Characterizing Biochars prior to Addition to Soils – Version I, Jan 2010

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Biochar is a vague term that applies to a potentially broad class of charcoal materials intended for addition to soils. Many raw materials and conversion processes can lay claim to producing biochar, and the resulting biochars will have different characteristics. **The purpose of this discussion is to formulate a simple scheme for characterizing biochars before addition to soils.** Efforts will be made to discuss the logic behind the individual characteristics, in addition to the limitations of the individual assays.

The presentation and content here is consistent with the paper titled "All Biochars are Not Created Equal, and How to Tell Them Apart", by McLaughlin, Anderson, Shields and Reed presented at the North America Biochar Conference in Boulder, August, 2009. (**http://cees.colorado.edu/biochar_characterization.html**). However, this discussion is new, in the sense that it attempts to simplify the logic and methodology in order to arrive at a characterization strategy that is widely accessible to many practitioners.

The general characterization scheme breaks the biochar into a small number of constituent parts, consisting of: Moisture, Ash, Mobile Matter and Resident Matter. Each constituent part can be further subdivided, as will be discussed. Initially, we will discuss the significance of each portion, how it is measured and what the measurement represents. Then we will discuss additional biochar consideration when added to soils.

Moisture: Moisture is the condensed water and can include some highly volatile organic compounds that evaporate from a sample of biochar. For most biochars, the vapors driven off during drying are water vapor, but some biochars will have lesser amounts of low boiling organic solvents (below 105 degrees Centigrade), typically methanol and acetic acid, which are easy to detect from their odor. The amount of water present in biochar can vary greatly, depending how it is made and whether it has accumulated moisture during shipping. For biochars that are measured and transacted by weight, it is only necessary to define how much of the biochar is not water, so the moisture is measured and subtracted from the biochar to measure uniformly the subsequent properties on a "dry basis".

To attain a convenient standard of "oven-dry biochar," any free water in the sample is removed by drying it at 105 C until a constant weight (that is, when no further weight is lost when drying is continued). This is typically overnight in a drying oven with internal forced convection. Caution should be taken when drying biochar by a fixed external temperature oven, such as the 105 C drying oven, that the actual biochar has reached the oven temperature and is not significantly cooler due to the evaporating moisture. This is especially important for thicker samples that may lack effective vapor circulation through the biochar.

Unfortunately, the moisture removed at 105 C is only one portion of the actual moisture contained in a biochar sample. Most biochars are hydroscopic and many biochars exhibit significant adsorption capacity for water vapor. The hydroscopic nature of biochar may be due to water of hydration within the ash present in the biochar or it may also be water molecules

associated with the organic portions of the biochar, including adsorbed water vapor. In the "All Biochars" paper, associated with Figure 17, there is a discussion on the need to dry biochars to 200 C in order to remove adsorbed water. Higher drying temperatures are appropriate for determining "moisture-free basis", as opposed to "oven-dry basis", for a biochar.

When drying biochars above 105 C to remove additional moisture, significantly higher oven temperatures may be necessary. It is recommended that the drying oven be set for 25 degrees Celsius higher than the target drying temperature and the oven be turned off when the biochar internal temperature reaches the target drying temperature. The biochar should remain in the drying oven until the maximum internal temperature is measured and noted. If the biochar internal temperature exceeds the oven temperature, the biochar has initiated oxidation reactions and the drying study should be repeated at a lower oven temperature. The biochar should cool in the drying oven or a sealed container to avoid hot biochar readsorbing moisture from ambient air.

Once cooled, the dried biochar can be weighed. The weight loss data should be reported with the highest actual drying temperature, perhaps abbreviated as "<moisture>@200 C" or "The biochar sample was dried, <moisture>@105 C overnight", to convey an appropriate amount of information efficiently.

Moisture is relatively easy to measure, but requires patience, especially if drying wet biochar or larger quantities for subsequent testing for other properties. A simple toaster oven can be used, with a thermocouple buried in the center of the drying biochar to measure the internal temperature. The sample of biochar should not be sealed, but contained in a vessel with openings in the top and bottom, such as a small tin can or drying dish. The top of the biochar should be shielded from the direct radiant heating of the toaster oven heater bars, perhaps with a piece of aluminum foil over the biochar sample with perforations in the foil to let the excess moisture escape and allow vapor circulation.

