All Biochars are Not Created Equal, and How to Tell Them Apart

Version 2 (October 2009), which supercedes the digital reprint issued at the
North American Biochar Conference, Boulder, CO – August 2009

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ABSTRACT

The use of charcoal as a soil amendment and for CO2 sequestration raises many questions about the characteristics of those "biochars" and their impacts on soils and organisms. This paper reviews and revises the analyses of the principal characteristics used to distinguish biochars, and presents a small survey of measured properties. Explicit terminology is proposed about "resident and mobile carbon and other matter" in biochars intended for addition to soils rather than for use as a fuel. Specific data are presented for commercial lump charcoals and Top-Lit UpDraft (TLUD) charcoals. Easy methods for informal testing of chars are presented to determine several key biochar characteristics. The major conclusions are: 1) Currently available biochars vary significantly in key properties, 2) Great attention should be taken to know the characteristics of any charcoals being added to soils, and 3) Reports of the responses (whether favorable or unfavorable) of plants and soils to biochar applications are of questionable value without corresponding knowledge of the characteristics of the applied biochars.

1. INTRODUCTION

Biochar is a term used to designate charcoal or biocarbon destined for addition to soils. As such, biochar is both a class of materials capable of sequestering carbon (CO2 equivalents) in soils and an ambitious goal of improving long-term soil productivity. Soil improvements attributed to the

addition of biochar include increased moisture retention, improved air permeability, elevated cation exchange capacity, increased buffering of soluble organic carbon, and synergistic interactions with soil microbial populations.

With many potential raw materials (called source feed-stocks) and multiple positive attributes, biochar remains an enigma. Its specific desirable properties are subject to debate and are the basis for ambitious ongoing research programs on what is important to the plants and soils. The goal of this paper is to review the key attributes of biochar and discuss the options for measuring said properties in any specific char that is being considered for addition to soil.

Potential biochar sources include conventional lump charcoal, residual char from open biomass burning (including forest fires), char residuals from gasifying stoves and furnaces, byproducts or co-products from fast and slow pyrolysis technologies, and carbonized biomass and agricultural residues manufactured in dedicated processes for specific feed-stocks, including chicken litter and bio-solids.

An informal but fairly exhaustive survey was made of readily available chars, and their differentiating chemical properties were measured. The trends and scatter in those measurements are discussed. Finally, options for informally testing candidate chars are presented. The unavoidable conclusion is that one knows what one is getting in a specific biochar only after the actual properties are measured, and never just because a supplier is claiming a product is suitable for use as a biochar.

2. BACKGROUND

2.1. What Biochar is Not

Much of the current understanding of the properties of biochar is derived from studies centered on the phenomenon known as “Terra Preta” in the Amazonian rainforests. Unfortunately, because of the anthropogenic nature of the ancient Terra Preta sites, it is difficult to reconstruct the causes and effects that created the enduring soil productivity that modern biochar seeks to replicate and possibly improve. However, some insights can be gleaned from the properties of carbon-rich substances and their observed effect in soils.

Biochar is carbon-rich, containing significant fractions of amorphous graphitic domains (as in “tiny pockets”) and additional organic carbon properties discussed below. The graphitic domains within the biochar have been documented to be stable in the soil for millennia, including samples isolated from historic Terra Preta sites. Although one might postulate that the presence of the graphitic carbon atoms results in the unique biochar properties, the answer is “likely not.” If the cause of improved soils were merely the presence of graphitic carbon atoms, then “carbon black” or “tire black” materials would perform similarly in the soil – which has never been observed. Neither have beneficial effects of coal residues in soil been observed in places where coal dust has been spilt over the ages.

Biochar also has properties and molecular structures that resemble activated carbon, a common industrial material that possesses unique adsorption properties for vapor and liquid phase organic molecules. As will be discussed, adsorption properties are believed to play a significant role in biochar phenomena, but adsorption effects alone do not account for the composite of observed biochar attributes. If adsorption alone were the dictating phenomenon, then powdered activated carbon would be the ultimate soil amendment – which is also not observed.

For example, Norit, an international activated carbon company, does market a product known as "GroSafe", which is a fairly typical powdered activated carbon product (see http://www.norit-americas.com/pdf/GroSafe_rev4.pdf). However, the technical literature explains its role in the soil to be for removing toxins, such as herbicides. As such, powdered activated carbon may be helpful in those locations where toxicity is present in the soil, but its efficacy does not extend to the other biochar attributes.

Similar logic can be applied to many common carbon-rich substances, such as shredded tires and pulverized plastics, etc. – and none of them exhibit any properties even vaguely similar to those of biochar. To the contrary, detrimental impacts on plants and soils are often observed. As such, little can be inferred in desirable biochar properties by observations of other natural and synthetic carbon-rich materials.

2.2. What Biochar is

Without intending to make a rigid definition, biochar can be broadly characterized as "thermally-modified biomass". This description is more of an acknowledgement of how the vast majority of existing biochar found in soils was formed than an actual requirement to qualify a material as biochar.

The thermal modification of biomass is significant because it results in a pivotal property of biochar – the ability to persist in the soil by not being susceptible to biological decay. Persistence basically makes biochar a soil "catalyst", in the sense of facilitating reactions beneficial to the soil dynamics, and not a consumed raw material. Soil raw materials are substances like fertilizers and other components that are either assimilated by living systems (plants, soil microbes) or gradually transformed, such as in the case of the breakdown of peat moss, compost or manure in soils.

In the absence of thermal modification, essentially all forms of biomass (plants, animals and microbes alike) are 100% biodegradable. This conclusion is based on the impossibility of the inverse: that some portion of biomass is not biodegradable. If a fraction of biomass were not biodegradable, no matter how *de minimus*, it would accumulate over the course of millions of years and easily be detected, perhaps even overwhelming the masses of renewable but biodegradable biomass.

It is important to recognize that biomass and biodegradability exist and operate in a relatively narrow temperature range – roughly 50 degrees Celsius on either side of room temperature. Below that temperature range, biological processes grind to a halt, and above that temperature range, the biological organic complexes thermally denature and lose their ability to function.

Within this biologically active temperature range, unmodified biomass is in a constant state of flux – growing, drying, and being recycled. Essentially every repetitive, biologically-created chemical structure and bond system present in living matter can be broken down and reused by other living species. This is why thermal modification, as in the conversion of biomass into charcoal, is so critical for providing persistence of carbon in the soil by inhibiting its biological degradation.

The specific thermal modification that converts biomass into biochar can be viewed from two closely related perspectives called "pyrolysis" and "carbonization". The pyrolysis perspective focuses on the chemical breakdowns that result in the liberation of pyrolytic gases. The carbonization perspective focuses on the chemical build-ups of the carbon atoms into solid structures. The bulk of pyrolysis and carbonization reactions occur in the temperature range from about 200 to 500 degrees C. One can think of pyrolysis and carbonization as simultaneous physical-chemical processes, changing the biomass into pyrolytic gases and charcoal.

At sufficient temperatures, generally above 300 degrees C, carbonization modifies the chemical bonds within the remaining solid such that they are less likely to be consumed as foods by living systems. The chemical bond modifications consist of dehydration, conversion of aliphatic bonds into aromatic bonds, and the consolidation of those aromatic bonds into local graphene complexes (http://en.wikipedia.org/wiki/Graphene). Living systems use enzymes to facilitate individual chemical reactions, and enzymes are very specific to the unique structure of the chemical bond being transformed. Carbonization randomizes the chemical bonds, creates locally varying molecular structures, and creates a much larger percentage of stable graphene chemical bonds. This diversity of chemical structures and overall greater bond stability thwarts the ability of living systems to supply appropriate enzymes to transform the carbonized bond structures. In a sense, carbonization converts biomass into a new form, termed biochar, which is more difficult to digest for the microbes - especially if there are sources of more palatable uncarbonized biomass available.

