantage that many analytical labs can perform the test and furthermore, butane has significantly less greenhouse warming impact than R-134a in the upper atmosphere. The drawback is that "Butane Activity" is much harder to measure in biochar, due to the lower molecular weight of butane as compared to R-134a, resulting in less measurable weight gain for a given extent of adsorption by the char.

Other challenge gases may be used, including cooking propane and even the gas used to refill butane lighters, which is actually isobutane. All these gases are lighter and create less weight gain in a char sample than R134a. However, by calibrating the test to a sample of activated carbon (available at any store selling home aquarium supplies), a rough yardstick for adsorption capacity can be created. Measure the response of the activated carbon and call that 100%. Good biochars will have between 20% and 40% of the weight gain of activated carbon. If the biochar has less than 10% of the weight gain of dried activated carbon, then the adsorption capacity is low; and any soil to which that biochar is added will gain little of the benefits attributed to the char's adsorption capacity.

Appendix C: Adsorption Theory in Carbonaceous Materials

Adsorption is a phenomenon where molecules, known as the adsorbate, are transferred from a bulk fluid phase, either gas or liquid, and align with a solid surface of the adsorbent. The effect of adsorption is to move the molecules being adsorbed from the higher entropy environment of either a liquid or gas phase, with the decrease in entropy being overcome by the energy (also known as heat) of adsorption. The thermodynamic of adsorption is depicted in Figure C-1.

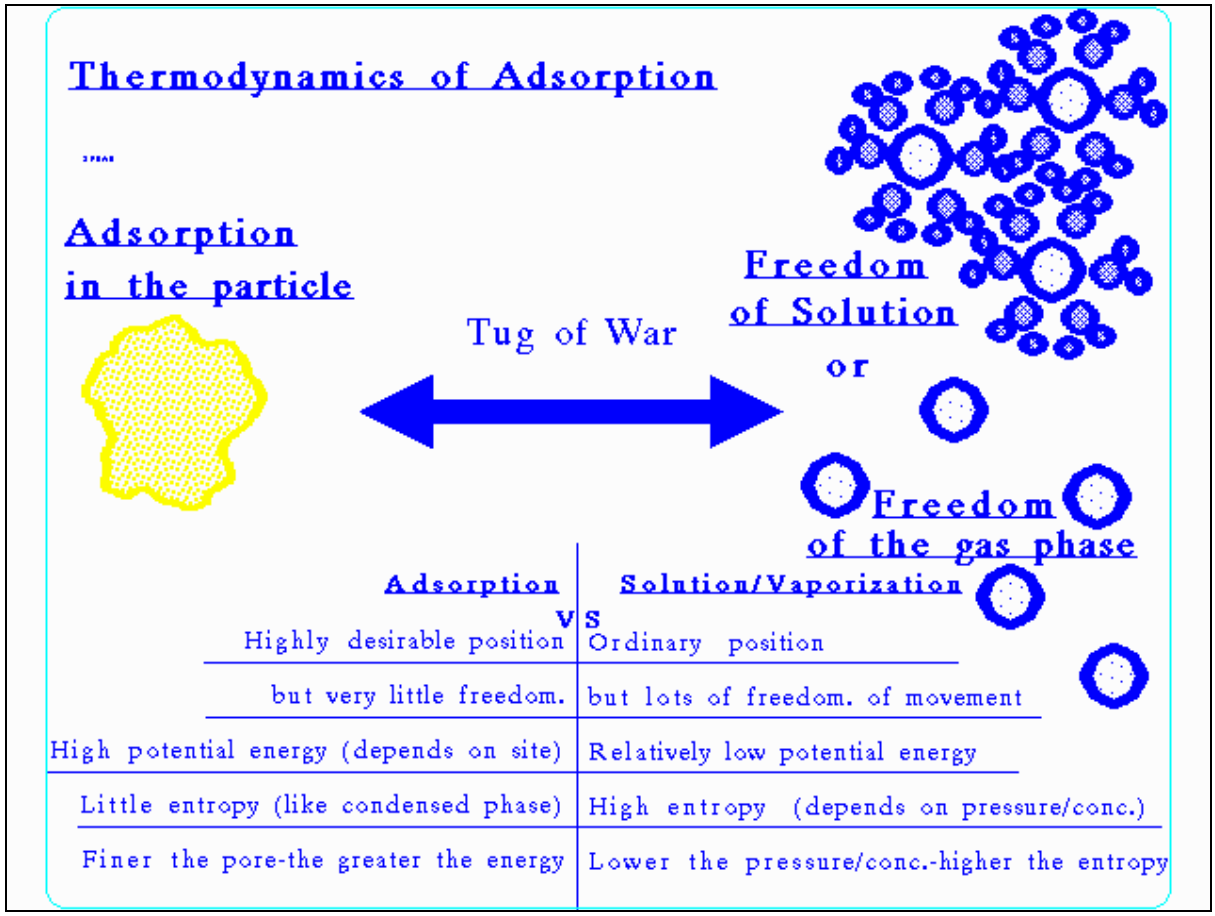


Figure C-1: Thermodynamics of Adsorption: Heat of Adsorption vs. Entropy of Fluid Phase

Adsorption is one of the fundamental forces of nature, like gravity and magnetism. Adsorption is due to a very short ranged molecular interaction known as "London Dispersion Forces", resulting from intermolecular induced dipole moments. While adsorption is responsible for some very commonplace phenomena, such as gases condensing into liquids, explaining it can be about as nasty as Chemistry gets. For the purist, the web will generally satisfy one's curiosity in short order (start at http://en.wikipedia.org/wiki/London_dispersion_force), or, for the less masochistic, a brief overview is provided in Figure C-2.