During heating to above 150C, some biochars may exhibit incremental carbonization, emit significant volatiles, and even smoke. This is an indication that the biochar is not fully carbonized, and is composed of a portion of torrefied wood. Therefore, drying should either be performed in a laboratory hood or other well-ventilated area. Biochars containing significant portions of torrefied wood are likely to behave differently in soil than fully carbonized biochars, and that area of research is ongoing by the soil and plant scientists. At this juncture, if a particular biochar is not stable at 200C during drying, one has learned a relevant insight into that biochar and should proceed accordingly.

Ash: Once one has a moisture-free biochar, the next subset of interest is ash, as in the fraction of the moisture-free biochar that is not organic. Biochar may be defined as stable soil *organic* matter, meaning that the ash fraction is really outside the portion unique to biochar. Ash should be measured by heating the moisture-free biochar, finely ground, in an open top ashing crucible heated in a muffle furnace to 500-550 Celsius in an atmosphere of air for at least 30 minutes. Depending on the sample, even for finely powdered samples, ashing can take much longer than 30 minutes. Ashed samples typically are a pale gray powder and exhibit NO black particles of residual carbon residue. Samples should be stirred and re-ashed if there is any concern of uncombusted organic material. Since low ash numbers are desirable, it is in the interests of the char producer to correctly execute the ashing procedure. Ashing yields a very stable material, so

erring on the side of excess time at temperature, under controlled temperature limits, will have no detrimental effect on the ash content of the biochar sample.

Mobile Matter: Within moisture-free biochars there is a portion of organic matter that will not be permanent in the soil. It can be lost by leaching into the soil or by digestion by soil microbes, but it is not likely to be released as a gas. Therefore, instead of using the term "volatile matter" (which comes from analyses of coal where this matter does become gaseous at high temperatures), the analogous term is "mobile matter" in biochar. Mobile matter is the portion of the moisture-free biochar that may migrate from the biochar into the soil, and serve as a source of organics for the soil microbes. In order to more accurately partition the organic portion of the biochar into Mobile Matter and the permanent Resident Matter, the proximate analysis temperature is lowered to 450 C and the biochar heated for 30 minutes at this temperature. The Mobile Matter portion is that material that leaves from the bone-dry biomass, leaving behind the Ash and Resident Matter constituents of the biochar. Notably, the proximate analysis crucible is covered and the Mobile Matter driven off in a manner that excludes air, in order to avoid oxidation of the residual Resident Matter.

Another convenient way to measure mobile matter that entirely avoids the issue of partial oxidation is to use small stainless steel pipe nipples with both ends capped. The ends are loosely threaded, finger tight and backed off a quarter turn, without any pipe thread compound or teflon tape. The entire stainless pipe assembly can be dried and weighed, then filled with moisture-free char and closed, but not tightly sealed, to allow the mobile matter to escape. The pipe assembly can be heated to drive off the mobile matter, cooled and weighted without emptying the char out, which improves the accuracy of the test. A 2.5" long ½"npt stainless nipple and end caps weigh less than 200 grams and holds about 2 grams of char, so the entire assemble can be weighed on most analytical balances to 0.1 mg (0.0001 gram) and yield excellent accuracy on the mobile matter loss.

Resident Matter: Resident Matter is the portion of the moisture-free biochar that is not ash, but is expected to remain stable in the soil for a very long time. It is calculated by subtraction, being the portion of the moisture-free biochar that is not Mobile Matter and not Ash. This material is analogous to "fixed matter" determination in the field of coal science and has also been referred to as "recalcitrant matter" in ongoing discussions on characterizing biochar constituents.

Analytical Sequence: A sample of biochar is dried to 175 C to 200 C to create at least 25 grams of moisture-free biochar. A sample of moisture-free biochar is separately ashed at 500-550 Celsius in air and another sample is subjected to air-free heating to 450 C for Mobile Matter removal. The Resident Matter portion is calculated by subtraction of the Ash and Mobile Matter fractions from the moisture-free biochar fraction.

The Analytical sequence outlined above parallels the ASTM D-1762 procedure for Chemical Analysis of Wood Charcoal, except the temperature ranges have been modified, with the drying temperature raised to 175C to 200C and the ashing and mobile-volatile matter temperatures lowered because biochar is destined for soil and not for a thermal energy furnace. With experience, the relative merits of these modified analytical procedures will be established, and adjustments might be made.