This raises a question: If a portion of carbonized biomass is immune to biological decay and if natural forest fires generate additional carbonized biomass on an ongoing basis, why isn't the world chock-full of accumulated persistent biochar? The basic reason is that there are very slow, non-biological, ambient temperature reactions between carbonized biomass and atmospheric oxygen, which slowly degrade exposed graphene bonds over the course of thousands to millions of years. As a result, long-term stable fossil carbon reservoirs of oil and coal are only found under anoxic conditions, buried deep in the earth and far from any oxygen. Even at ambient temperatures, oxygen is reactive with all carbon-carbon and carbon-hydrogen bonds, given enough time.

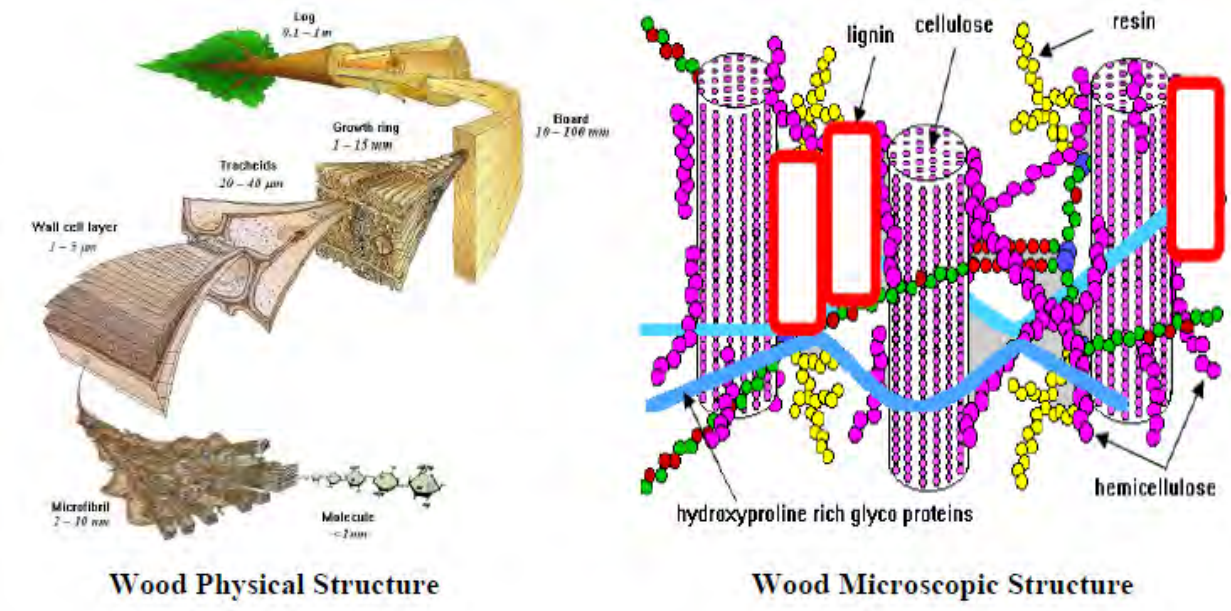
3. CONVERTING BIOMASS TO BIOCHAR

Before delving into the qualities and measurable properties of available biochars, it is useful to briefly review the conversion process that transforms biomass into biochar. Since we are interested in the biochar, the residual solid, we will focus on the carbonization reactions. The

carbonization process will be described for the most common application, which is the conversion of wood-derived ligno-cellulosic biomass into charcoal, but the carbonization reactions apply to any carbon-rich previously-living material.

Woods is primarily a combination of hemicellulose, cellulose and lignin, with trace resins and inorganic salts. While accurate, this description under-represents the molecular-level complexity of the plant structure, as depicted in Figure 1.

FIGURE 1: PHYSICAL AND MICROSCOPIC STRUCUTURE OF WOOD



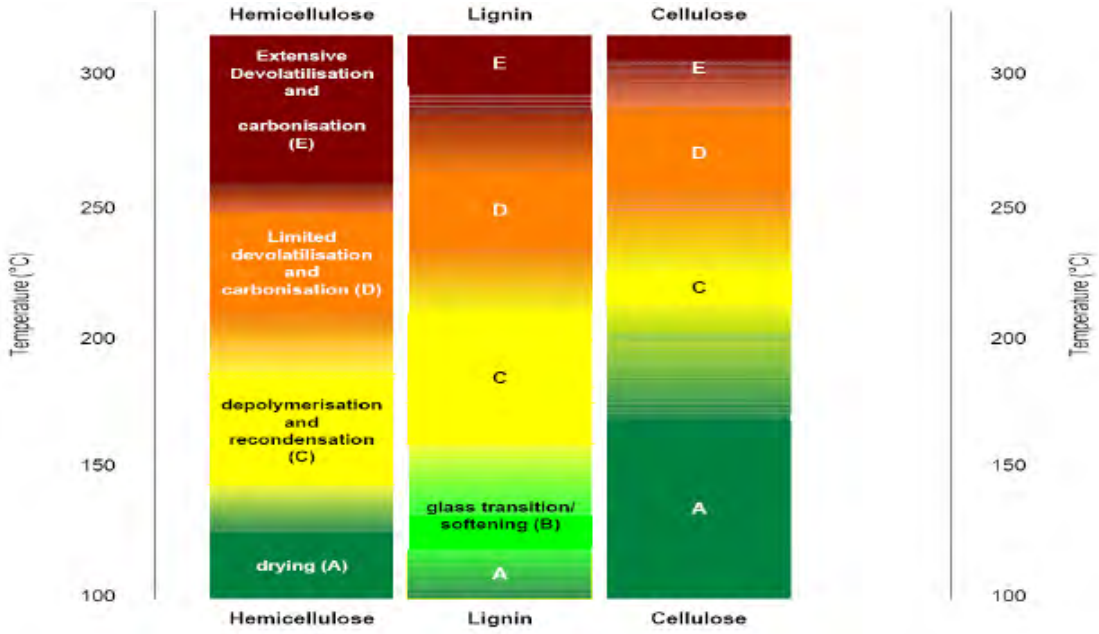
From: http://www.techtp.com/Torrefaction for High Quality Wood Pellets.pdf, page 7 of 36

During carbonization, the various components of the biomass are modified by chemical transformations that occur within specific temperature ranges. All of these transformations are basically initiated by the instability of the individual chemical bonds within the biomass at the elevated temperatures involved in carbonization. Realizing that living things spend their entire formative and functional lives in a very narrow temperature range, it is not surprising there occurs a wholesale rearrangement of biomass as the temperature rises significantly above ambient. Consider the dramatic changes that occur when cooking an egg that becomes hard-boiled by simply raising the biomass to only 100 degrees Celsius for a short period time without the loss of moisture from inside the shell. Analogously, but at much higher temperatures, carbonization takes that thermal transformation process of biomass through many phases, as shown in Figure 2.

As can be seen in Figure 2, all three of the major components of biomass (hemicellulose, lignin and cellulose) are thermally transformed between 200 and 300 degrees Celsius. Figure 2 depicts the principal decomposition reactions, where the individual constituents of the biomass

"devolatilize" and release a mixture of gases, known as volatiles, and "carbonize" to form a more carbon-rich residual solid, which is the char.