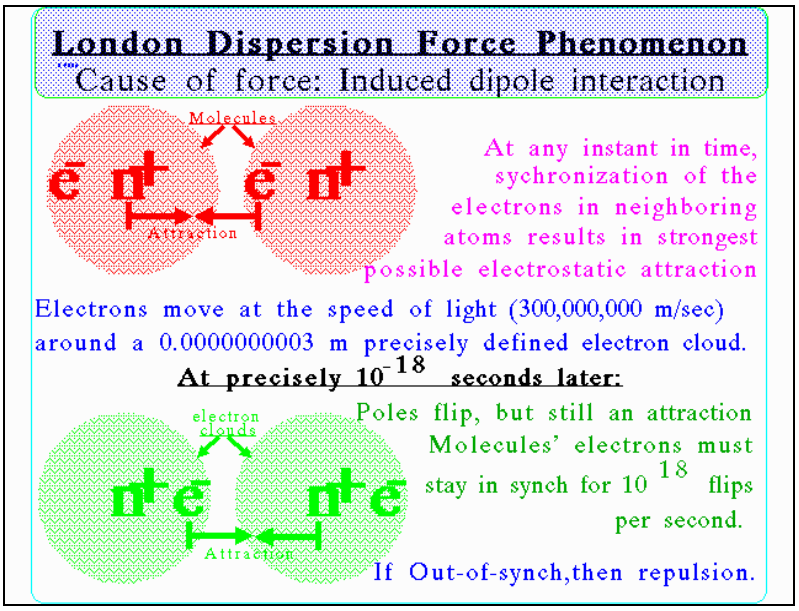


Figure C-2: London Dispersion Forces resulting from attractive intermolecular induced dipoles

For the situation of adsorption on the internal surfaces of the carbonaceous materials, including activated carbon and biochars, one source of dipoles is the surface of the adsorption site. The other source of dipoles is the adsorbate molecule. The adsorption force is additive, and consists of the sum of all the possible dipole-dipole interactions, as depicted in Figure C-3.

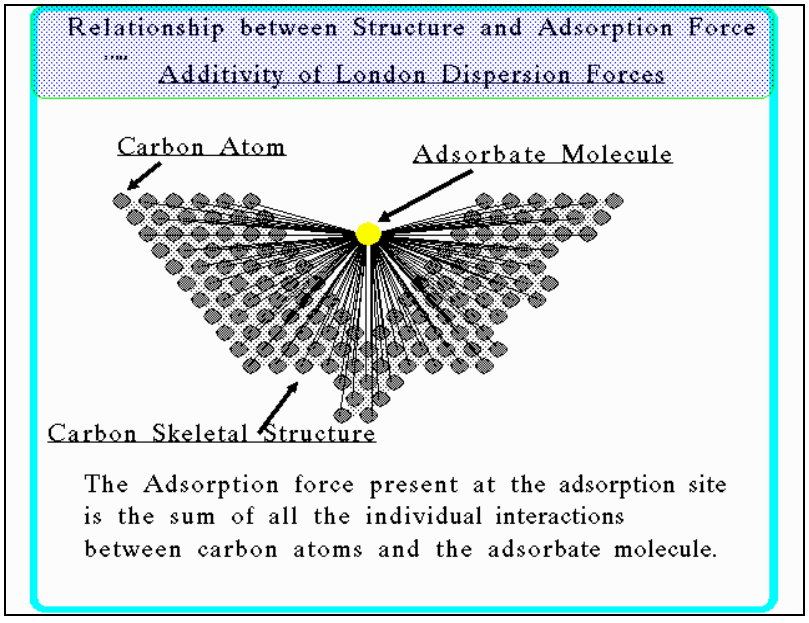


Figure C-3: Adsorption Force is the sum of all the attractive forces at the adsorption site

The magnitude of the individual London Dispersion Force between the adsorbate and the surface carbon atoms of the adsorption site is shown in Figure C-4.

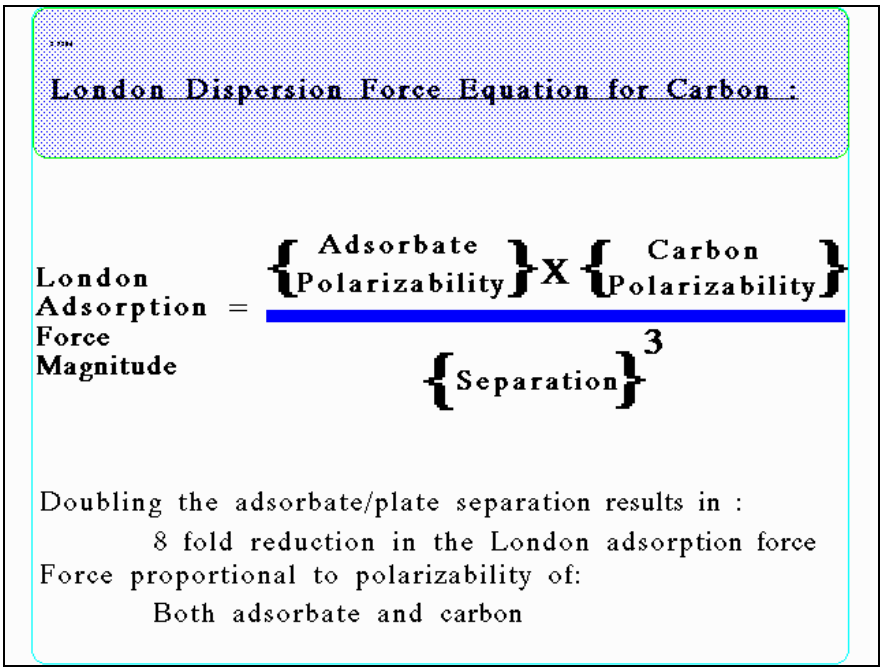


Figure C-4: London Dispersion Forces are proportional to the product of Polarizibilities

Figure C-4 introduces a new property of molecules and chemical bonds known as polarizibility. It is basically the ease by which a chemical bond or the electron cloud of free electrons around an individual atomic nucleus can be distorted by an external electromagnetic field, which results in the individual electrons participating in dipole-dipole interactions. Additional characteristics of "Polarizability" are shown in Figure C-5.