The residue from the Mobile Matter analysis can be saved and tested for carbon content, yielding a measure of **Resident Carbon** contained in the Resident Matter portion of the biochar. This metric may prove useful in estimating the amount of carbon dioxide equivalent is represented by each unit of that biochar, with the weight of Carbon Dioxide Equivalent or "CO2e" being 3.67 times the weight of Resident Carbon. 3.67 represents the ratio of the molecular weights of carbon dioxide (CO_2 is 12 + 16 + 16 = 44) verses that of carbon alone (C = 12).

As mentioned above, one potential impact of Mobile Matter, upon being leached from the biochar, is its interaction with soil microbes. Depending on the soil and crops, additional soluble soil carbon may be good (by promoting microbial activity in the soil) or may have drawbacks (such as stimulating microbial competition for available soil nitrogen). In addition, Mobile Matter is not stable and will likely not be present in the soil after one or a few growing seasons. As such, Mobile Matter is likely of lower value in a biochar than an equivalent amount of Resident Matter.

Measuring biochar pH and TDS: The above set of tests breaks the sample of biochar into its constituent components and provides insight into the make up of the specific tested biochar. There are additional tests useful to predict the effect of the addition of the biochar to a specific soil.

Starting with a sample of biochar, a critical set of measurements provides insight into the short-term impact of adding the biochar to a specific soil. Those tests are pH and Conductivity, also known as Total Dissolved Solids or TDS. The first measurements are made on a sample created by mixing a portion of pure biochar with neutral pH water that has low conductivity. Ideally distilled de-ionized water is used, but DI water may be hard to obtain outside a research laboratory. Fortunately, many bottled waters are acceptably pure, consisting of purified tap water with small amounts of salts added for "flavor." One brand, Aquafina, is essentially bottled de-ionized water.

After obtaining a source of dilution water and measuring the starting pH and TDS with inexpensive handheld meters, a biochar slurry is created; one part biochar for 10 parts water by weight. Depending on the biochar, the biochar may take some time to become wet and release entrapped air. It is possible to approximately measure the biochar pH and TDS after a short mixing and settling cycle, although the floating biochar may influence the TDS measurement. Thus, initially, after mixing or shaking and then settling for ten minutes, the pH and TDS of the slurry are measured. If the TDS is extremely high, then serial dilutions should be made to estimate how severe the TDS contribution from the biochar will be to the soil.

Many biochars are difficult to wet for a number of reasons. Either the biochar has elevated levels of condensed hydrophobic oils and tars, or there is a significant fraction of torrefied wood in the biochar, or the biochar has a significant fraction of micropore sites that require water vapor to migrate and condense in the pores to "wet them out". The former two conditions are not favorable when using the biochar as a soil amendment, whereas the later is highly desirable. One method of differentiating between the bad and the good is to heat the biochar slurry to promote the migration of the water vapor into the pores.

A simple method of accelerated "wetting" of biochar borrows from the home canning practices of heating a canning jar, with the lid loose, in a pan of boiling water. Simply make up a 10

weight percent slurry of dry biochar in a pint canning jar, boil for 30 minutes in a covered saucepan with a small layer of boiling water, so the jar is surrounded by steam, Upon cooling, the microporous biochars will sink and the less desirable hydrophobic biochars will continue to float, providing a rough partitioning of the biochar components. Subsequently, the TDS and pH can be measured on the wetted biochar slurry, providing additional insight on the likely impact of the biochar when added to soil and allowed to equilibrate with soil moisture levels.

TDS and pH are measuring two different properties in the biochar slurry. TDS is a measure of the total dissolved salt content of the water, including all the fertilizers and neutral salts that are in solution. It is not necessarily a bad thing, but too much salt has an adverse effect on most plants. This is a significant concern with biochars made from sources containing manure, such as chicken litter. Biochars with significant ash content have a much greater likelihood of elevating TDS, since soluble salts are measured as ash.

On the other hand, soil pH is much more critical, especially if the biochar pushes the pH farther in an unfavorable direction, either to a high pH or too low. Many biochars have a significant "liming" effect and can elevate soil pH. For many soils, this is a good thing, but alkaline soils may not tolerate additional lime loading.