FIGURE 2: THERMAL MODIFICATIONS OF WOOD CONSTITUENTS



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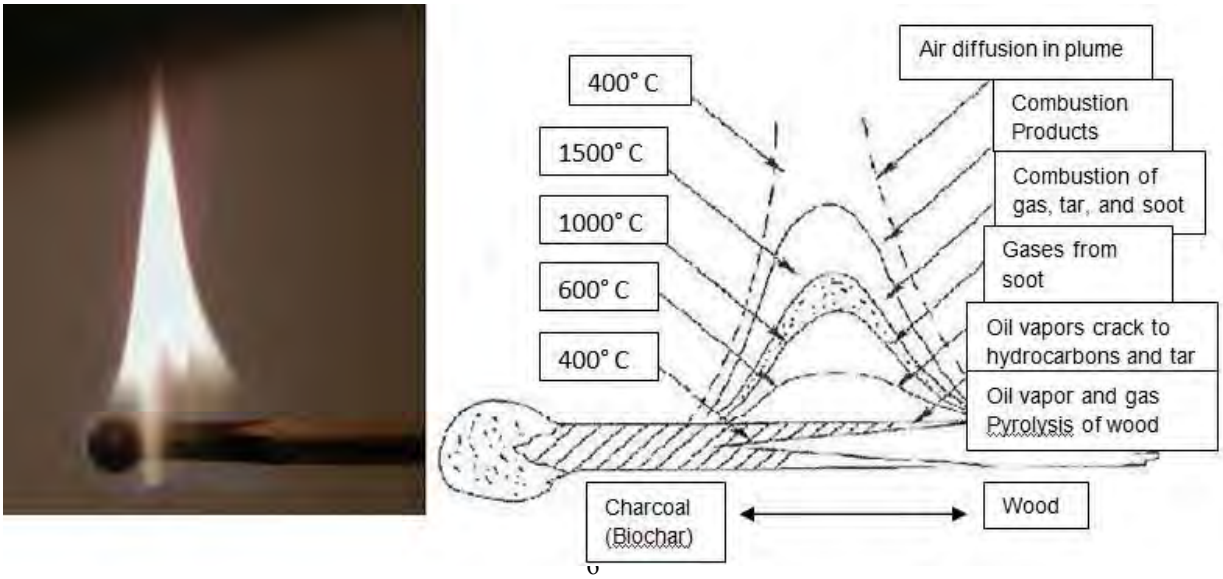
With terms like depolymerization and devolatilization, the molecular-level science may seem much more complicated than the everyday applications of the phenomena. Figure 3 shows a simple example of the entire carbonization process – the burning of a wooden match. As the flame progresses along the wooden match, it heats the wood and drives off the volatiles, leaving the carbonized char as the residual solid.

FIGURE 3: A MATCH CONVERTS WOOD INTO CHAR AS IT BURNS



Another common example of carbonization is the burning of dry wood, such as campfires - especially if the fire is quenched with water, saving the glowing charcoal from being turned to ash. A more dramatic example is the "toasting of marshmallows – gone wrong", where the roasting marshmallow catches fire and converts [carbonizes] into a residual mass of crispy char while the soft white center generates a fireball of volatiles that rapidly burn in the available oxygen from the air. Note that in all of the above cases, a solid charcoal remains, meaning that the reactions of the residual graphitic carbon atoms with oxygen, called char-gasification, is not taking place. If char-gasification occurs, the char is converted to ash and the carbon atoms are converted to gases, mainly carbon dioxide and lesser amounts of carbon monoxide.

4. DISSECTING BIOCHAR INTO PROXIMATES AND ULTIMATES

4.1. Overview

One of the challenges in characterizing biochar as a class of materials is that it is new and unique in the world of material testing. Until biochar is understood sufficiently to establish the hierarchy of preferred properties, it will have to be characterized by established tests that were developed for other materials. One such standard set of tests is the ASTM procedures intended for the characterization of solid fuels, especially coals. These procedures can be applied to charcoal that is intended for burning and such testing yields appropriate measurements, as they relate to the burning of charcoal as a fuel.

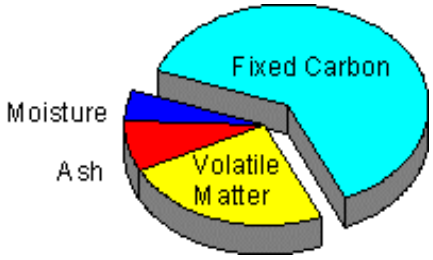
Two popular ASTM tests for coals, known as Proximate and Ultimate Analyses, measure how a specific coal or coal-like sample will perform when utilized in a solid fuel combusting process. Figure 4 summarizes the basic breakdown of the Proximate and Ultimate Analyses as developed for the characterization of coals.

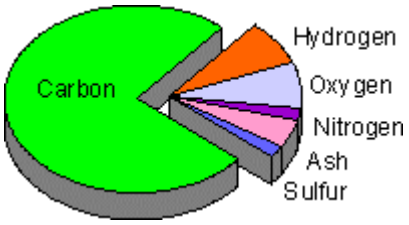
The principal shortcoming of using coal characterizations for biochar comes down to different destinations for the two materials. Coal is a fuel, and the ASTM coal tests measure properties that predict performance when used as fuel, especially the amount of available thermal energy. Biochar is a soil amendment that will not be subjected to high heat. As such, the coal tests are measuring properties of the biochar that would be relevant were it to be burned like coal, which is unlikely. Still, the basic partitioning of properties associated with coal analyses has merit in differentiating biochars, subject to some minor modification of the testing procedures and associated interpretation of the testing results, as will be discussed.

FIGURE 4: PROXIMATE AND ULTIMATE ANALYSES OF COALS

Proximate Analysis
Determines (on an as-received basis)

- **Moisture content**
- **Volatile matter** (gases released when coal is heated).
- **Fixed carbon** (solid fuel left after the volatile matter is driven off, but not just carbon).
- **Ash** (impurities consisting of silica, iron, alumina, and other incombustible matter).





Source: U.S. DOE - EIA, Coal Data: A Reference, 1989.

Ultimate Analysis
Determines the amount of carbon, hydrogen, oxygen, nitrogen, and sulfur.

- **Btu -** Heating value is determined in terms of Btu both on an as-received basis (including moisture) and on a dry basis.
- The carbon is from both the volatile and fixed matter, not differentiated.

From: http://www.coaleducation.org/ky_coal_facts/coal_resources/coal_properties.htm

4.2. Revising Testing Conditions to facilitate the Interpretation of the Data

When coal is combusted, the incoming pulverized coal fuel enters the combustion chamber and virtually instantly is heated to over 1000 degrees Celsius. In that environment, the coal powder immediately dehydrates, releases all the volatiles that will vaporize at 1000 degrees Celsius, and the remaining mass consolidates into volatile-free "char" particles. The volatiles burn rapidly in vapor-phase reactions and the char particles burn like miniature charcoal briquettes, where the oxygen in the combustion air reacts on the surfaces of the particles in a diffusion-controlled regime often called "glowing combustion". Furthermore, any ash remaining after coal combustion has been exposed to temperatures as high as 2000 degrees Celsius, and never less than 1000 degrees Celsius.

As such, the coal tests seek to partition the composite coal into moisture, "volatile matter" that vaporizes as the mass is heated up to 1000 degrees Celsius, "fixed carbon" representing the amount of incoming coal that converts into char and burns as such, and ash, in a form representative of what will remain after the combustion process. For these reasons, the volatile matter test heats the coal up to 950 degrees Celsius in an inert atmosphere and any matter that exits is considered volatile matter. The ash is liberated/generated by exposing the coal to air at

800 – 900 degrees Celsius until all the available carbon is reacted to carbon dioxide and any metal salts are converted to the corresponding metal oxides. The resulting ash accurately represents the ash that exits the coal combustion process under conditions of complete carbon burnout. It should be noted that the "Fixed Carbon" portion of the coal proximate analysis is not pure carbon; it is whatever is not ash and does not volatilize at 950 degrees Celsius.

Coal proximate analyses are readily available from commercial laboratories and not too difficult to perform in any lab with a muffle furnace, appropriate crucibles and an analytical balance. Unfortunately, the partitioning of a biochar sample into coal proximate analysis fractions does not provide much insight into how biochar actually partitions when used as a soil amendment, that is, when the char is subjected to temperatures and conditions that are encountered in soils.