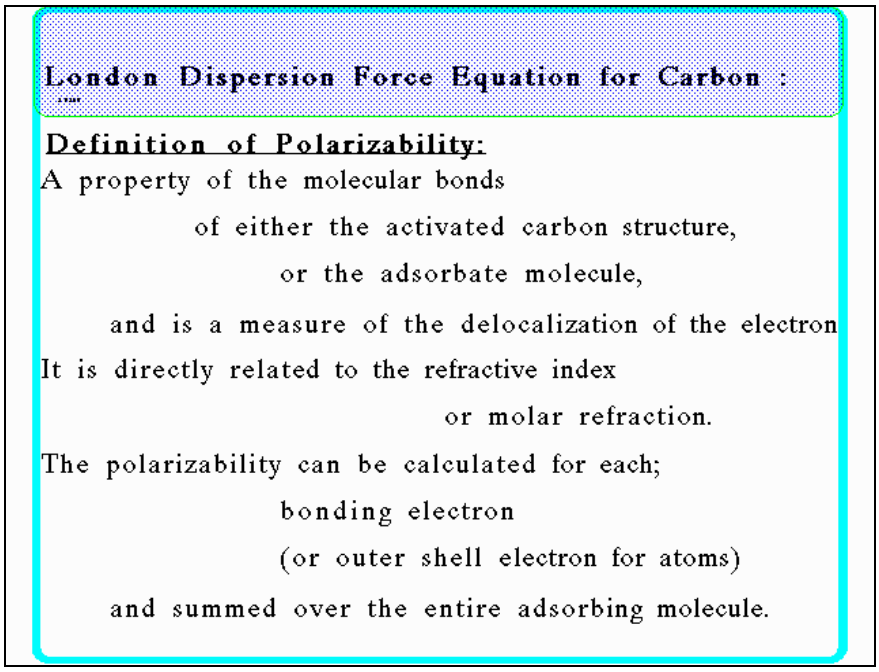


Figure C-5: Characteristics of "Polarizability" for free electrons and covalent bonds

The key to adsorption in chars, and the importance of graphene sheets and graphitic domains, lies in the polarizibility of the delocalized conjugated pi electrons in the graphene structure. Organic sigma bonds are barely polarizable, and even individual pi bonds, such as with ethylene and diatomic gases, participate in adsorptive attractions to a limited extent. The most significant sources of polarizable bonds in organic molecules are individual aromatic rings, such as toluene and phenolics, and larger pi electron "surfaces" found in graphene sheets and on the surfaces of multiple layer graphitic domains.

Since adsorption forces are additive for all the possible adsorbate-adsorbent interactions, higher adsorption forces can be created by combining the effects of multiple surfaces on an individual adsorbate, as shown in Figure C-6.

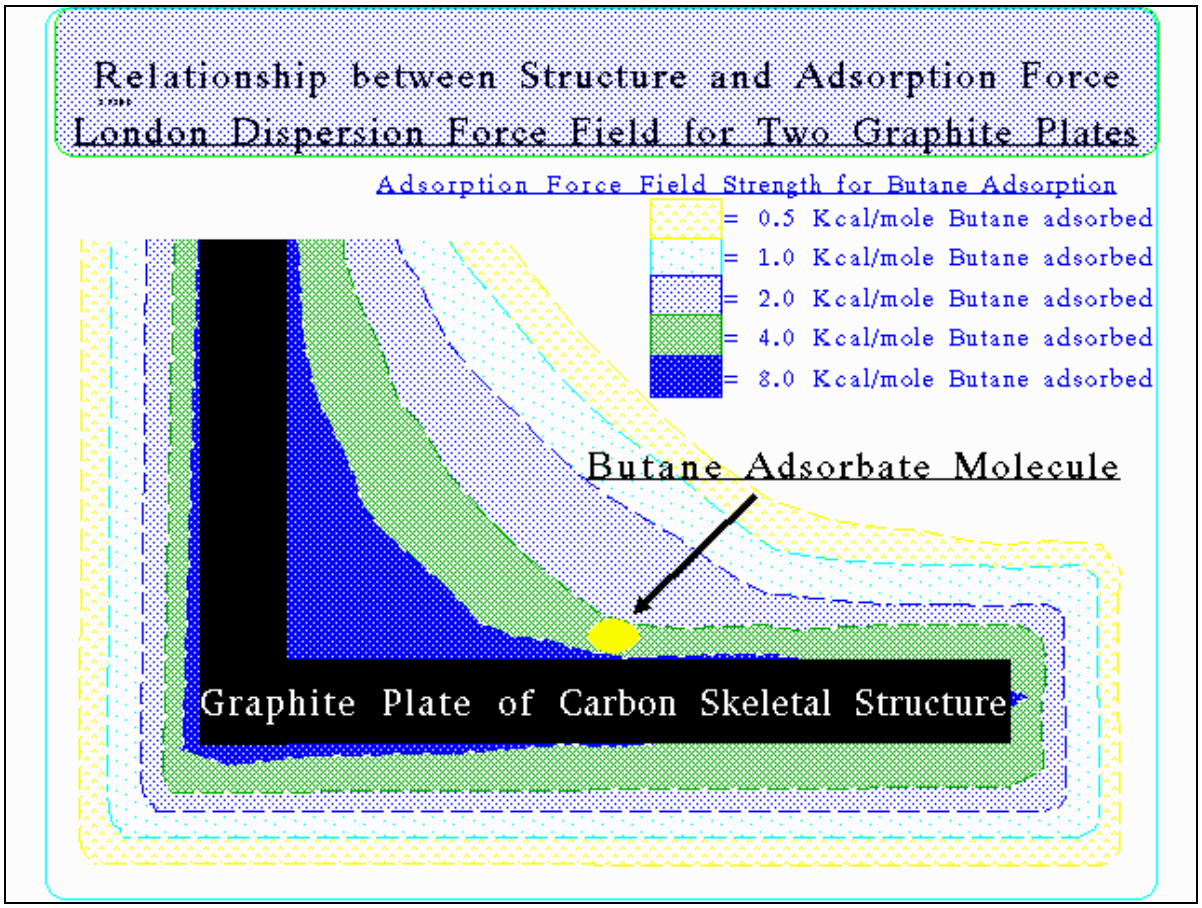


Figure C-6: Higher adsorption sites occur where multiple surfaces combine adsorption forces

When one combines the fact that the pi bonds of the graphene sheets have the highest polarizibility of any common organic substance with the combinations of multiple surfaces to form the veritable infinity of possible adsorption sites within chars, one arrives at a complex three-dimension adsorptive volume, with a distribution of localized adsorption energies, as depicted in Figure C-7.