Initial pH and TDS measurements on the biochar-water slurry will give indications of how much of an individual biochar can be added to a given soil. As a further check, the actual proposed soil-biochar blend can be made up and this combination tested for pH and TDS. For a proposed soil-biochar blend, the pH and TDS are done at "saturation", where the slurry contains as little water as possible that still fully covers the soil and biochar solids, since the soil will not typically have a significant excess of free water except during rare rainfall events. Measuring soil properties at saturation are standard analytical methods used by soil scientists and it is anticipated that some standard soil methods will be adopted in the future.

This final pH and TDS tests are measuring the conditions that will actually be created in the soil for the potential soil-biochar ratio being tested. **As such, if the pH is unacceptable or the TDS increase excessive, the biochar should not be added to the soil in the portion being measured.** If unacceptable soil pH or TDS levels are predicted, either a lower biochar-to-soil ratio or utilize alternate source of biochar – and retest.

Additional Biochar testing: Additional tests for soil and plant compatibility are the "Germination test" and the "Worm avoidance test", which are discussed on pages 8 & 9 of "A Guide to Conducting Biochar Trials", by Julie Major, PhD, Extension Director for the International Biochar Initiative (see http://www.biochar-international.org/extension for Guide and additional discussions).

The final two properties of biochar that are broad indicators of biochar properties are Cation Exchange Capacity or CEC and Adsorption Capacity. CEC measures the extent that the biochar will behave like an ion exchange material. Adsorption capacity measures the extent that biochar behaves like activated carbon in the soil. The "All Biochars…" paper explores these properties in detail and the reader is referred there for that discussion. THE DISCUSSION ON ADSORPTION CAPACITY IS PROVIDED AS APPENDIX A.

One final biochar property that is expected to play a pivotal role in arid soils is the extent that biochar improves the composite soil's moisture retention capacity. This is an area where current soil research is developing appropriate methods and the reader is urged to let that research be completed before emphasizing this quality in a specific biochar. Furthermore, in growing situations where soil moisture is not limiting in plant productivity, the moisture retention impact of the biochar on the soil is expected to be of less consequence.

As a parting comment, every biochar added to soil should have a retained sample stored in case there is a need for additional analytical testing. Relatively dry biochar in a sealed jar will store at ambient conditions for years without significant change. A pint jar of a biochar sample is absolutely indispensable in determining what went wrong, or right, with a given biochar trial.

In conclusion, any biochar can and should be tested prior to addition to the soil. Some tests characterize the biochar and allow predictions of the relative performance in the soil. Other tests alert the user of undesirable soil consequences, including pH changes and elevated TDS, that may result from the biochar addition and lead to poor crop growing conditions. Since the tests are easy to perform and the consequences highly desirable to know in advance of adding the biochar to the soil, do the tests first, consider the test result implications and proceed accordingly.

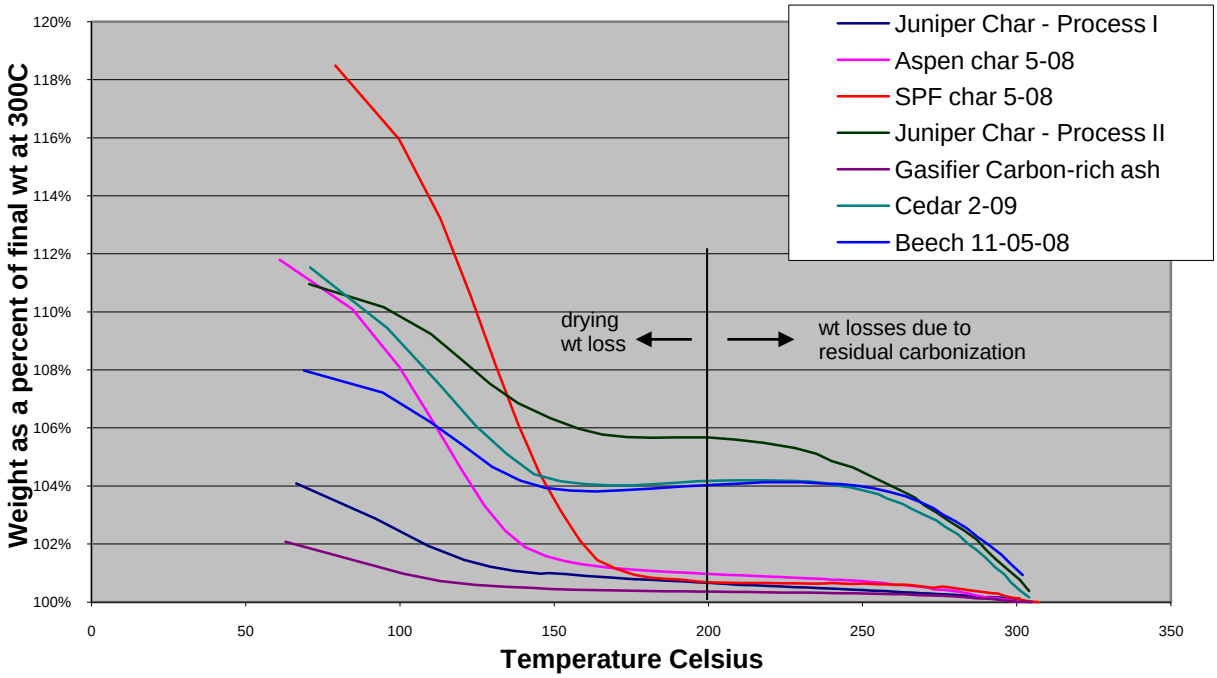
APPENDIX A: Section 7.3 of the "All Biochars" paper, Version 2, Oct 2009