Therefore, we propose and present below a *modified thermal analysis methods* to yield more insight into the metrics relevant to distinguishing one biochar from another. The modifications are adjustments of the temperatures utilized during testing to be more aligned with the temperatures encountered during pyrolysis and carbonization. The specific modifications presented here are not cast in stone and may well be further manipulated as better insights into pivotal biochar properties are developed. At this juncture, we are trying new things and seeing what can be measured and subsequently interpreted.

To avoid confusion with the standard ASTM tests for coal, we call our methods "Modified Proximate Analysis" and "Modified Ultimate Analysis". When these analyses were performed and reported for this paper, we made the following changes in the analytical protocol:

1. The term "Fixed" is changed to be "Resident." Resident does not mean absolute permanence in the soils, but half-life of over 500 years seems to justify the "resident" terminology. Others have used the word "Recalcitrant," but that does not have a specific connotation and seems a bit esoteric.

2. The term "Volatile" is changed to be "Mobile," as in "being able to be removed, but not necessarily being made into a gas". Mobile means a lack of permanence, as in the case of hydrocarbons that can be digested by microorganisms. Others have used the word "Labile," but that has the same communication issues as "Recalcitrant".

3. The grouping "Fixed Carbon" was renamed "Resident Matter." The difference between "fixed" and "resident" has been explained above. The usage of the term "matter" is to allow a partitioning in the ultimate analysis test of the carbon fraction separate from the non-carbon fraction of the resident matter. In summary, Resident Carbon plus Resident H & O (plus typically inconsequential other chemical species) is equal to the total Resident Matter (formerly grouped as Fixed Carbon in the terminology of proximate coal analyses).

4. Similarly, "Mobile Matter" is the sum of "Mobile Carbon" and "Mobile H & O."

5. The threshold temperature for vaporizing the Mobile Matter away from the Resident Matter has been lowered to 450 degrees Celsius.

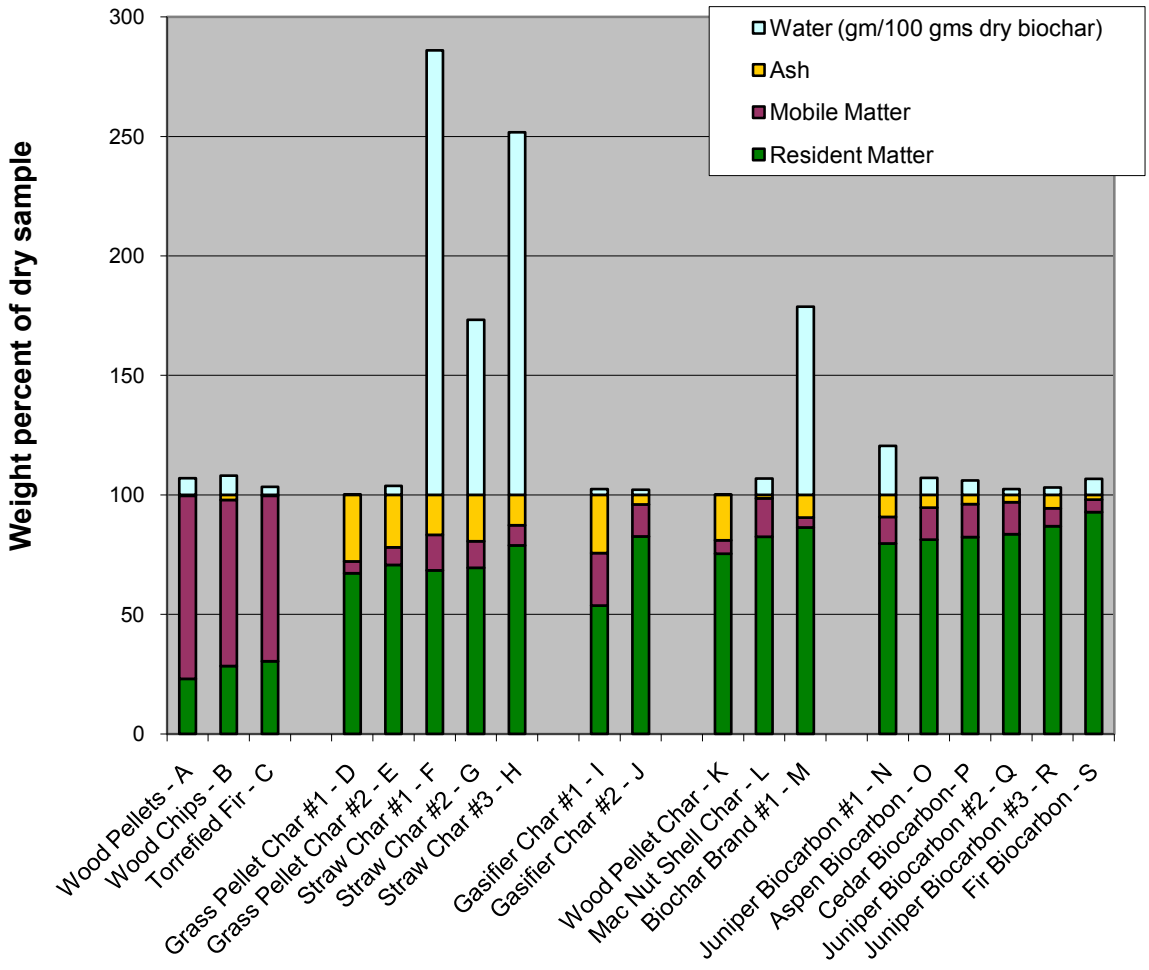
6. The ashing temperature, in the presence of air, is performed at 500-550 Celsius. This temperature range produces a Mobile Matter fraction that minimizes additional generation of volatiles by the incremental carbonization of the biochar sample, which occurs whenever a char is heated above the highest treatment temperature (HTT) that the char has previously experienced during production. The lower ashing temperature also avoids converting the alkaline hydroxides and carbonates into metal oxides, thereby potentially providing a more representative sample of the ash present in the biochar sample.

   The drying of the biochar samples remained the same as in the coal assay, with drying in the presence of air at 105 Celsius until stable sample weight is obtained.

4.3 Test Results Using the Modified Proximate Analysis

Nineteen representative biomass and biochars were tested with the Modified Proximate Analysis and the results are shown in Figure 5.

FIGURE 5: MODIFIED PROXIMATE ANALYSES OF CHARS



The sample set used for Figure 5 is not comprehensive of the universe of potential biochars and the data is from a single measurement of each sample. But the data serve to demonstrate the diversity of measured properties. Figure 5 has the main constituents of chars normalized to provide the portions on a dry sample basis, with residual water presented above the 100% level. Residual water is not an intrinsic component of a char, but is due to post-carbonization practices such as cooling with water addition or storage and transport conditions that allow hydroscopic chars to acquire moisture.

The chars in Figure 5 appear in groups broadly representative of the major types of raw materials and chars. The three entries (A, B, C) on the left of Figure 5 are pre-carbonization materials and reveal very high mobile ("volatile") and corresponding low resident ("fixed") portions. The five grass pellet and straw chars contain elevated levels of ash associated with the potassium and phosphorus typical of grasses as compared to wood-derived chars. The two gasifier chars (I and J) reflect the specific conditions of the gasifier operation, with more aggressive conditions leading to higher ash levels as more of the carbon portion of the biomass is reacted away [char-gasified] into the vapor phase. The three middle chars (K, L, M) are from various raw materials and processes and reflect the specifics of the individual manufacturers. The six wood-derived biocarbons on the right are from a single carbonization process, so the variability is associated mostly with the source biomass. Wood-derived chars generally have low levels of ash, although elevated ash may appear in the char if the wood is contaminated with soil during harvesting and/or transportation to the biocarbon conversion facility. In general, the specifics of an individual char derive from a combination of the properties of the starting biomass and carbonization conditions, with most factors being within the control of the various biochar producers.