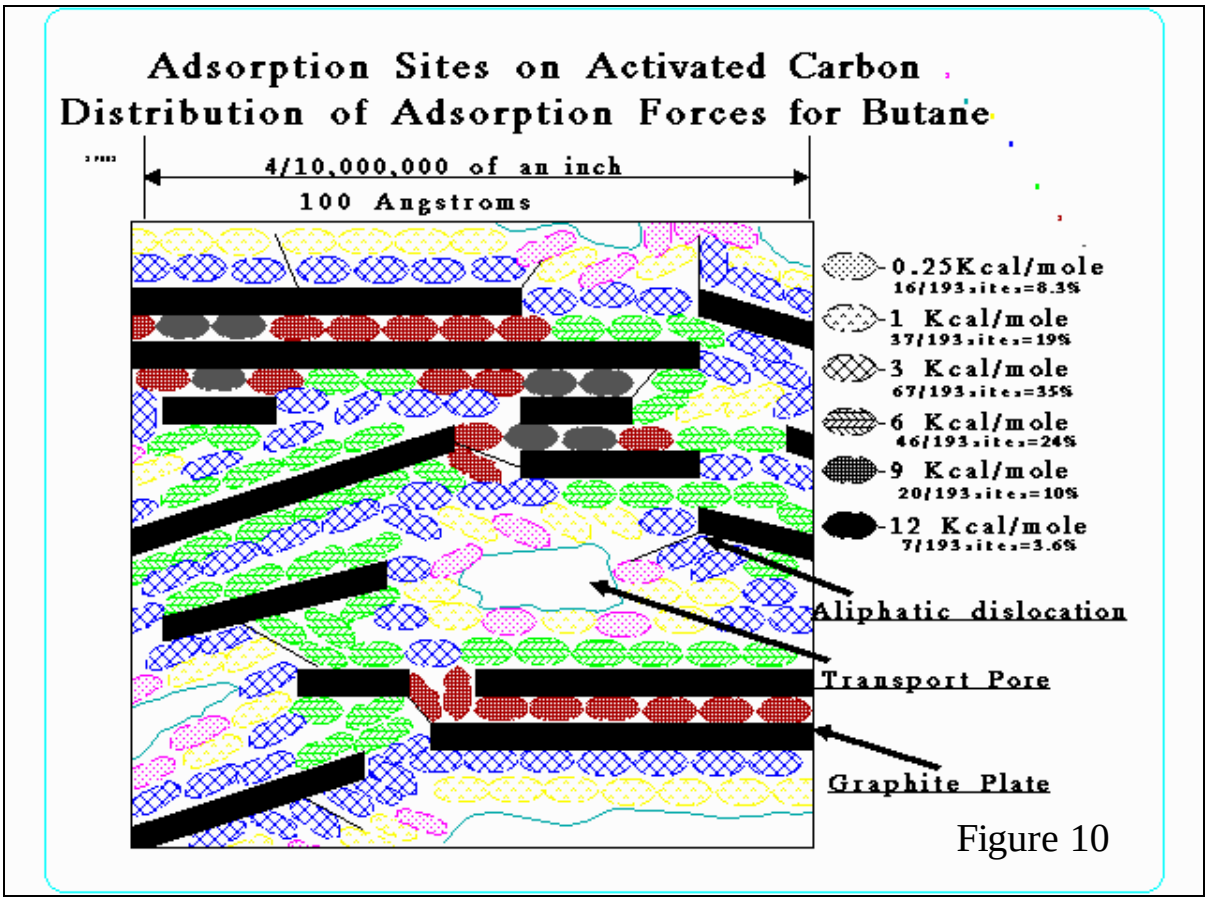


Figure C-7: Calculating the distribution of butane adsorption energy sites in activated carbon

Figure C-7 is, of course, in two dimensions and shows a simplification of the adsorption energy fields mapping using butane as the test adsorbate and depicting the graphitic domains as a collection of dislocated flat plates. This model is accurate for activated carbon, which has essentially just graphitic plates remaining after the carbonization and activation processes used to make activated carbon. Biochars would be a more complicated situation where, depending on the HTT, a significant portion of the microporous volume would be composed of non-aromatic linkages that would not appreciably contribute to local adsorption energy forces.

In summary, based on a body of knowledge gained from the study of activated carbon and the science underlying adsorption in carbonaceous materials, it is reasonable to attribute the development of adsorption capacity in biochars to the development of graphene sheets and graphitic domains during carbonization. The trends of char transformation as a function of HTT match the trend toward acquiring the graphitic content necessary to exhibit adsorption phenomena in biochars. Since graphene sheets display the same attractive adsorption forces for adjacent graphene sheets as for any potential adsorbate, it is reasonable that at elevated HTTs, the three-dimensional structure weakens to a point where graphene sheets consolidate into multi-layer graphitic domains, creating the multi-graphene layer surfaces and multi-adjacent surface adsorption sites necessary for activated carbon-like high energy adsorption sites.

Appendix D: McShields Biochar Characterization Procedure

1) Oven-dried Sample and Residual Moisture

A relatively large (10 to 20 gram) weighed sample is placed in a shallow dish and left overnight in a drying oven set to 200 deg. C Percent moisture is the weight loss during drying and includes some VOCs that escape when the sample is heated to 200C. This Oven-dried Sample used for the additional tests below.

