

Presentation Title: Analytical Options for Biochar Adsorption and Surface Area

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Abstract:

Adsorption is a pivotal property that distinguishes biochar from other carbon-rich natural products. Adsorption also distinguishes superior biochars from less effective “agricultural charcoals”. Since biochar is so new, there are no analytical methods developed specifically to measure adsorption in biochar, nor any experience base to relate adsorption to biochar impact when added to growing systems.

Micromeritics Analytical Services and Soil Control Labs, representing the commercial options for surface area testing and soil property testing, have performed the available traditional analytical methods for adsorption and surface area on a suite of “standard biochars”. In addition, a research technique known as “Gravimetric Adsorption Capacity Scan” has been performed on the same standard biochars.

The standard biochars consisted of a sequence of retort biochars produced over the range of temperatures where adsorption increases and decreases (350 to 900 Celsius), in addition to a series of TLUD micro-gasifier biochars that exhibited a several-fold difference in adsorption capacity. The analytical tests included BET and isotherm analysis with traditional challenge gases (N₂, CO₂, Butane), in addition to the R134a adsorption capacity mapping of the GACS analytical technique.

The results of the various tests are compared and contrasted, along with a discussion of how each test is measuring adsorption or surface area. The relative merit of each test in predicting relevant biochar properties and associated performance is evaluated. Each test measures something different and each test has its own strengths and shortcomings – these will also be summarized.

Background: Biochar versus Charcoal

Biochar is an enigma. It came into existence 600 million years ago, when plants adapted to dry land growth, and lightning strikes caused fires that converted biomass to char. Even today, most of the stable soil carbon is attributed to open fires, such as the systematic burning of the Midwest plains by the Native Americans. Forest fires are documented to convert 1 to 2 percent of the biomass to stable char, representing the portion of the forest that was heated sufficiently to become resistant to biological decay, yet stopped short of becoming ash. “Terra Preta” is an example of anthropogenic char being credited with improving soil fertility in the past, and biochar can be viewed as the modern adaptation of such practices.

Biochar and charcoal are similar materials with different purposes. Charcoal, a fuel and metal reductant, is considered to be the oldest man-made material. The advantage of charcoal is that it burns with less smoke, which is advantageous when cooking indoors. In addition, charcoal burns hotter than wood, which allows it to be used for metal forming, such as in blacksmithing.

For the sake of clarity, this paper will refer to any biomass that has been heated sufficiently to turn black, and not burned completely to ash, to be “char”. Those chars that are intended for use as fuel in cooking or metal processing will be designated “charcoal”, and those chars intended for utilization as a soil amendment will be “biochar”.

Irrespective of labels and history, chars are a pretty well defined class of materials, being thermally-modified biomass that has turned black. As such, chars should have definable, measurable physical and chemical properties. For charcoal, since it is a fuel, the major metrics are energy content, volatile matter, and fixed carbon. These measures have established assays from the coal industry, and accurately predict how charcoals will behave when used in their intended applications, typically either cooking or metal processing.

Biochar is a different challenge, since it does not matter how it burns. What matters is how the biochar interacts in the soil dynamics of moisture, fertilizer and microbial populations, and how stable it is to degradation in that environment. This paper will focus on “Adsorption”, which is the property of biochar that mimics the effects of activated carbon. This analogy is like comparing CEC in biochar to ion exchange resins and other soil constituents that exchange inorganic ions (clays, humic acids) and ash to the behaviors of similar soluble inorganic salts. First we will attempt to put adsorption’s unique characteristics, and role in soils, into perspective, and then delve into the options for measuring “adsorption”, as the property may or may not manifest itself in individual biochars.

Background: Adsorption versus Absorption

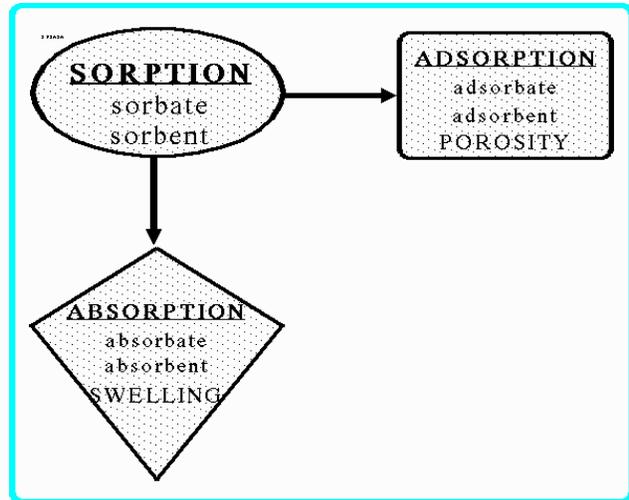
Starting with <http://en.wikipedia.org/wiki/Sorption>: **Sorption** is a physical and chemical process by which one substance becomes attached to another. Specific cases of sorption are:

- Absorption - the incorporation of a substance in one state into another of a different state (e.g., liquids being absorbed by a solid or gases being absorbed by a liquid)
- Adsorption - the physical adherence or bonding of ions and molecules onto the surface of another phase (e.g., reagents adsorbed to a solid catalyst surface)
- Ion exchange - an exchange of ions between two electrolytes or between an electrolyte solution and a complex

Setting ion exchange aside as a property that is captured by CEC in biochar characterization, we will focus on distinguishing adsorption from absorption in chars. As will be seen, both phenomenon are present in biochars.

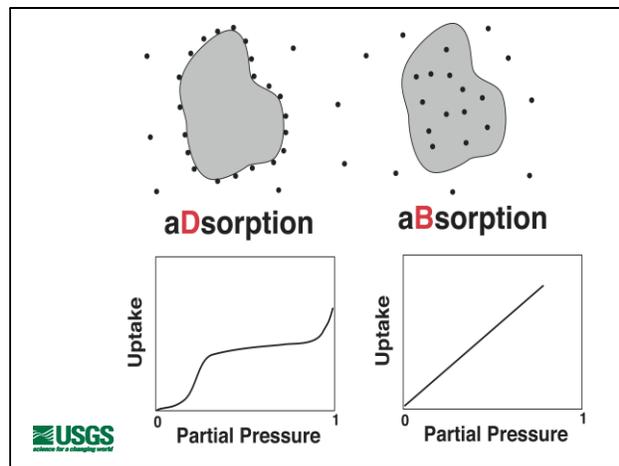
Figure 1 (right) provides a guide to semantics and identifies the pivotal characteristic that separates adsorption versus absorption. In absorption, the absorbent (the media receiving the absorbate) swells and increases in volume as additional material is absorbed. In adsorption, the adsorbent has existing internal volume, typically characterized as porosity, which is filled by adsorbate, but the external size of the adsorbent remains unchanged.

Fig. 1



The distinction is depicted in figure 2, with the additional insight that the underlying mechanism can be identified by the characteristic shape of the isotherm relating the uptake to the partial pressure of the sorbate in the case of vapor phase sorption (slide provided by D. Rutherford of the USGS).

Fig. 2



Shown below (fig. 3 and 4) are the water vapor isotherms of pine wood and pine wood char produced at different temperatures (data provided by D. Rutherford of the USGS). As is evident on figure 3, the pine wood and lower temperature pine wood chars have water vapor isotherms dominated by absorption. In contrast, figure 4, shows the isotherms of higher temperature chars, and shows isotherms characteristic of adsorption as the mechanism of water vapor uptake. It is possible for materials to evidence both absorption and adsorption simultaneously, with each

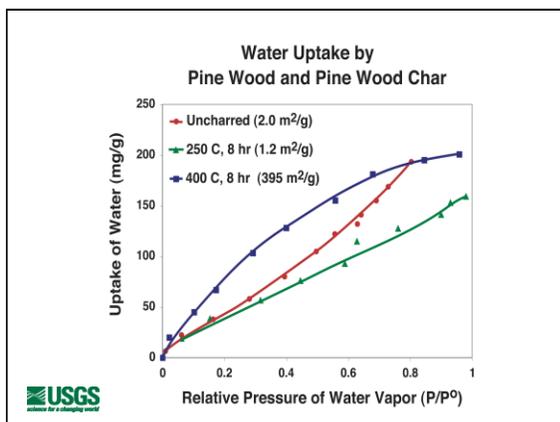


Fig. 3

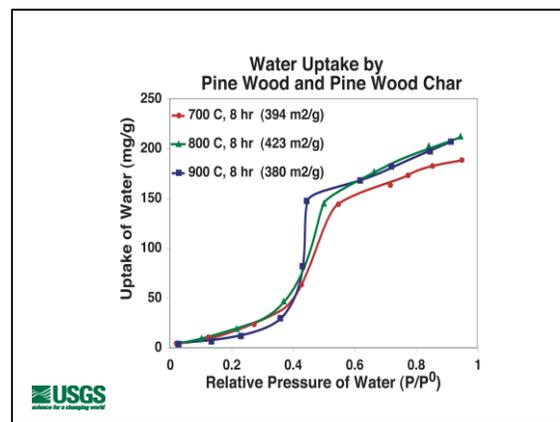


Fig. 4

phenomenon occurring in discrete microscopic regions within the bulk material, depending on local composition.