4.4. Test Results Using the Modified Ultimate Analysis

The focus of ultimate analysis testing is to measure the individual chemical levels in the composite sample to gain further insight into specific properties that are of interest during the use of the substance. For coal, that means measuring the elements shown in the second half of Figure 4, with the goal of calculating the heating value or total energy content of the coal. The name "ultimate" is somewhat of an historical misnomer, because in a world prior to expensive analytical instruments, "ultimate analysis" techniques were much more work than the "proximate analysis" and were considered to be about as much as could be known about a sample of coal.

The Modified Ultimate Analysis of biochars builds off the same analytical measurements as for coal, but since biochar is not intended for use as a fuel, we need to rethink what we are learning from the partitioning of the char into individual elements or chemical classes. Furthermore, depending on the source of the biomass for the char, there are some chemical species, particularly sulfur, that are unlikely to be present at significant levels in the resulting char, but are a major concern in coal.

For this paper, a conventional analytical instrument, a LECO Corporation CN2000, was used to combust a small dried sample of char and to measure the level of carbon dioxide and nitrogen oxides in the off gases. By calibrating the instrument on known standards, the instrument calculates the weight percentages of carbon and nitrogen in the original sample. By coupling the

ultimate analysis with the proximate analysis, after subtracting out the moisture and ash levels in the sample, one can determine the relative portions of carbon, nitrogen and, by difference, any remaining organic fraction in both the mobile (volatile) and resident (fixed) matter. The remaining organic fraction represents the sum of the hydrogen, oxygen and sulfur in the sample. Since sulfur is expected to be present at negligible levels, the organic fraction is interpreted to represent the sum of the weight of hydrogen and oxygen in the sample. For clarity, it is labeled as "Resident H & O" and "Mobile H & O" in the figures.

In addition to low sulfur levels, most chars exhibit low nitrogen levels, attributed to the loss of nitrogen from the char as either ammonia or oxides of nitrogen during the carbonization process. The figures do include "Resident N" and "Mobile N" measurements, but they are usually so minor that it is hard to visualize and can normally be neglected or included in the "H & O" portion of biochars derived from relatively clean biomass sources.

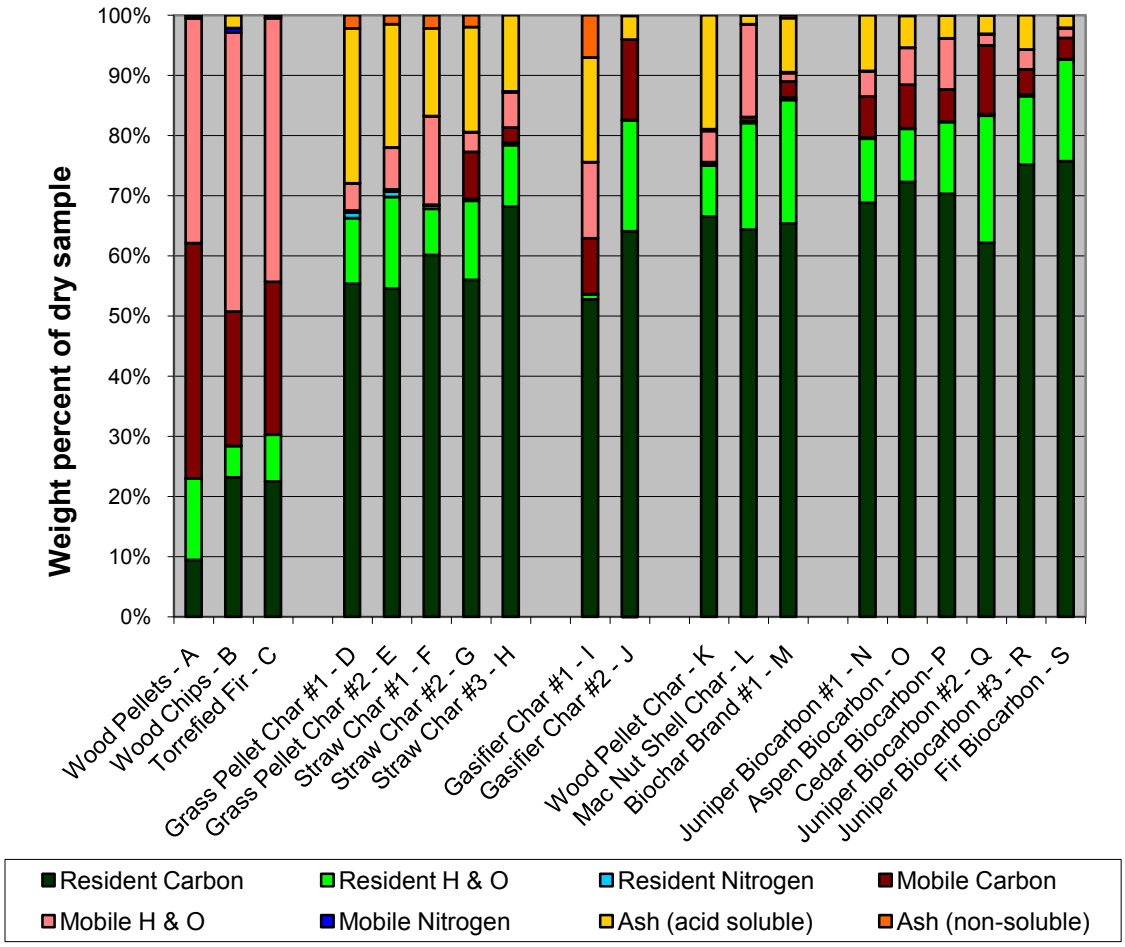
As such, the major partitioning that emerges in the biochar "Modified Ultimate Analysis" is to divide the char sample into 1) the "Resident Carbon" portion of the Resident Matter, 2) the hydrogen and oxygen portion of the Resident Matter, called "Resident H & O", and the analogous 3) Mobile Carbon and 4) Mobile H & O portions of the Mobile Matter. Since the proximate analysis isolates a pure ash sample, it is also possible to evaluate 5) the acid-soluble ash and 6) acid-insoluble ash by acidifying the acid and recovering the acid-insoluble fraction. 7) Resident N and 8) Mobile N can also be detected, but are often in amounts too small to be of significance in plant and soil science.

The ultimate analyses of the nineteen samples from Figure 5 are shown in Figure 6. It should be kept in mind that Figures 5 and 6 represent a very small set of samples, with only one or two samples representing whole classes of chars. As such, the reader is cautioned from drawing overly broad conclusions from such a limited number of actual analytical results. However, it is clear that the various components of the char samples can be dissected into a finer group of chemical partitions by use of "modified proximate and ultimate analyses" evolved from the analytical methods for coal.

A word of caution is necessary with respect to the ash levels indicated in Figures 5 and 6. Figure 6 shows the total ash of Figure 5 broken into two fractions (acid soluble and non-soluble), and the acid soluble fraction is always the majority of the total ash from uncontaminated wood. One needs to question the origin of the acid soluble ash fraction, especially in biochar derived from clean wood. Most of the ash in clean wood is made up of phytoliths, which are silica that has gone up into the tree to provide structure and support, and cations (sodium, potassium, calcium and magnesium) that form neutral salts with available anions, such as bicarbonates, carbonates, bisulfates, sulfates, hydroxyl groups, etc.

The concern is that the ashing conditions used in the analytical procedure may convert the cations from one salt form to another, whereby changing the molecular weight of the salt and weight contributed to the ash content of the biochar sample. For example, sodium hydroxide (molecular weight 40) could be converted to sodium carbonate (molecular weight 84) under the conditions of the ashing test. Thus, any sodium hydroxide would generate a weight of ash a little over twice the actual weight of sodium hydroxide in the original biochar.

FIGURE 6: MODIFIED ULTIMATE ANALYSES OF CHARS



As such, it is recommended that the absolute magnitude of ash measurements in biochars be taken with the proverbial "grain of salt", especially the acid soluble fractions. Higher ash levels generally mean that higher levels of non-organic "something" are present in the char. What those ash constituents are, and whether they could impact local soil conditions, needs to be understood before utilization as a biochar.