The drying temperature is higher than the typical 105C used in most drying procedures due to the ability of chars to adsorb and retain moisture above the atmospheric boiling point of liquid water. Figure D-1 shows the weight loss trends during the heating of the char samples during the GACS assay. The 200C drying temperature is chosen to take advantage of the apparent plateau in the weight loss trends in the vicinity of 200C, prior to any additional weight losses associated with incremental carbonization observed in chars pyrolyzed at temperatures below 400C.

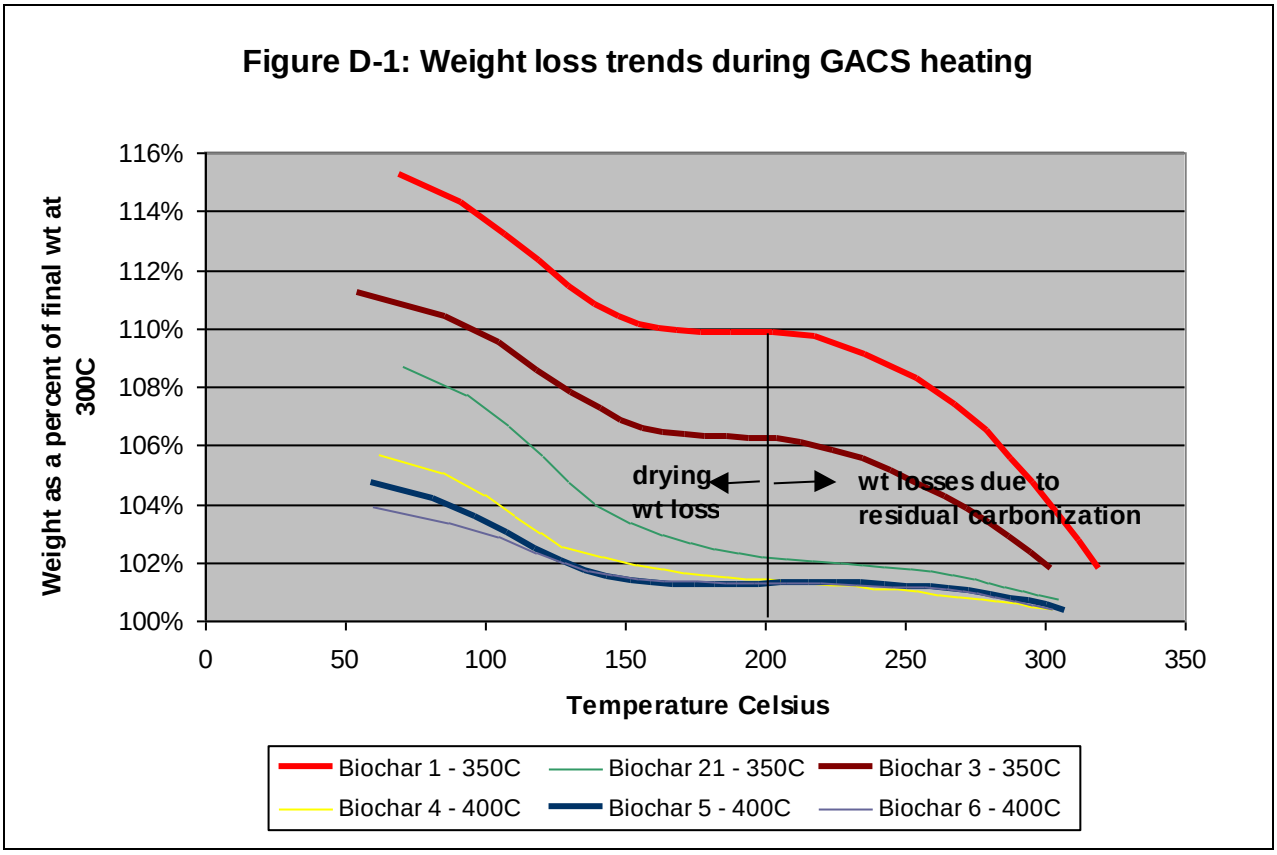
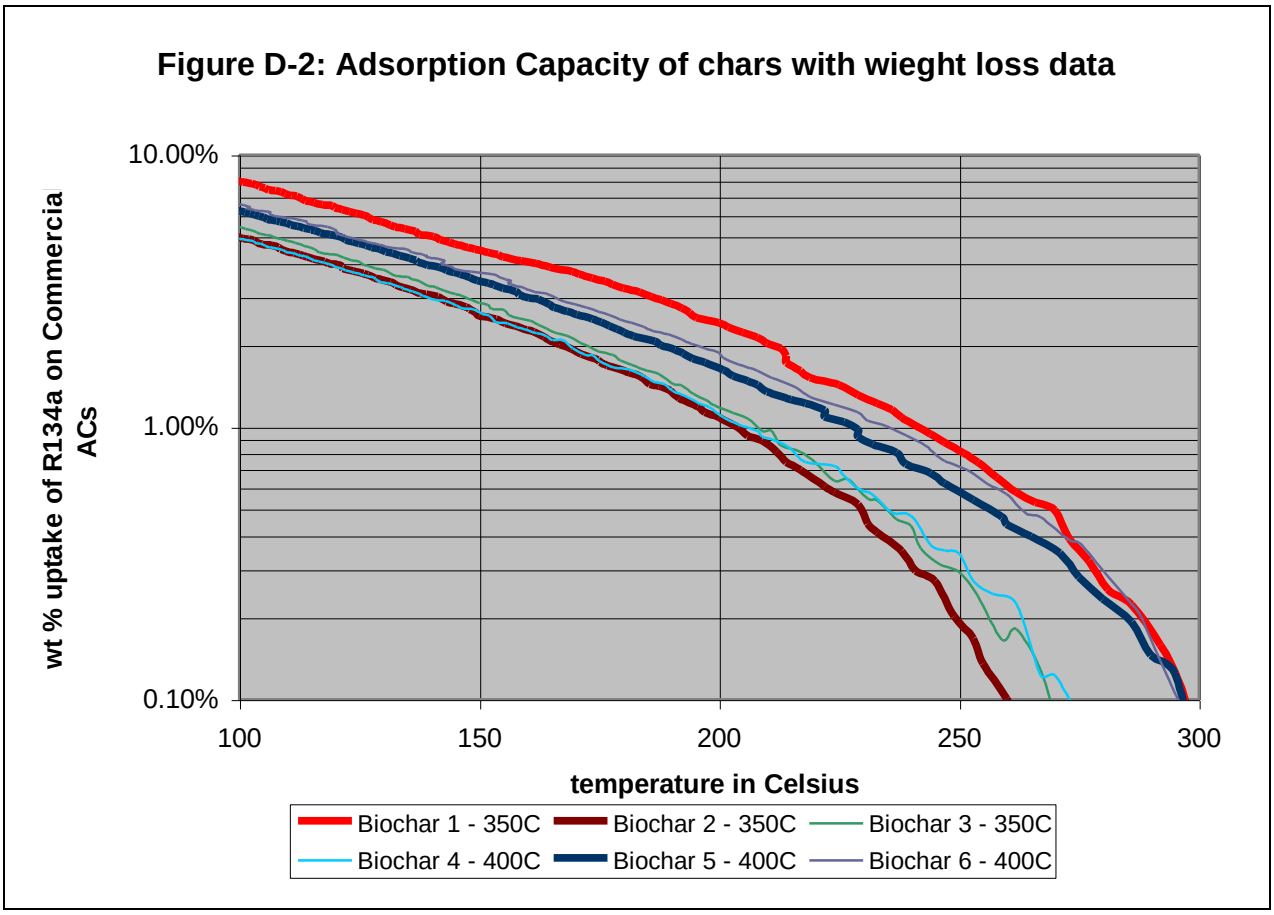