While the amounts of water uptake are similar in all the samples of pine wood and char, there is one important difference between materials that aBSorb and materials that aDSorb, which relates to the implications on the physical structure of the solid material. Materials that aBSorb have elastic structures that can stretch and swell as additional aBSorbate is present, whereas materials that aDSorb have rigid structures that have internal voids that act as the locations for adsorption.

In chars, and especially in biochars, the property of resistance to biological decay is attributed to the formation of graphitic structures, which are rigid. In contrast, the starting biomass is elastic and capable of absorbing, as are the lower temperature biochars. The underlying concept is that as the carbonization temperature increases, a greater fraction of the remaining solids is more highly graphitized and contains less of the elastic biomass-like structures. The elastic structures may consist of unmodified biomass (cellulose, hemicellulose, lignin, etc.) or newly formed non-graphitic substances that may share many properties with bio-oils (also known as mobile matter, labile matter or tar).

As we discuss the utility of the analytical methods for measuring adsorption and surface area in biochars, it is important to remember that biochars may consist of unmodified biomass, condensed non-graphitic bio-oils and tars, and graphitic structures of varying size and extent – depending on the individual biochar sample and how it was made. While pyrolysis temperature is the most dominant variable in biochar properties, carbonization processes vary in the extent that they remove bio-oils as they form versus deposit them in the developing graphitic structures.

Biochar Standards: Retort versus TLUD biochars

In order to evaluate the various options for measuring adsorption and surface area in the diverse universe of biochars, biochars samples were prepared over a wide range of conditions. One set of standards was taken from previous work presented at the US Biochar 2010 Conference in Iowa titled “Schenkel and Shenxue revisited” which explored the properties of a homologous series of retort biochars over a range of temperatures from 200C to 900C. The original paper and appendices can be downloaded at www.acfox.com in the presented papers section. Retort chars are made by heating biomass in the absence of oxygen or air, and represent one prevalent method of creating biochars.

Another method of making biochars involves controlled pyrolysis with partial oxidation of the biomass and biochar in a method known as “micro-gasification”, which is used in making improved cookstoves that use waste biomass as fuel (search “HERA-GIZ micro-gasification” and at www.acfox.com). Improved cookstoves using micro-gasification are often referred to as “TLUD” cookstoves, which is an acronym for “Top Lit UpDraft”. TLUD biochars differ from retort biochars in that some of the wood gas and char is oxidized to provide the heat to convert the biomass to biochar. Depending on how the TLUD is operated, a range of adsorption in the biochars can be produced, as discussed in “How to make high and low adsorption biochars for small research studies” (at www.acfox.com).

Two sets of four biochar standards were assembled, representing a wide range of adsorption generated over typical operating conditions in retorts and TLUDs. The retort biochars consisted of residual samples from the original 2010 work, pyrolyzed at 364C, 500C, 700C and 900C. The TLUD biochars were created using a range of fan assisted primary air in the 1G Toucan TLUD, with samples at Natural Draft = ND = 0V, 3V, 6V and 9V, where the V stands for the voltage applied to the forced primary air fan.

Each of the biochar standards was homogenized by grinding to a coarse powder with a mortar and pestle, then split into identical sets of eight standards and provided to Micromeritics Analytical Services and Control Laboratories Inc. (www.compostlab.com). Micromeritics and Control Labs performed standard commercially available analytical tests on the samples. Hugh McLaughlin also analyzed the eight samples using the Gravimetric Adsorption Capacity Scan method, which will be discussed next.

Baseline Adsorption: Gravimetric Adsorption Capacity Scan (GACS)

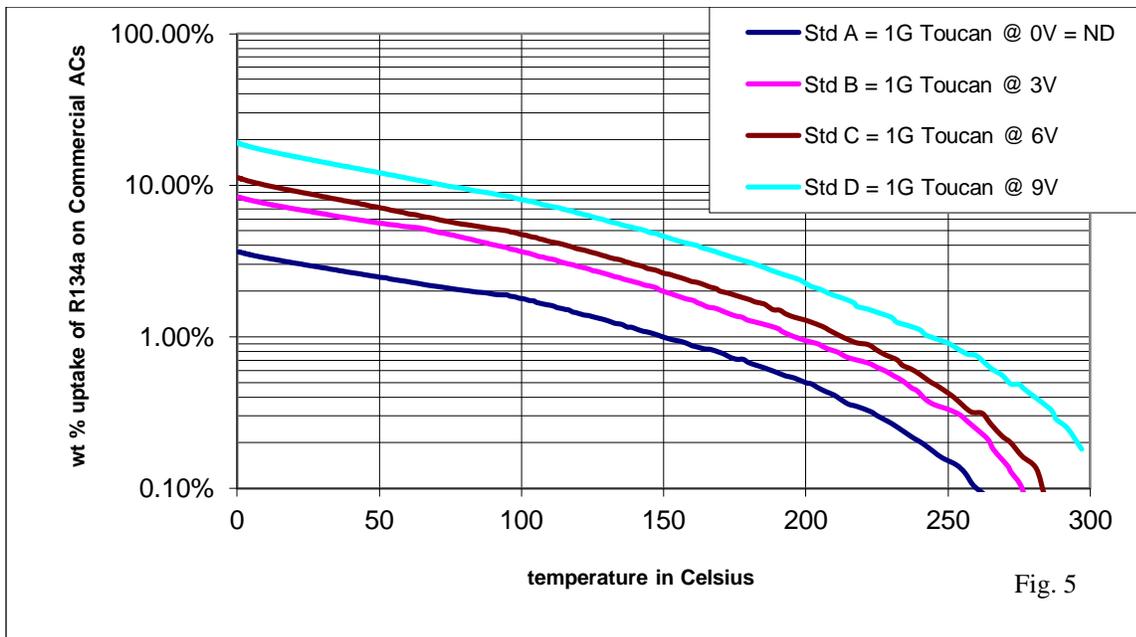
The intent of this paper is to compare available analytical methods for measuring adsorption and surface areas in biochars, and evaluate the value of each of the metrics generated. The current state of the art assay for adsorption in activated carbon research is a technique that measures the actual adsorption occurring over a broad range of adsorption energies. The specifics of the assay is discussed in “Appendix B: GACS assay for measuring Adsorption Capacity” from the 2010 paper (at www.acfox.com).

Because the GACS test measures the adsorption phenomenon over a wide range of conditions, it will be used to provide the baseline characterization of the biochar standards. However, that is not to imply that GACS is better or more accurate than the other analytical methods being evaluated – it just represents one starting place.

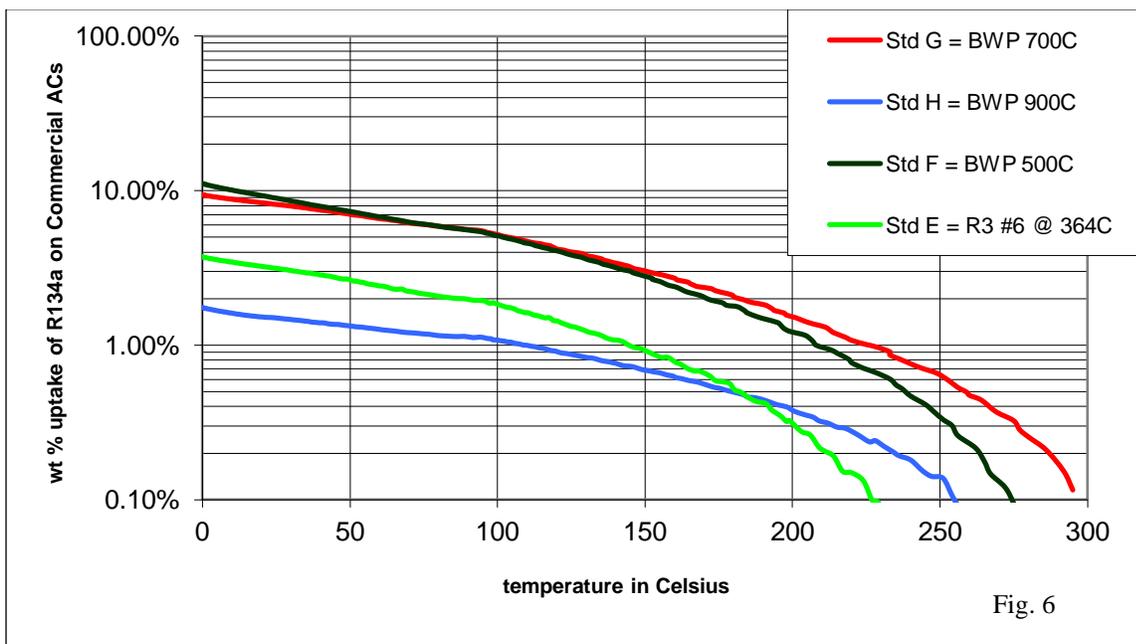
Because the GACS method was developed for activated carbon studies, there are some concerns when measuring biochars. Specifically, most activated carbons have been exposed to temperatures over 800C, whereas many chars are made a much lower temperatures. Since the GACS test exposes the sample to 300C, there is a tendency for lower temperature biochars to initiate additional incremental carbonization, which alters the samples and interferes with the interpretation of the GACS results. The GACS method also removes some mobile matter from the biochar sample during the initial heating in nitrogen, as adsorbed water is removed, which also influences the adsorption capacity subsequently measured.