7.3. Adsorption Capacity

Surprisingly, adsorption capacity is one test that is accessible to the home practitioner. It does take some practice and it helps if you obtain a sample of activated carbon to use as a standard reference. Small quantities of activated carbon are available at pet supply stores, since it is used in home aquarium filters.

The approach is to prepare a **very dry** sample of the candidate char, and then "challenge" it to adsorb a known vapor source. The drying of the char is critical, because adsorbed water will artificially lower the observed adsorption capacity. The drying method described previously is used, but the recommended temperature is around 200 degrees Celsius. The reason for the higher drying temperature is shown in Figure 17, which shows the weight losses of seven different char samples as they are heated from room temperature to 300 Celsius in a nitrogen atmosphere. As can be seen, there is a plateau in the weight loss between 175 C and 225 Celsius, which corresponds with the desorption of the adsorbed water vapor and any light volatile compounds such as methanol, acetic acid, acetaldehyde, etc., which also diminish the adsorption capacity of the char, resulting in an incorrectly lower measurement of the Adsorption Capacity.

FIGURE 17: WEIGHT LOSS CURVES FOR A SET OF SEVEN CHARS



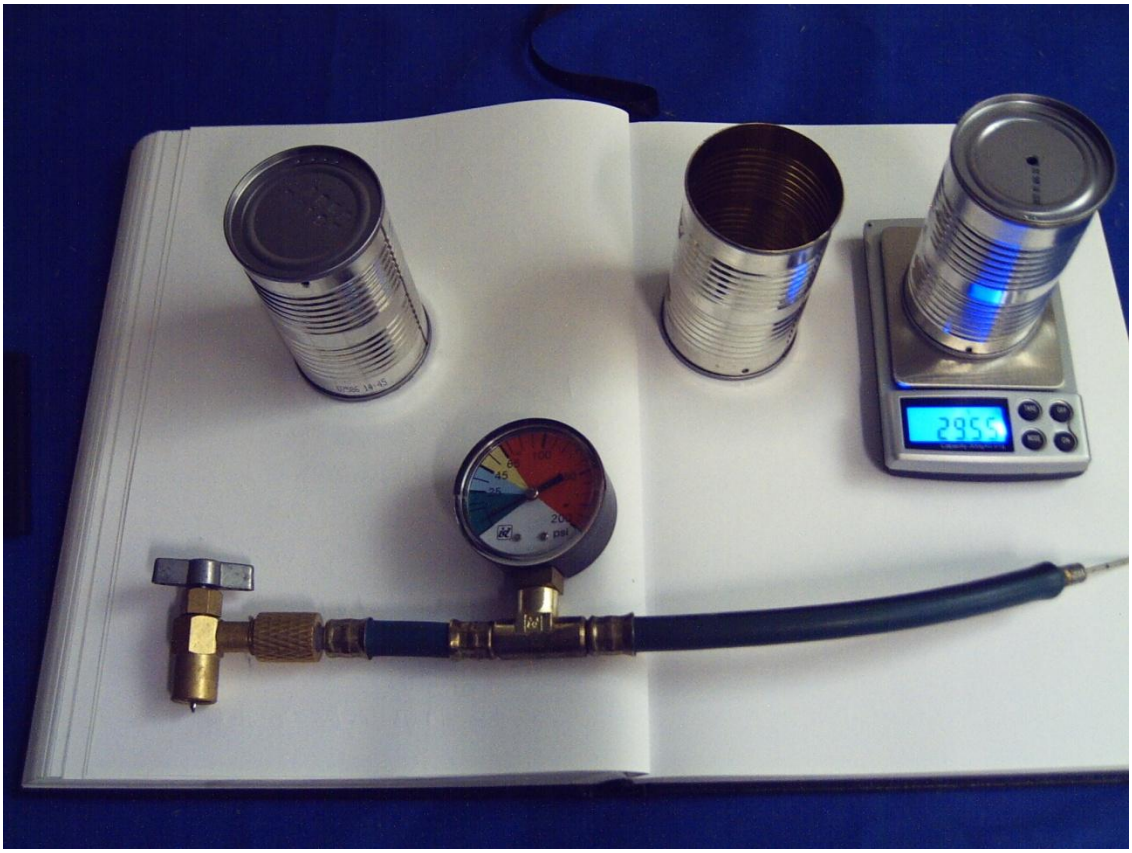
Prior to drying, the candidate char should be crushed and sieved to yield a coarse granular material, with granules between 1 and 5 mm in diameter. After the char is dried to approximately 200 degrees Celsius, it is cooled in a container with a sealed lid to avoid uptake of atmospheric moisture. Once cooled, a weighed clean dry tomato paste can is filled about one half way with dry granular char and weighed again.

The "challenge gas, R134a, is obtained from any auto supply store in a 12 ounce cans. An R134a dispensing device, with a metering valve and supply tubing, is also required. Modify the dispensing device by cutting the flexible hose and screwing an inflation needle used to pump up soccer and basketballs into the cut end of the hose. Inject the R134a slowly into the bottom of the tomato paste can through a small hole drilled in the unopened end of the can. As the R134a is admitted into the char, some R134a will be adsorbed and the heat of adsorption will be released – the container may get