Figure D-2 shows the adsorption capacity trends for the chars utilized for Figure D-1. All the chars had appreciable adsorption capacity. However, the weight loss was not correlated to adsorption capacity. As such, it was concluded that the weight loss is a measure of the residual moisture in the chars, typically due to post-production wetting, and removing the moisture to 200C represents the most reliable method to assure consistent char conditioning prior to further characterization by the McShields Procedure.



2) Total Carbon, Total Nitrogen and Total Hydrogen & Oxygen (HO)

Total Carbon and Total Nitrogen determined on a dry fraction from Step 1 using a Leco C/N analyzer or equal. The Total Hydrogen & Oxygen (HO) is calculated as a portion of the weight remaining, after it is corrected for the ash, as determined in Step 5 below.

3) Total Resident Matter and Total Mobile Matter

A second fraction of dry sample from Step 1 is packed into a tared 2" long x 0.5" id pipe. Pipe and sample weighed to get the dry weight of sample. The pipe is flushed with nitrogen gas and capped at both ends. One cap is loosened one turn to let any pyrolysis gases escape. The pipe is placed into a furnace and heated for four hours at 450 deg. C. Pipe cooled and weighed. The remaining weight represents the sum of Total Resident Matter and the Ash. Initial weight minus the sum of the Total Resident Matter and Ash is the Total Mobile Matter.

As discussed in the main paper and reproduced here: "The mobile matter is postulated to represent that portion of the biochar that is unstable over time in the soil. The principal mechanism for loss of the mobile matter in the soil is believed to be the migration from the biochar into the soil pore water and subsequent metabolization by soil microbes. At this point, and pending further research by the soil scientists and vetting this assay against other available

analytical options such as Soxhlet Extraction with a water miscible solvent, the mobile-resident partition is just a practical and convenient analytical procedure that generates a metric for comparing chars. At this juncture, perhaps it should be treated as a premise, awaiting validation by others and based on future research results."

4) Resident Carbon, Resident Nitrogen, Mobile Carbon and Mobile Nitrogen

Carbon and nitrogen determined on the resident matter using a Leco C/N analyzer or equal. The Mobile Carbon and Mobile Nitrogen are calculated by subtracting the resident value from the total dry values, accounting for the ash present.

5) Total Ash, Acid soluble Ash and Non-acid soluble Ash

A known weight of the Total Resident Matter created in Step 3 is heated in a tared dish to 550 deg. C in air until the ash left is white. Percent ash in the Total Resident Matter is calculated and the corresponding values for the Oven-dried Sample. A few milliliters of dilute (approx 5N) HCl is added to the dish containing the ash and warmed for a few minutes. The acidified ash is washed through tarred GF Whatman 934-AH filter paper. The residue and filter paper is dried and Non-acid soluble Ash determined. Acid soluble fraction determined using Total Ash and subtracting the Non-acid soluble Ash fraction.

The ashing temperature has been lower from typical ashing temperatures used to determine ash content in fuels, such as coal and charcoal, to avoid the calcination of the carbonates present in the char. As discussed in http://en.wikipedia.org/wiki/Calcination:

> Calcination reactions usually take place at or above the thermal decomposition temperature (for decomposition and volatilization reactions) or the transition temperature (for phase transitions). This temperature is usually defined as the temperature at which the standard Gibbs free energy for a particular calcination reaction is equal to zero. For example, in limestone calcination, a decomposition process, the chemical reaction is
>
> $$CaCO_3 \rightarrow CaO + CO_2(g)$$
>
> The standard Gibbs free energy of reaction is approximated as $\Delta G°_r = 177{,}100 - 158\ T$ (J/mol). The standard free energy of reaction is zero in this case when the temperature, T, is equal to 1121 K, or 848 °C.

In this manner, by lowering the ashing temperature to 550 Celsius, the loss of a portion of the ash as vapors is avoided and the accuracy of the partitioning of the char into constituent parts is improved.