In summary, GACS is certainly not perfect and the measured results need to be subjected to the same balanced evaluation of what is actually being learned about the biochar sample, and under what conditions, that is necessary to interpret the information content of the other analytical methods.

The GACS results are shown below, in figure 5 for the TLUD biochar standards. As can be seen, the adsorption increases across the entire range of temperatures with the increased forced air voltage during carbonization.



The GACS results are shown below, in figure 6, for the 2010 Retort biochar standards. The pattern of adsorption is much less regular for the range of increasing carbonization temperatures. Focusing on the adsorption capacity at 100 Celsius, the adsorption goes through a maximum at intermediate temperatures, and then decreases at higher carbonization temperatures. This phenomenon is explored in detail in the 2010 “Schenkel and Shenxue revisited” paper and is attributed to the collapsing of the carbonaceous matrix and graphene sheets into denser multi-layer graphitic domains.



Traditional surface area and volumetric adsorption methods

Historic analytical methods used for the characterization of the surface area and porosity in solids are based on physical adsorption. The best-known and most commonly used method for evaluating specific surface areas of solid materials is the BET method based on the theory of Stephen Brunauer, Paul Hugh Emmett, and Edward Teller published in 1938.

The specific surface area is “measured” in the following way (see also http://en.wikipedia.org/wiki/BET_theory): A sample of dry porous material is equilibrated with known amounts of nitrogen vapor and the experimental adsorption isotherm is constructed, typically at 77 K (minus 196 C or minus 321 F), the boiling point of liquid nitrogen. The BET equation is fitted to the experimental adsorption isotherm and a point of inflection is located that represents the monolayer surface capacity, i.e. the number of adsorbed molecules covering the surface with a single layer of nitrogen molecules. This quantity multiplied by the cross sectional surface area of one nitrogen molecule to calculate the surface area of an adsorbent. While the BET equation was developed for a flat uniform surface assuming multilayer adsorption mechanism; it has been also applied to porous materials such as activated carbons and zeolites.

Another quantity that can be obtained from gas adsorption of microporous carbon materials is the micropore volume, V_m . The best-known method of evaluating this quantity for microporous carbons is the Dubinin-Radushkevich equation (DR), derived on a thermodynamically based set of assumptions for the volumetric filling of micropores.

In this work, we compare the results obtained from N_2 BET and CO_2 DR methods and their predictive power for the two sets of biochar standards, the previously described Retort and TLUD biochar standards. The volumetric adsorption measurements of N_2 at minus 196 C and CO_2 at 0 C were performed using an ASAP 2420 (Micromeritics) instrument. Prior to measurement, the samples were dried by degassing over night under vacuum at 200 C, which is consistent with the other techniques used in this study to remove any adsorbed water vapor.

The CO_2 and N_2 isotherms for both the TLUD (fig. 7 and 9) and Retort (fig. 8 and 10) Chars are shown below. The quantity of CO_2 adsorbed for each sample increases with the increased energy applied to the different char types. The N_2 isotherms also correlate when comparing the TLUD chars, but the retort chars demonstrate that N_2 is not a good adsorbate for these materials.

Fig. 7, CO2 TLUD Isotherms

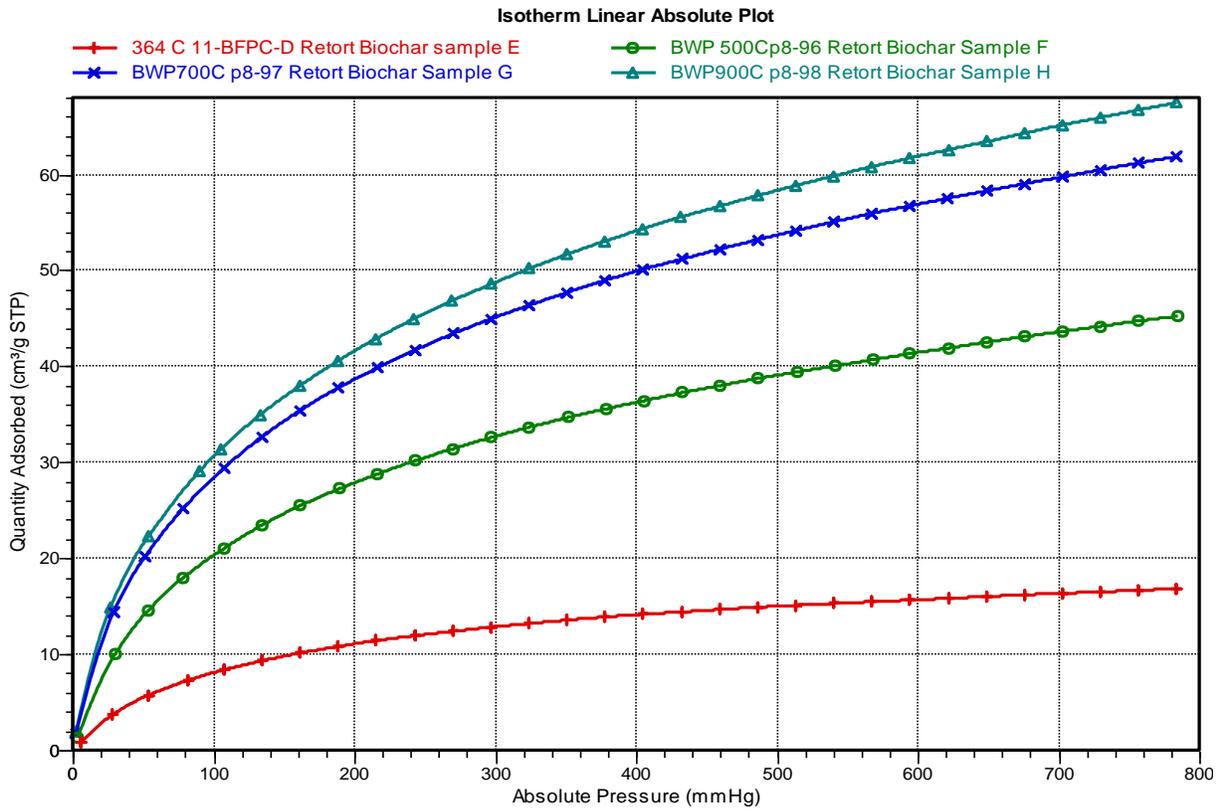
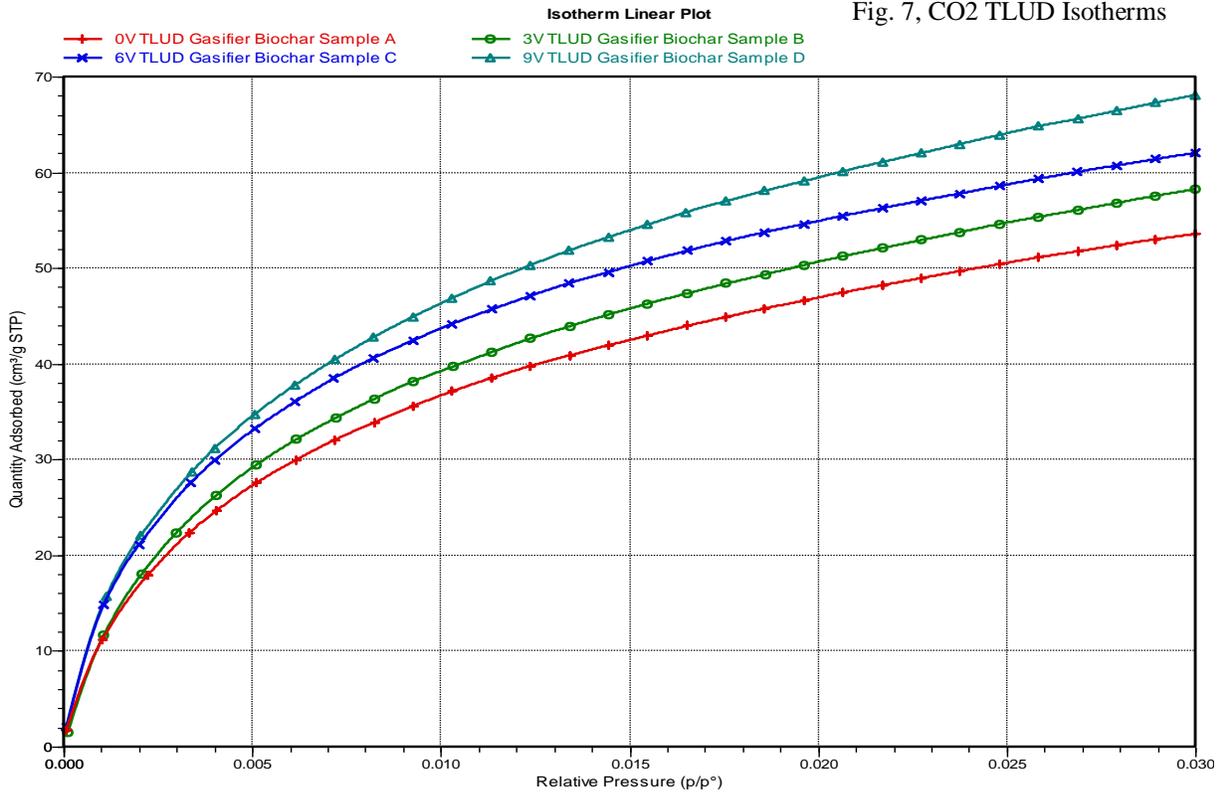