warm to the touch. The addition of R134a should continue until the char will adsorb no additional challenge gas. In general, the R134a addition can continue until the temperature of char returns to the starting temperature, since the excess R134a will enter as a cold vapor and eventually cool the char mass. A simple insertion meat thermometer can improve the accuracy of determining the endpoint of the R134a addition. The container should be shaken periodically to assist the equilibration process by mixing the char contents. When completed, the weight of the container, char and adsorbed R134a allow the calculation of the percentage of weight increase caused by the R134a.

In general, chars with good adsorption capacities show a noticeable temperature rise and significant weight gain, such as ten or more percent of the weight of the original char when the sample temperature is near ambient. In contrast, chars with low adsorption capacities (zero to four percent) will show little temperature rise during R134a addition and essentially no weight gain due to the adsorption of R134a. The difference becomes obvious with relatively little practice. The adsorption test conducted on activated carbon will yield very high percentage increases in weight and a noticeable temperature rise during R134a addition.

ADDITIONAL COMMENTS:

The Adsorption Capacity apparatus is shown below. The adsorption capacity assay can be quantified by terminating the test when the temperature of the adsorption returns to a fixed temperature, with 25 Celsius being recommended. An insertion thermometer in the center of the biochar sample can be used to monitor the temperature. When conducting the test, the addition of the R134a results in a temperature rise, which should be continued until the sample temperature returns to 25 C due to the cooling effect of the refrigerant being added to the biochar. At that time, the weight gain measured and reported as "R134a uptake at 25 C" in weight percent of the mass of dry biochar tested. As a rule of thumb, each weight percent of R134a gain at 25 C is the equivalent of approximately 20 square meters of BET surface area per gram of biochar.



Adsorption Capacity apparatus showing an inexpensive scale, accurate to 0.01 grams, is needed to weigh the samples. Acceptable units are available on "ebay" for less than $20 that read to 0.01 grams up to 200 grams.