6) Resident Hydrogen & Oxygen (HO) and Mobile Hydrogen & Oxygen (HO)

Total Resident Matter less the Resident Carbon, Resident Nitrogen and Total Ash is Resident OH. Mobile HO is calculated from the Total HO less the Resident HO.

Appendix E: Data reduction and smoothing for laboratory chars

The McShields Procedure partitions the char into a small number of constituent parts and seeks to minimize the total laboratory effort and expense of analysis. With this method, several components are calculated by difference, based on sample weights and measurements of specific constituents, such as carbon and nitrogen. While efficient, in such a calculation, errors tend to propagate and amplify, since if one measurement is in error in one direction, another calculated measurement is in error in the opposite direction.

Figure E-1 shows the raw data for the measurement of the constituents of the laboratory chars, in addition to the trend of "Char Yield". One can envision that there are overall unifying trends, but individual data points appear to evidence local inconsistencies that are not reconcilable with the overall evolution of the char properties with HTT.

Figure E-1: Trends in Laboratory Chars

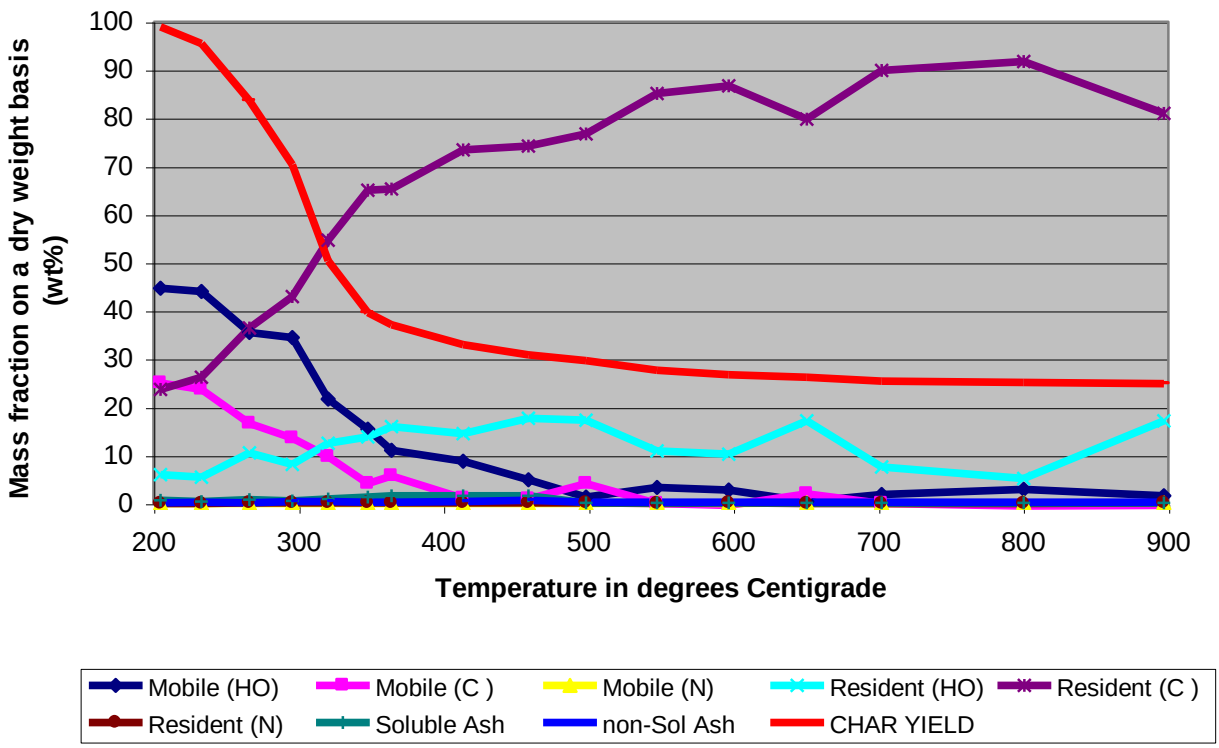


Figure E-2 shows the data for the partitioning of Mobile, Resident and Ash, which represents the data collected directly by weights and the treatment of the char sample at 200C, 450C in the absence of air and 550C in an ashing crucible. The data shows smoother overall trends, but the interaction of the Mobile and Resident assay in the vicinity of 265C is apparent, where it is hypothesized that some mobile matter did not escape the ampoule, resulting in a mobile content being artificially low and the corresponding resident matter being incrementally higher. In

addition, the ash content shown in Figure E-2 is uniformly minor, owing to the high purity of the starting biomass, hardwood pellets, and the ash content is normalized out of subsequent data sets.