We suspect that much of what the tests show to be ash is actually closely held in the resident matter, therefore behaving in soils quite differently if applied as part of the biochar versus being applied as loose ash, with potentially significantly different rates of release and consequences over time on the soil, plants and microorganisms.

Similarly, the pH of an ash sample can reflect the conditions of the ash formation during the analyses more than the actual pH of the original char at carbonization temperatures. Furthermore, the pH of fresh biochar samples may not accurately reflect their pH impact in the soils, especially after the biochar has equilibrated with atmospheric carbon dioxide, which converts many of the alkaline hydroxides into corresponding carbonates and shifts the pH lower.

5. ADDITIONAL PIVOTAL BIOCHAR PROPERTIES AND ANALYTICAL TESTS

Two additional biochar properties are believed to be pivotal in the unique properties of biochar in the soil; these will be discussed at length.

The two remaining biochar attributes are a challenge both to measure analytically and to understand their role in the soil. They are known as Cation Exchange Capacity, or CEC, and Adsorption Capacity. Conceptually, the former is the extent to which biochar has ion exchange properties and the later is the extent that biochar has activated carbon properties. Many biochars exhibit significant and measurable amounts of CEC and adsorption capacity, and these properties may lie at the heart of the unique and dynamic role of biochar in the soil.

5.1. Cation Exchange Capacity (CEC)

Cation Exchange Capacity takes a sample of char and converts all the cations to one form, then displaces them with another cation, and finally quantifies the displaced cations to measure the CEC. The CEC method used for this paper consisted of the following procedure:

> A sample of dried char is shaken/centrifuged/drained three times with sodium acetate solution, then shaken/centrifuged/drained with 2-propanol three times. The alcohol rinse removes excess cations present in solution, but not bound to the char. The sodium-loaded char is then shaken/ centrifuged/drained with ammonia acetate solution three times. The total solution from the three ammonia acetate rinses is measured for sodium level and the CEC calculated in milli-equivalents per 100 grams of dry starting char.

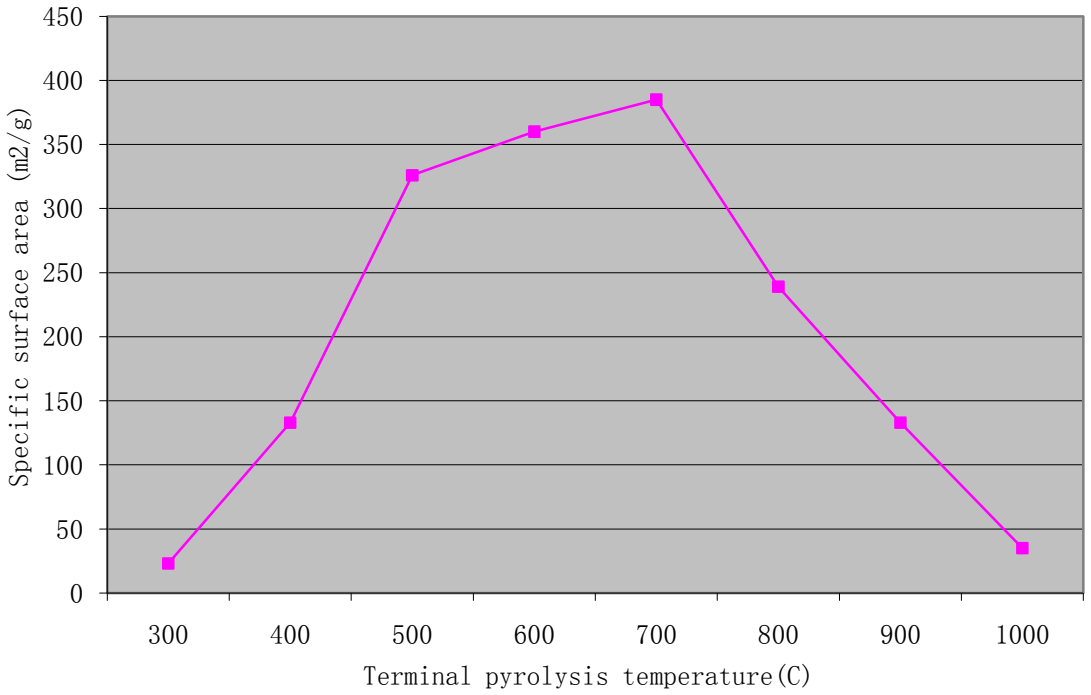
CEC is not a very common analytical test and exact procedures vary from lab to lab. As such, this analytical test will benefit from additional methods-development work. Better and more standardized CEC methods, specific for biochar, are anticipated in the future.

Further complicating predicting the roll of CEC in a specific biochar is the documented development of additional CEC within the soil over time and depending on soil conditions (see "Oxidation of black carbon by biotic and abiotic processes", C.H. Cheng et al. / Organic Geochemistry 37 (2006) 1477–1488). As such, it is likely that measuring the CEC of a char determines the current level of the CEC property at the time of measurement, but does not indicate what additional CEC may come into existence in the future.

5.2. Adsorption Capacity

Adsorption Capacity is another property that is poorly understood in biochar. One characteristic of the adsorption capacity phenomenon in chars is shown in Figure 7, where a sequence of chars, carbonized over a range of Higher Treatment Temperatures (HTT), shows a dramatic variation of measured BET surface area. [Note to readers: BET stands for Brunauer-Emmett-Teller, the three scientists that published the method in 1938. Although the BET measurement has some limitations that we discuss shortly, it is a useful measurement for this initial discussion of surface areas being impacted by increasing carbonization temperatures. Furthermore, the BET method is the historic measurement of surface area that appears frequently in the literature.]

FIGURE 7: VARIATION OF CHAR BET SURFACE AREA WITH HTT



From http://terrapreta.bioenergylists.org/files/TrainingManual.pdf - bamboo charcoal

The qualitative phenomenon shown in Figure 7 has been confirmed for many chars and always occurs. Individual chars will exhibit a quantitatively different absolute surface area at any given temperature, but the characteristic rise and fall is highly reproducible. The development of surface area above 300 Celsius is attributed to the formation of localized graphene regions within the char as the residual solid becomes progressively more carbon-rich. The decline of surface area above 700 Celsius is attributed to "calcination" [high temperature treatment] of the developed graphene plates, resulting in the coalescence of the individual graphene regions into larger, denser, but less porous amorphous graphitic carbon complexes – similar to the char formed en route to making activated carbon.

Because surface area and adsorption capacity are properties of the graphene portion of the char itself, the property is formed at the time the char is created and is unlikely to further develop in the char when placed into soils. The adsorption capacity of a char can deteriorate after creation, perhaps by having something either occupy the adsorption sites or physically blocking access to the adsorption capacity by coating the outside of the char particles. As such, measuring the adsorption capacity of a freshly made char yields the upper ceiling for the life of the char with respect to this property.

In terms of what biochar contributes to soil dynamics, adsorption capacity is believed to contribute the bulk of the moisture retention and most of the capacity to buffer soluble organic compounds. . As such, these characteristics may be pivotal in the stimulation of the microbial populations in the soil by stabilizing the minimum moisture and carbon source levels in the soil

and elevating microbial survival rates during times of drought and shortages of other soluble carbon sources.

Adsorption capacity is measured by "challenging" the char with a known substance, usually an organic vapor, and measuring the extent of uptake 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.