Fig. 8, CO2 Retort Isotherms

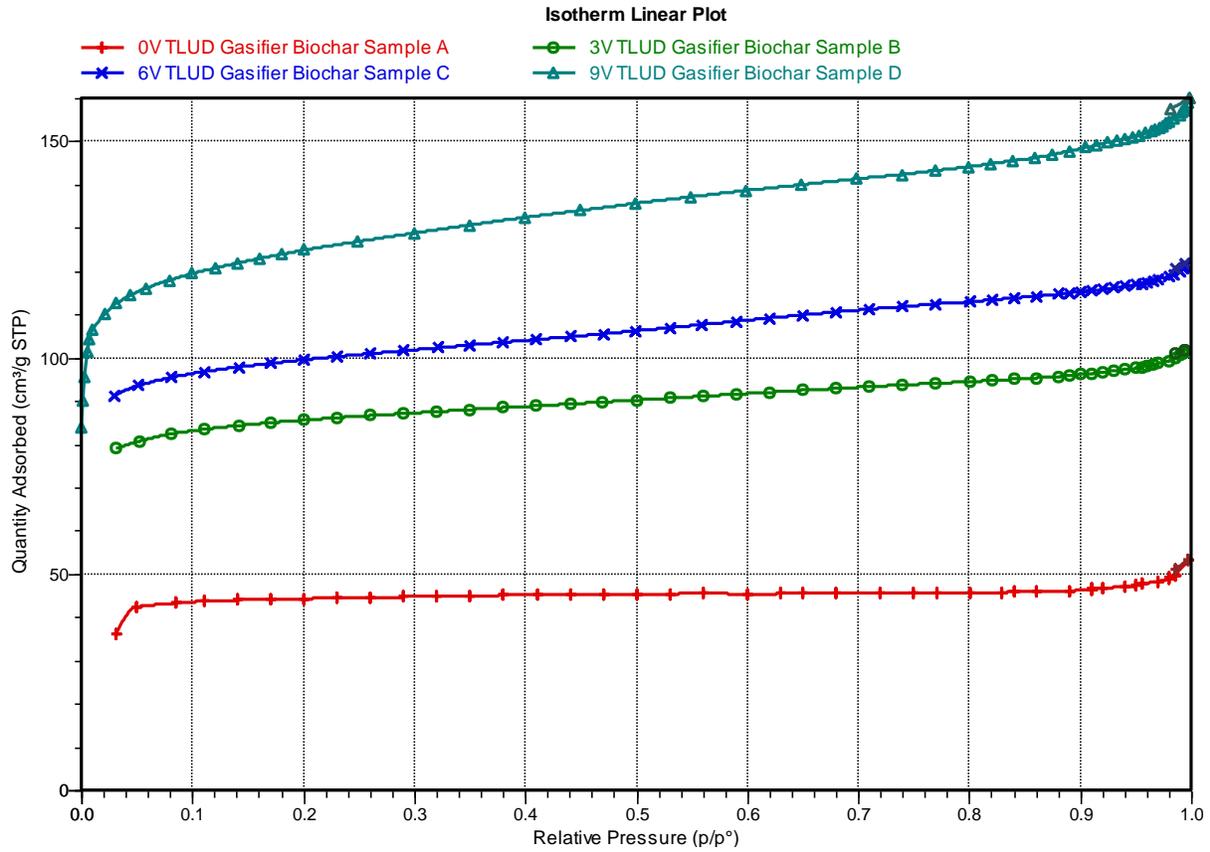


Fig. 9, N₂ TLUD Isotherms

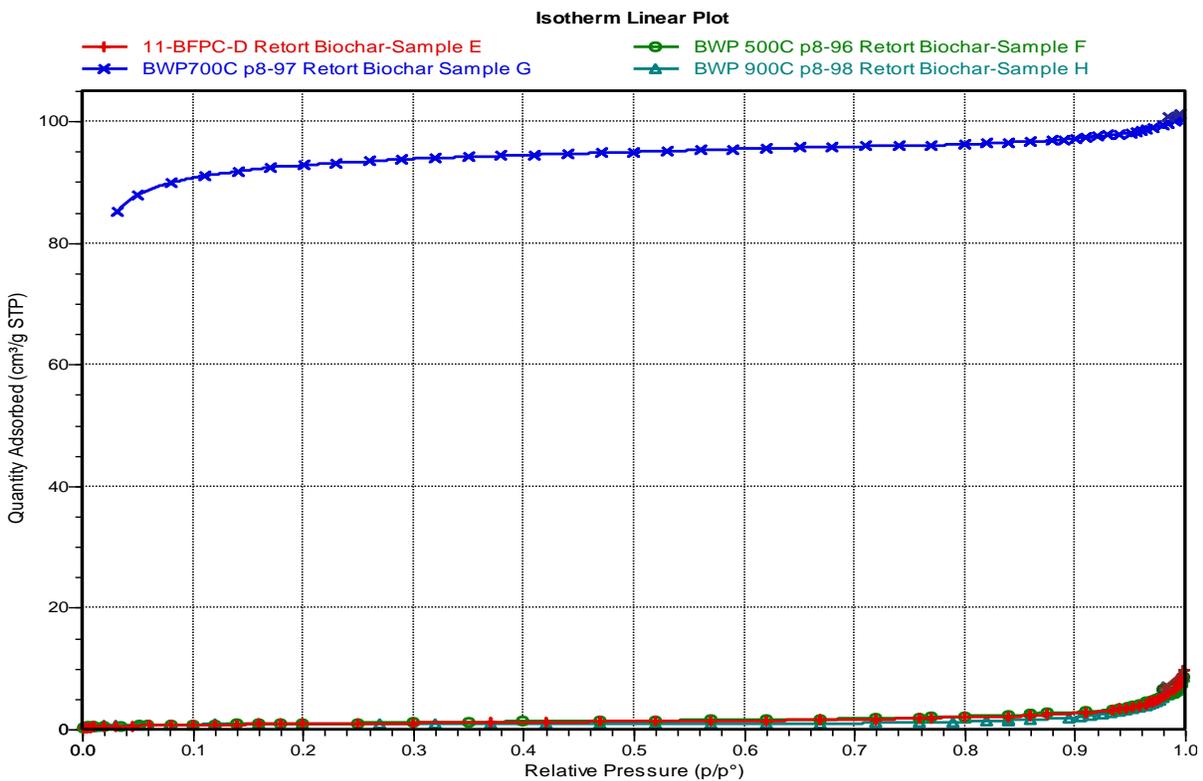


Fig. 10, N₂ Retort Isotherms

Figure 10 shows the N₂ isotherms for the retort chars and demonstrates the problem we see quite often on highly microporous materials. The diffusion rate of N₂ molecules into micropores of these retort chars at minus 196 C is extremely slow and these pores are effectively inaccessible to N₂ molecules. On the other hand, the CO₂ molecules at 0 C can easily adsorbed into the micropores of the same materials at the much higher temperature. This example supports the conclusion that CO₂ at 0 C is a better probe than N₂ at minus 196 C for such microporous materials as biochars.