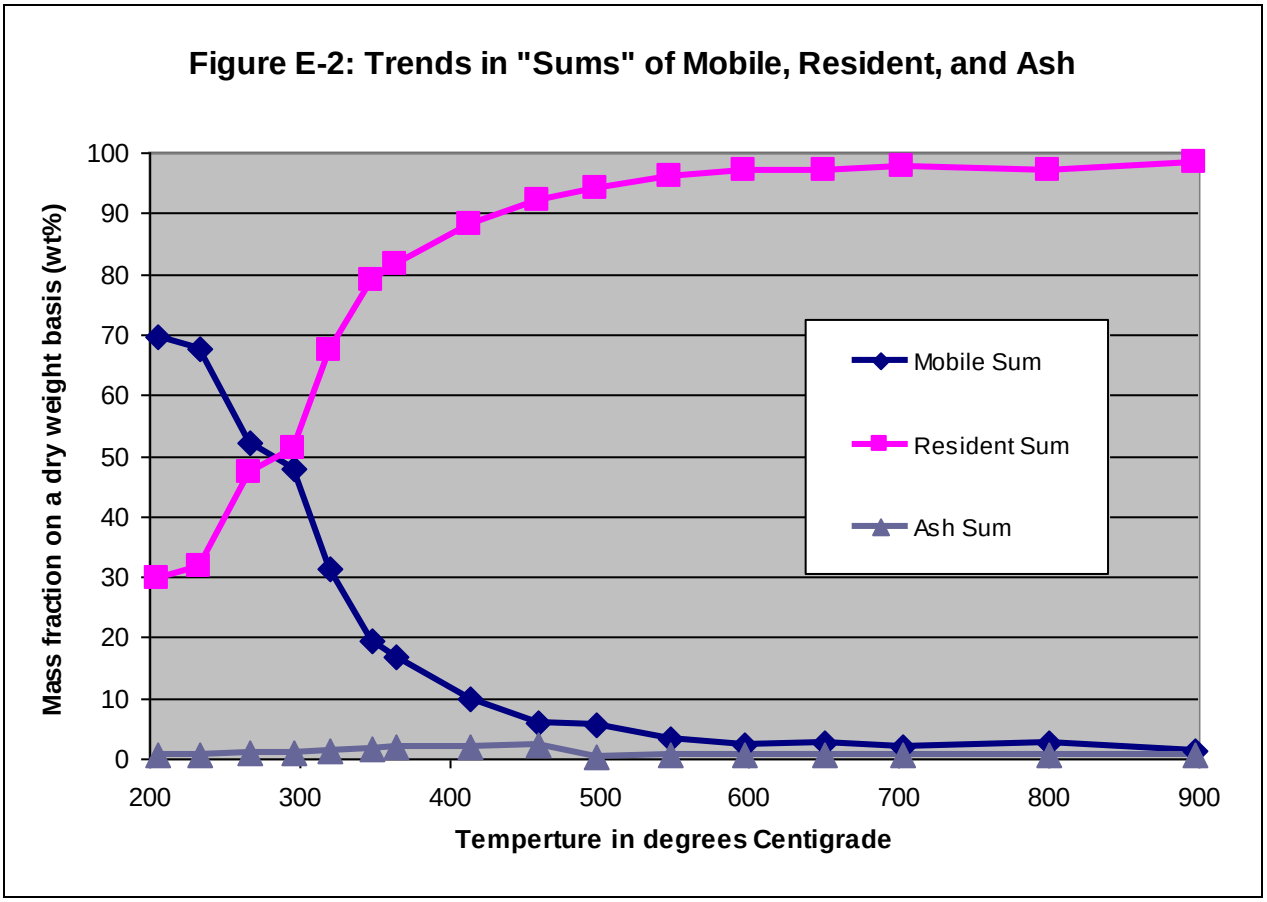


Figure E-3 shows two locations where the measured Carbon content is lower and the resulting calculated HO content is elevated. In order to allow the dominant underlying phenomena to be analyzed, it was decided to smooth the data to correct for the suspected analytical interactions. Alternately, one could replicate the entire experimental and analytical procedure in anticipation that the statistical averaging would dampen out the variations. However, since the creation of the laboratory chars represents approximately 250 hours of dedicated lab effort and the subsequent analysis by the McShields Procedure, efficient as it may be, represents another 150 hours of effort, one must temper one's zeal at triplicate or higher repetitions. In light of the lack of suitably skilled slave labor, or the modern day equivalent known as "the Graduate Student", it was decided to smooth the available data set and proceed.

Figure E-4 shows the resulting smoothed data for the laboratory chars. This data is utilized for the subsequent analysis in the main paper.

Figure E-3: Interactions between measured Carbon and HO by difference

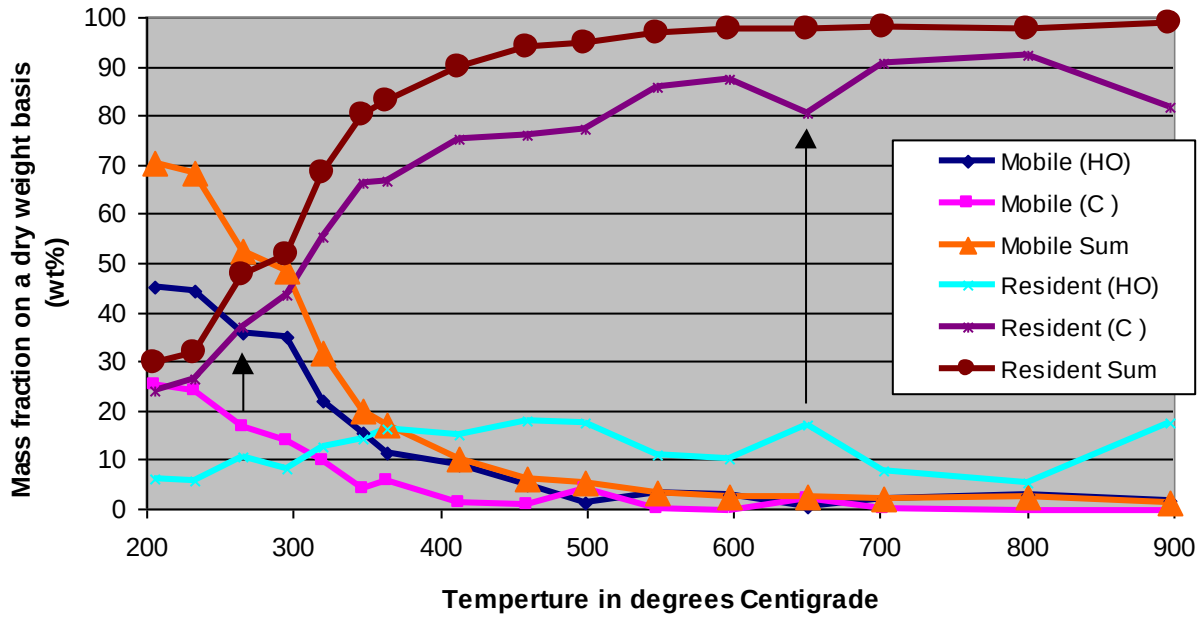


Figure E-4: Smoothed Carbon and HO data for analysis