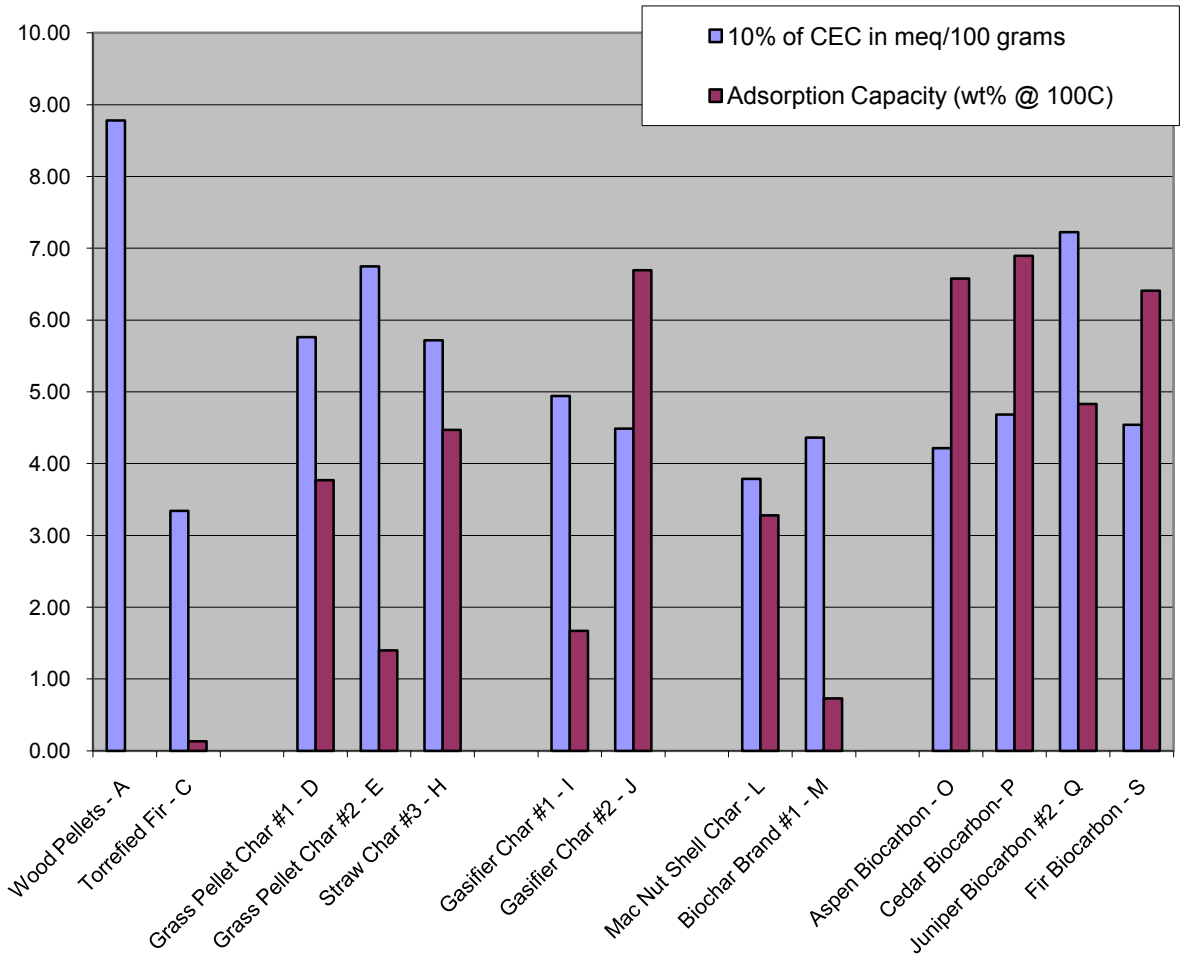
The adsorption capacity test used for this paper is known as "GACS" or Gravimetric Adsorption Capacity Scan. The GACS method is similar to another esoteric method known as the GRPD test for activated carbon, which was developed, in turn, from a test known as TACTIC (developed by Calgon Carbon Corporation 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 adsorption conditions and measure the extent of adsorption.

For this paper, the standard 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 either 100 degrees Celsius or 125 degrees Celsius. The assay is basically a means of comparing relative adsorption capacities within a group of chars. 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. Interested individuals are invited to contact the Corresponding Author for additional information about the GACS assay.

Figure 8 shows the CEC and adsorption capacity of eleven chars and two wood-samples previously discussed in conjunction with Figures 5 and 6. Some samples from Figure 5 and 6 did not have both the CEC and adsorption capacity measurements available and those samples are not included in Figure 8. The CEC data is shown on Figure 8 at 10% of the measured CEC level to allow a common y-axis for both CEC in units of meq/100 grams and adsorption capacity in units of weight percent R134a @ 100 degrees Celsius.

Figure 8 shows significant variation of both CEC and adsorption capacity in the selected eleven chars and two woods. All the samples tested showed good levels of CEC, but considering how few samples there are, one should not jump to conclusions about what does and doesn't lead to CEC in a char.

FIGURE 8: CEC AND ADSORPTION CAPACITY OF CHARS



Adsorption capacity showed more dramatic trends, with the two pre-carbonization materials having little or no adsorption capacity, as would be expected from the trend of the low-temperature side of Figure 7. The adsorption capacity of the chars in Figure 8 seems to reflect the specifics of different carbonization process more than the specific starting material. This is not unexpected considering the carbonization process creates the internal structures in the starting biomass as the volatiles are driven off and the solid char is formed. Furthermore, of the two examples of gasifier chars, Gasifier Char #1 used woody biomass as the fuel for gasification and represents a wood-gasifier char, whereas, Gasifier Char #2 was residual char from a char-gasifier. Of the chars shown in Figure 8, letters H, L, O, P, Q & S were all produced in the same carbonization process and seem to share uniformly elevated levels of adsorption capacity.

From this discussion in Section 5, we conclude that future research about CEC and adsorption capacity could indeed be fertile ground [pun intended].

6. POTENTIAL SOURCES OF BIOCHAR

6.1. Overview

Potential biochar sources include conventional lump charcoal, char residuals from gasifying stoves and furnaces, by-products from fast and slow pyrolysis technologies, residual char from open biomass burning (including forest fires), and carbonized biomass and agricultural residues (including chicken litter and biosolids) manufactured in dedicated processes. Figure 9 summarizes a few of the many characteristics that can be used to classify biochars.

FIGURE 9. Table of Potential Sources of Biochar

Type / Issue	Incidental	Traditional	Gasifier	Other Modern Industrial Processes	
Application	**Fire Residual**	**Lump Charcoal**	**Biomass to Energy**	**By-Product or Co-product**	**Sole product**
Description (Highly generalized)	Fireplace Forest fire Incineration	Primitive kilns Modern kilns	Downdraft Updraft Top-Lit UpDraft (TLUD)	Traditional retort Specialized retort Fast Pyrolysis Bio-Gas & Bio-Oil	Biocarbon for energy Biochar for soil
Oxygen Present during carbonization	Oxic - Uncontrolled	Oxic or Anoxic	Oxic	Anoxic (usually)	Anoxic or Oxic
Commercially available for biochar?	No. Basically destructive.	Yes. Established product – for cooking	Biochar usually is NOT the primary objective.	Biochar usually is NOT the primary goal in initial efforts	Initial efforts specific for making biocarbon

It is not the intent of this section to make judgments about what constitutes the good and bad characteristics of biochars, nor to say which methods of pyrolysis are better than others. Our purpose is to alert the readers to the fact that fundamental differences exist between biochars because of the pyrolysis methods, even when the starting biomass is exactly the same.

At industrial scales, unavailable to average people, technologies have existed for decades for the purpose of dry distilling wood and collecting the volatiles, such as “wood alcohol” or methanol. They are now discovering that the by-product of charcoal has increased value as an additional product called biochar. Other large-volume sources may become commercially available in the near future.

Each of the carbonization methods can be further differentiated as being either a continuous or batch process. Both types can produce good and not-so-good biochar. The difference between them is that continuous production systems, which tends to be larger in size, lend themselves to steady-state operation, if appropriate monitoring is performed and if the product specifications are what the biochar user desires. A batch system, which favors smaller and less complex equipment, allows the user to easily customize the pyrolysis process, but can produce wide fluctuations in some characteristics, especially if monitoring and process controls are not rigorous.