Water vapor adsorption isotherms using Dynamic vapor sorption (DVS)

As previously discussed, an important characteristic of biochars is their capacity for water sorption. This assay is performed under conditions much closer to those found in the soil and using a sorbate, water vapor, identical to that found in growing systems. In contrast, N₂ BET and CO₂ DR methods use conditions and sorbates that are far removed from those found in soils, but potentially better suited for the characterization of porous solids. Indeed, in the scientific literature, measuring water sorption is a much less frequently utilized analytical procedure.

Gravimetric water vapor sorption experiments were carried out using the DVS-HT instrument (Surface Measurement Systems, Alperton, UK). This instrument measures the uptake and loss of vapor gravimetrically using a recording ultra-microbalance with a mass resolution of $\pm 0.1 \mu\text{g}$. The vapor partial pressure ($\pm 1.0\%$) around the sample is controlled by mixing saturated and dry carrier gas streams using electronic mass flow controllers. The temperature is maintained at the desired temperature $\pm 0.1 \text{ }^\circ\text{C}$.

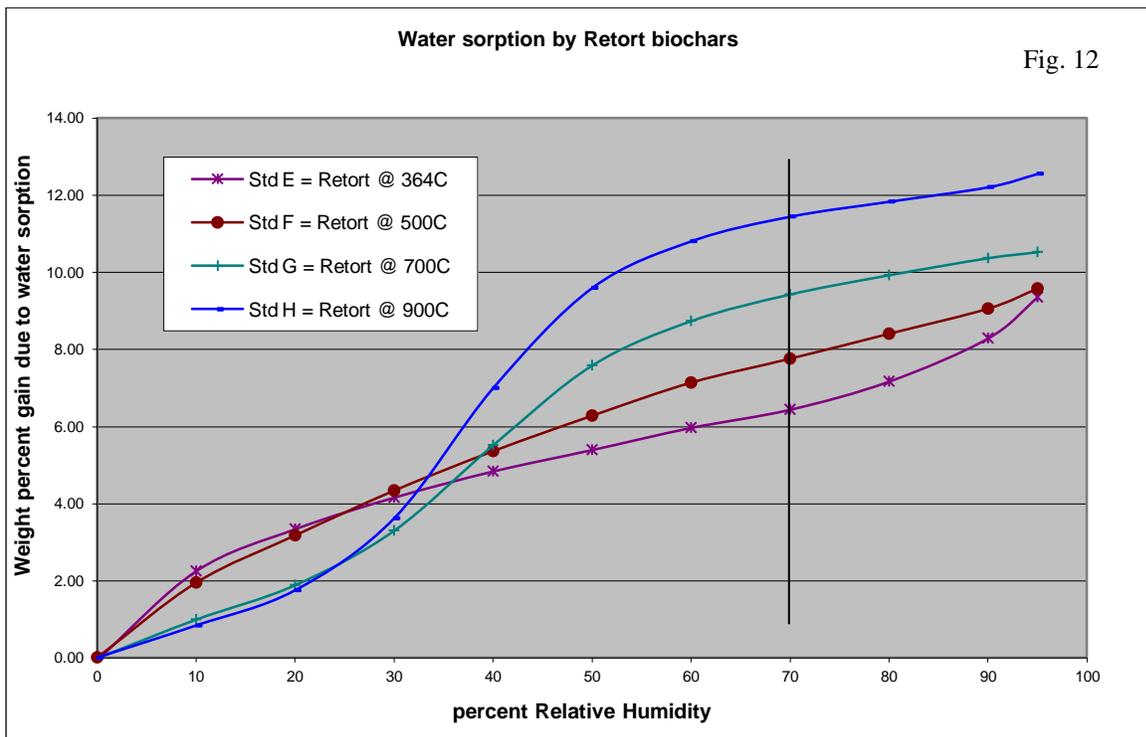
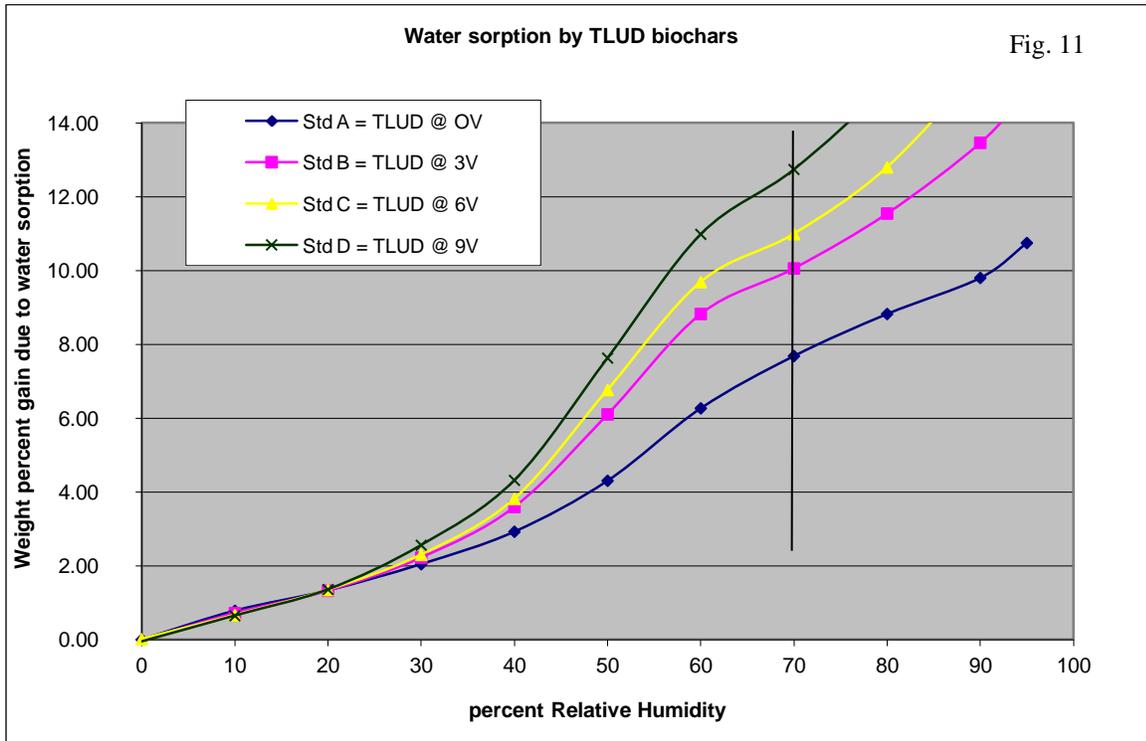
The samples (7-15 mg) were placed into the DVS-HT instrument at 25 $^\circ\text{C}$ where they were initially dried in a 400-sccm (standard cubic centimeters) stream of dry air ($< 0.1\%$ relative humidity) for 4 hours to establish a dry mass. The samples were then exposed to a step changes in relative humidity (RH) and maintained at these conditions while monitoring the sample mass. The RH profile was as follows: 0 to 90% RH in 10% RH steps (sorption isotherm) and back down to 0% RH in a similar fashion (desorption isotherm). The mass was allowed to reach equilibrium at each step change in humidity.

The equilibrium points at the end of each step were used to determine the water sorption and desorption isotherms. Identical conditions were used for all samples.

Figures 11 and 12 show the water vapor sorption data for the TLUDS and Retort biochars. Note that the y-axis scales are the same, allowing for relative comparison of the extent of water uptake. The value at 70% Relative Humidity is noted by the vertical line, with this quantification being used to compare relative capacities as related to other biochar properties.

From the shape of the water vapor isotherms at low RH, it is apparent that two of the Retort biochars, Standards E & F, exhibit a very different isotherm shape than the other six standards. From the earlier discussions, one would attribute this behavior to the sorption mechanism being more aBorption and less aDorption than the other more characteristically “S” shaped isotherms. The mechanism for this may be important from a research perspective, but from a practical

application we are more interested in the water capacity at higher relative pressures, say 70% relative humidity.



Additional testing per IBI Standards and Butane Activity

Control Labs tested the TLUD biochar standards in this study following Test Category A: Basic Biochar Utility Properties of recently adopted IBI testing format. The data collected on the Retort biochars is available in the prior publication based on these samples. In addition to the IBI Test Category A, all samples were subject to additional specialized tests. The major biochar quality constituents that we tested for were H:C ratio, H,C,N, & O values, moisture content, and ash. Based on calculations using these values obtained in testing we were able to calculate the high heating value (HHV) for each specific biochar sample. In addition to IBI protocol we included tests for energy content, butane activity, as well as liming values. The summary of the Test Category A results on the TLUD biochar standards is shown below in table 1, and available at www.acfox.com.

Table 1



Summary of Dry weight data - TLUD Samples

	TLUD A	TLUD B	TLUD C	TLUD D		
Moisture	0.0	0.0	0.0	0.0	percent	Declaration ASTM D1762-84 (105c)
Total Ash	2.3	3.4	3.6	4.0	percent	50% Max ASTM D 1762-84 (750c)
Organic Carbon	85.3	85.9	85.9	84.0	percent	Declaration CHN by dry combustion
Inorganic Carbon	0.07	0.10	0.15	0.21	percent	Declaration HCl treated
Hydrogen/Carbon (H:C)	0.40	0.33	0.29	0.28	molar ratio	0.7 Max
Hydrogen	2.9	2.4	2.1	2.0	percent	Declaration CHN by dry combustion
Total Nitrogen	0.75	0.69	0.67	0.66	percent	Declaration CHN by dry combustion
Total Oxygen	8.7	7.6	7.5	9.1	percent	Declaration by difference
pH value	NA	NA	NA	NA	units	Declaration Ahmedna et al (2002) (1997)
Liming (neut. value)	1.1	1.8	4.9	5.9	% CaCO3	Declaration Rayment & Higginson
Liming (carbonate value)	0.6	0.8	1.2	1.8	% CaCO3	Declaration ASTM D 4373
Calcium (Ca)	1.3	2.7	3.0	2.8	percent	Declaration
Magnesium (Mg)	0.3	2.0	2.7	2.3	percent	Declaration
Activity (Butane) ^c	4.1	6.3	8.4	10.6	g/100 g	Declaration ASTM D 5742 (butane)
Bulk Density	17.84	14.35	13.79	14.38	lb/cu ft	Declaration
Sulfur (S)	0	0	0	0	percent	Declaration
**Energy (HHV)	13855	13733	13596	13171	(Btu/lb)	Calculated from CHNO
Mobile matter	2.02%	1.51%	1.54%	1.82%	percent	Wt loss at 450C - McShields Method

The butane activity measured on the biochar standards is based on ASTM D5742 - 95(2010) Standard Test Method for Determination of Butane Activity of Activated Carbon. This method takes a dried sample of carbon at 25 Celsius and measures the weight gain upon being equilibrated in pure butane at one atmosphere. Butane Activity measures total adsorption capacity above a relatively low adsorption energy threshold and represents essentially the total micropore volume of the porous adsorbent. While the total adsorption capacity measured by Butane Activity is worth knowing, a significant portion of this capacity is too low in adsorption

energy to be of any practical value in an actual adsorption application. However, butane activity has the advantage of being relatively low cost for the required apparatus and, like all ASTM tests, should be reproducibly measured by any qualified analytical resource.

A critical concern for measuring butane activity is the proper drying of the sample prior to testing. The concern stems from the fact that adsorbed water vapor occupies the same adsorption sites as butane, so residual adsorbed water vapor decreases the amount of butane uptake and influences the adsorption measurement.

Summary of Adsorption and Surface Area results – searching for correlations

The original choice of GACS as the baseline assay for adsorption is somewhat arbitrary, but intentionally chosen as to not bias one commercially available method over other analytical options. At this phase of biochar “science”, it is difficult to know what properties of biochar are pivotal in soil performance. In light of this, we are focusing on which available analytical methods seem to be measuring the same phenomena, or at least mimicking each other. A summary of the analyses for both sets of biochar standards are shown below in table 2.

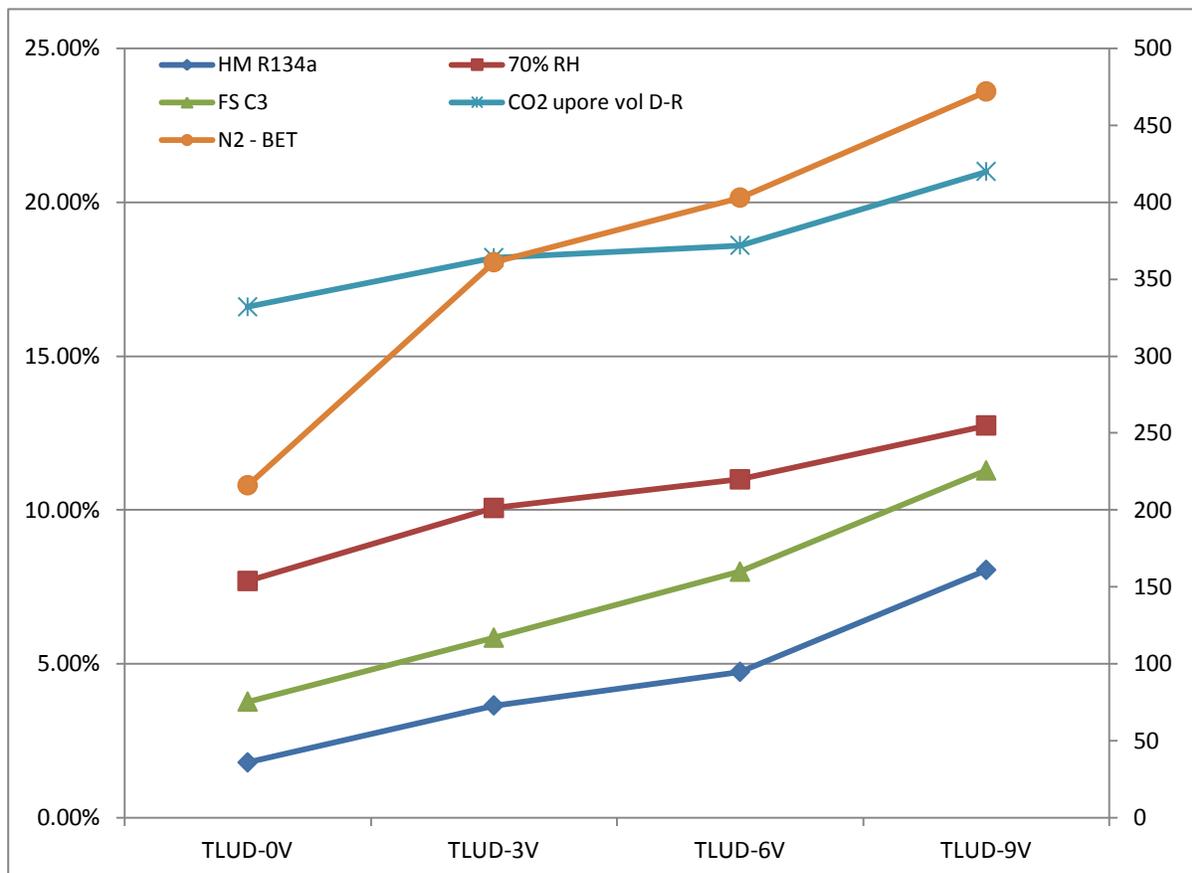
	R134a	Water uptake at 70% RH (%wt change)	Butane	CO2 Vol Ads (cc/g)	CO2 upore vol D-R (cc/g)	BET - N2 (m2/g)
Sample A - TLUD 0V	1.79%	7.69%	3.77%	53	0.166	216
Sample B - TLUD 3V	3.64%	10.06%	5.85%	58	0.182	361
Sample C - TLUD 6V	4.74%	10.99%	7.99%	62	0.186	403
Sample D - TLUD 9V	8.05%	12.74%	11.28%	68	0.21	472
Sample E - Retort 364C	1.84%	6.44%	2.89%	17	0.05	2
Sample F - Retort 500C	4.56%	7.76%	4.47%	45	0.139	9
Sample G - Retort 700C	4.86%	9.43%	6.27%	62	0.188	389
Sample H - Retort 900C	6.80%	11.45%	3.07%	67	0.207	80

Table 2

In addition to the adsorption results, as measured by the R134a-based GACS results and summarized as the weight percent adsorption of R134a by bone-dry biochar at 100C, there are several other metrics available on the two series of biochar standards. The HTT or Heat Treatment Temperature, the highest temperature during carbonization, provides a logical sequence for the Retort standards. The TLUD biochars are ranked in order of severity of carbonization, as measured by the voltage supplies to the fan supplying the primary air to the micro-gasifier. Both sequences of biochars also have additional measurable properties, including elemental properties and composite metrics, such as “mobile matter”, which is the portion of the organic material that volatilizes at 450C under controlled conditions.

With the TLUD class of chars, all of the techniques did a reasonably good job of correlating adsorption capacity to energy applied. In other words, all of the techniques should do a good job of predicting performance of the char based on the reported capacity or surface area. See figure 13 for a graphical representation of these different parameters.

Fig. 13



The Retort biochars exhibited much more complex dynamics as the HTT was varied from 364C to 900C. The R134a adsorption, Butane capacity, and even the BET surface area, exhibited an internal maximum between 500C and 700C. The water adsorption and CO2 adsorption isotherms exhibited similar increasing adsorption capacities with increased temperatures as evidenced in figure 14.

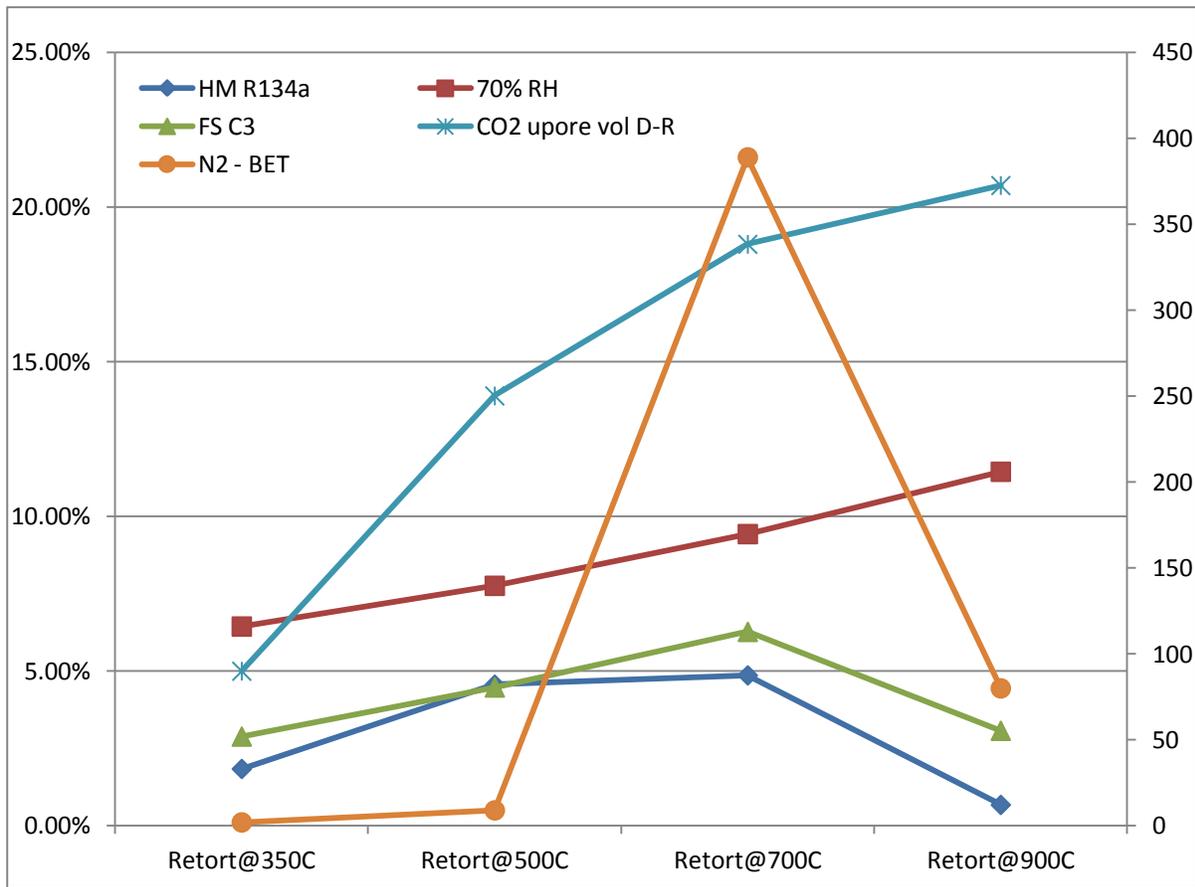
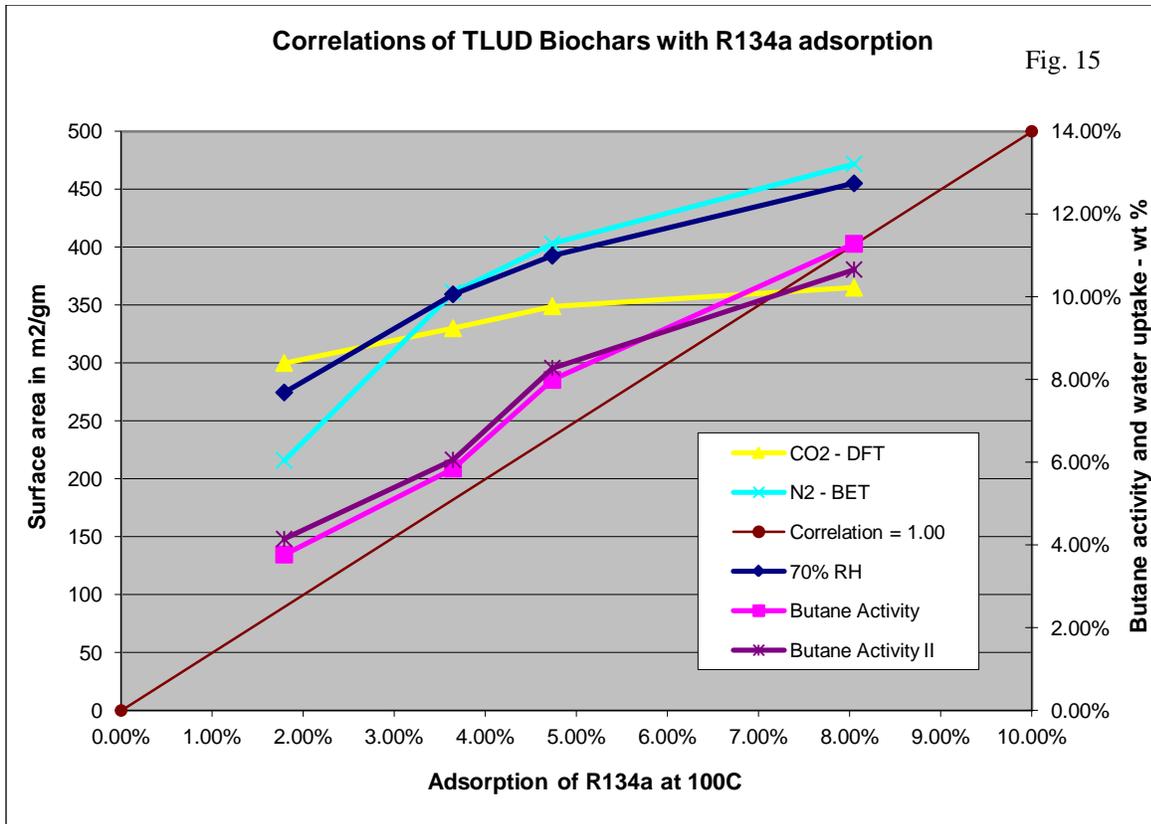
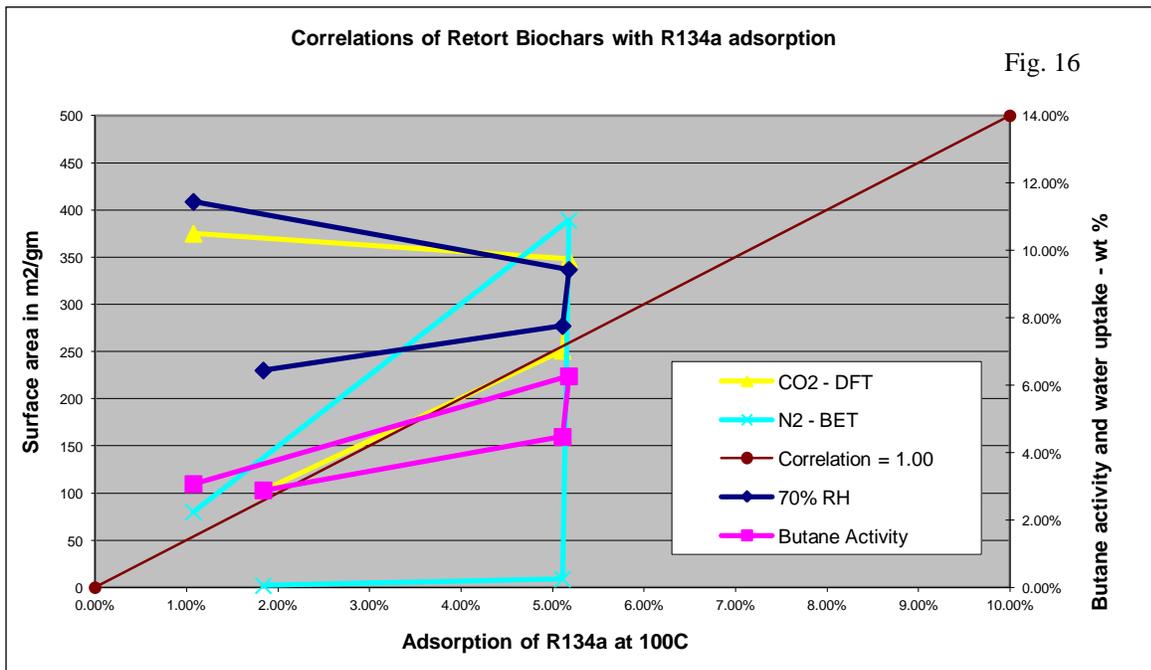


Fig. 14

The correlations of the other adsorption and surface area assays with R134a adsorption are shown below in Figure 15. In general, all metrics showed positive correlations with R134a and each other, with butane activity showing the best dynamic range of measurement and best prediction of a purely linear correlation without y-intercept correction factor, as shown with the “Correlation = 1.00” line.



In contrast, the correlations are less well-behaved for the Retort Biochars, as shown on Figure 16.



As shown in Figure 17, while none of the correlations above are exemplary, the butane activity correlation is significantly better than the others, with the N₂ – BET exhibiting especially erratic behavior. Looking at the Retort Biochars as correlated by HTT provides additional insights, as shown below. In this plot, the CO₂ – DFT data is correlating with the 70% RH (relative humidity) data and the butane activity is correlating with the R134a adsorption, with the N₂ – BET exhibiting no apparent systematic trends for the limited data set.

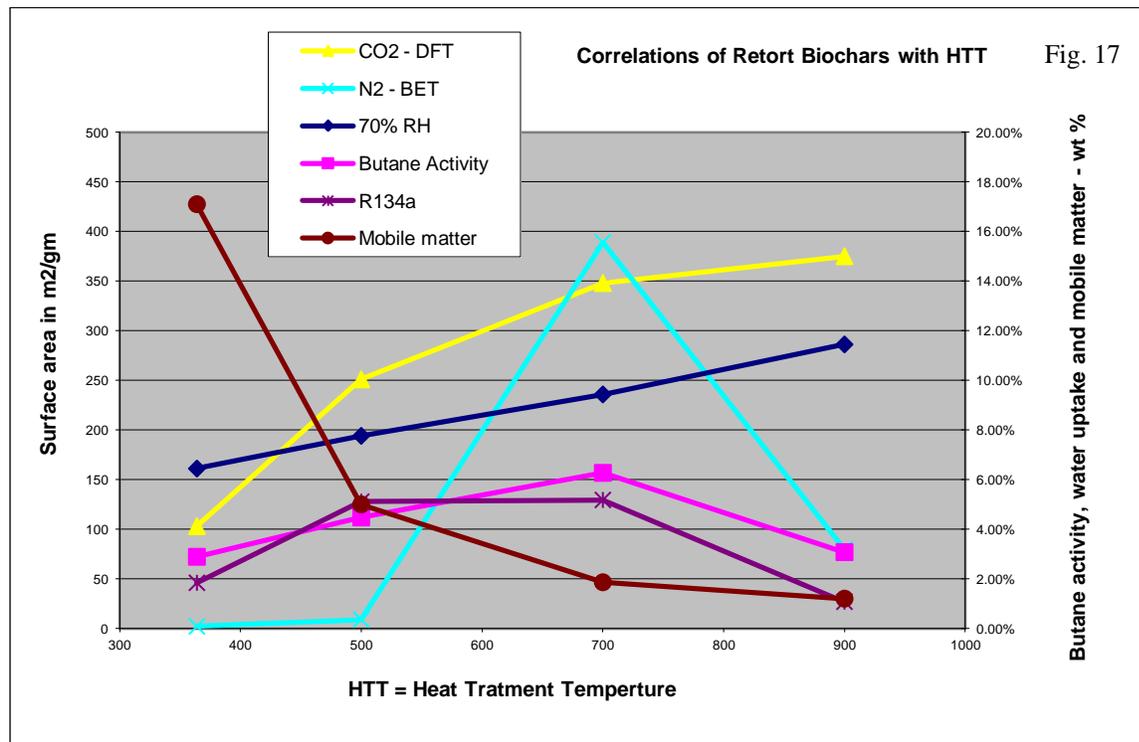


Figure 17 also shows the mobile matter levels measured in the Retort biochars. The mobile matter levels in all of the TLUD biochars were uniformly low, less than 2% for all samples. In contrast, the lower temperature Retort biochars have significant levels of mobile matter, representing a potential interference in the measurement of microporous properties, since mobile matter would be expected to reside in microporous sites within the solid media.

Observations and Conclusions

The paper set out to clarify the analytical options for measuring adsorption and surface area in biochars, and has ended up delineating exactly how difficult it can be to arrive at measurements that quantify one phenomenon without having interferences from other factors. One underlying driver is the variability that is encountered within a homologous series of biochars, created by varying one set of carbonization conditions and realizing that many things are happening simultaneously within the char. Biochars are basically a class of materials that extends from “over-torrefied biomass” to a molecular-scale mixture of ash and graphite.

It may be more appropriate to view biochar as a mixture of several discrete phases, composed of sparingly-modified biomass, bio-oils and condensates that form during pyrolysis and remain to an extent dependent on the carbonization conditions, and newly created clusters of graphene and graphitic complexes that may and may not overlap in space. Biochar is clearly a heterogeneous material, with variations on the molecular scale. The challenge is when one wants to measure a property that is functionally and quantitatively different in different phases. Thus, water vapor is taken up in elastic biomass by adsorption and in rigid graphite structures by adsorption, and both mechanisms are likely modified with by the presence of bio-oils.

The standard analytical methods assigned to adsorption and surface area are proven techniques developed and optimized for materials other than biochars. N₂ BET and CO₂ DR methods were developed to characterize catalyst supports and other rigid matrix materials, such as zeolites. Butane activity is intended to measure the ability of activated carbons to capture vapor phase organic solvents in the absence of interferences, such as in solvent recovery operations where a pure solvent is evaporated to leave behind a less-volatile material initially applied dissolved in the solvent. All these analytical methods have developed over many years and optimized to be accurate in very specific sets of conditions on proven materials. Unfortunately, biochar is a new material and none of the existing analytical methods were vetted with data generated by testing the properties of biochars.

Maybe the best outcome is a set of observations, based on what seems to be working better than other alternatives. Such as set of observations would include:

1. CO₂ at 0C is a better adsorbent for highly microporous carbons, providing more reliable measurements than N₂ at -196C because of the higher testing temperature. The diffusion into the pore and equilibration rates of CO₂ are much faster than N₂ at -196C for identical samples.
2. Butane Activity was the only measurement that captured the R134a measured loss of adsorption capacity at very high HTT in the Retort biochars. For situations where the analytical instrumentation are not accessible for CO₂ surface area, Butane Activity, as per the ASTM procedure, represents a reliable method to track trends in biochars.
3. CO₂ and water adsorption demonstrated an increase in capacity and micropore adsorption for the higher HTT retort Biochars which may be more representative of the true working capacity of these chars, but that will need to be determined with real world studies.
4. The size of the adsorbate molecules play a role in adsorption, potentially explaining why CO₂ and water, provide higher adsorption results for the high temperature Retort sample.
 - a. Nitrogen cross-sectional area is 16.2 Å²
 - b. CO₂ cross-sectional area is ~14.2 Å² (on carbon)
 - c. Water cross-sectional area is ~ 10.5 Å² (on carbon)
 - d. Butane cross-sectional area is ~ 39.5 Å²
 - e. R134a cross sectional area is ~ 34.0 Å² (calculated from liquid density at 25C)

5. The TLUD biochar standards exhibited a wide range of adsorption and surface area measurements that correlated well for all analytical methods. This is noteworthy, since the TLUD chars differed only in severity of carbonization conditions and insignificantly in all other elemental properties such as carbon content and mobile matter.
6. Lower HTT Retort biochars had unusual properties that may be attributed to the higher levels of residual bio-oils and mobile matter. Biochars with lower levels of non-graphitic carbon seemed better behaved in most analytical testing methods.

There is very little research indicating which property, be it adsorption versus surface area versus water uptake by absorption versus water uptake by adsorption, is beneficial, and to what extent, in various growing situations. If and when the soil scientists determine what properties are of most value in biochars, the process of refining the production conditions and measuring the desired properties will be greatly simplified. There is a high probability that all the “adsorption” or “surface area” measured by the current suite of analytical options is not participating in soil dynamics – because the test method included the particular property in the assay, but the soil does not actually exploit the property in the growing system.

In conclusion, this paper will not be the final word on measuring adsorption in biochars. In fact, we may never have the final answers, especially if we don’t know how to ask the final questions.

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