Currently, of all these sources, there are only three that are realistically accessible to the individual interested in using biochar. One is purchasing conventional lump charcoal; the second is small-scale use of simple drum retorts; and the third is making your own char residuals from Top-Lit UpDraft (TLUD) gasifying stoves.

6.2. Lump Charcoal from Commercial Sources

Conventional lump charcoal was a widespread product prior to WWII, but has been replaced by charcoal briquettes after the war. Currently, most charcoal briquettes are a mixture of powdered devolatilized coal, a small portion of raw or carbonized sawdust, and intentional ash additives - intended to create the "complete charcoal cooking experience." All that lovely white ash, indicating the coals are ready for cooking, is limestone, straight from the mine.

Nowadays, lump charcoal is a boutique cooking fuel, which is gaining popularity and distributed almost anywhere outdoor cooking supplies are sold, including most hardware stores. It is generally made from clean wood scraps, such as residues from furniture making, and appears as solid lumps that still exhibit the grain of the original wood. While it is not inexpensive, lump charcoal is certainly affordable in the smaller quantities that a home garden might require to achieve recommended biochar levels in the soils of 3 to 10 weight percent of the soil mass in the root zone.

However, an underlying issue remains: *Is lump charcoal a good candidate for use as a biochar?* Furthermore, there are many varieties of lump charcoal, as can be investigated by visiting a web site called www.nakedwhiz.com. The site reviews the cooking properties of lump charcoals, but was a valuable resource by supplying over a dozen various lump charcoals for testing. This data set was augmented by a large number of varietal charcoals from Real Montana Charcoal, which makes small batches of charcoal from individual wood species. Thus, an additional survey was made of how charcoal varies as a function of the wood species when made within the same basic production process.

The lump charcoals were tested for total mobile matter, adsorption capacity, and relative density. The goal was to judge the relative variability of the charcoal properties and see if any one property could be inferred from another, such as lower density charcoals correlating with higher adsorption capacity per unit weight, etc. It should be noted that for this set of data, the Mobile Matter assay temperature was the coal volatile matter setpoint of 900 degrees Celsius, which removes a small increment of additional volatiles over the previously discussed 450-Celsius setpoint now proposed for the biochar modified proximate and ultimate analyses.

Mobile matter is an important property in biochar for two reasons. First, there is evidence that mobile matter leaches into the soil and provides a soluble carbon source, which can cause a short-term nutrient deficiency for the plants by stimulating soil microbe growth that competes with the plants for available nitrogen. The mobile matter levels in lump cooking charcoal are a concern because the charcoal is expected to light without the addition of liquid charcoal starter. As such, in order to aid lighting, lump charcoal are often made under carbonization conditions that leave higher levels of low molecular weight volatiles in the charcoal and, thereby, achieve the desired lighting qualities.

Second, the elevated amounts of mobile matter are likely to disappear within a single growing season and not contribute to the long-term properties of the soil. As such, mobile matter portion in biochar is bought and paid for, but represents less long-term value as a soil amendment. Water and ash provide similarly reduced long-term value in the biochar, but most people recognize that situation and purchase accordingly.

In addition to the Mobile Matter assay, Adsorption Capacity was tested because that is a crucial property of biochar that is created at the time of manufacture and unlikely to improve over time. The results of testing 15 randomly selected commercial lump charcoals are shown in Figure 10.

In general, the best of the lump charcoals had adsorption capacities comparable with the biocarbons shown on the right of Figure 8, when the adsorption data is compared at the same adsorption temperature (done by the corresponding author, data not presented here). Unfortunately, the average lump charcoal mobile matter was over twice the average level of 10% for biocarbons shown in Figure 8. Furthermore, it is apparent from Figure 10 that one cannot infer the mobile matter or adsorption capacities based on the relative bulk density, although there appears to be a weak inverse correlation of adsorption capacity and bulk density.

Eighteen samples of Real Montana Charcoal were obtained and tested for adsorption capacity to see how the adsorption capacities vary from species to species of wood, holding constant the specific carbonization process. Figure 11 shows the Real Montana Charcoals adsorption capacity data, plotted in addition to the adsorption capacity data of Figure 10 for commercial lump charcoals.

As shown in Figure 11, selecting within a single carbonization method does reduce the variability of both the relative density and the adsorption capacity. Considering that the average Real Montana Charcoal adsorption capacity was 70% higher than for the selection of lump charcoals, and that only one other lump charcoal significantly exceeded the average of the Real Montana family, it is clear that there is value to be realized by testing lump charcoals for desired properties. Or in other words, the adsorption capacities have been found to vary as much as 700% (a seven-fold difference) between samples of commercial charcoals, and therefore their application into soils as biochars should be conducted with forethought and caution, including measurement of their individual properties prior to soil application.

FIGURE 10: COMMERCIAL LUMP CHARCOAL PROPERTIES

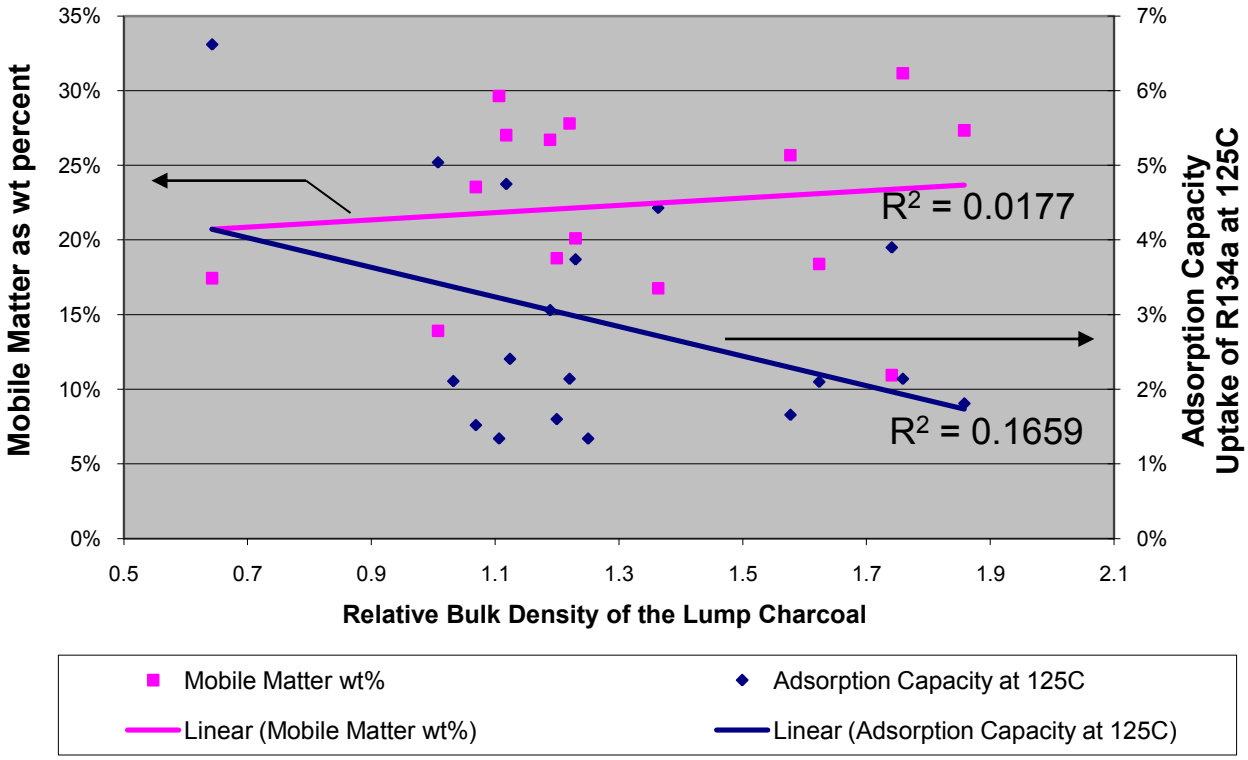
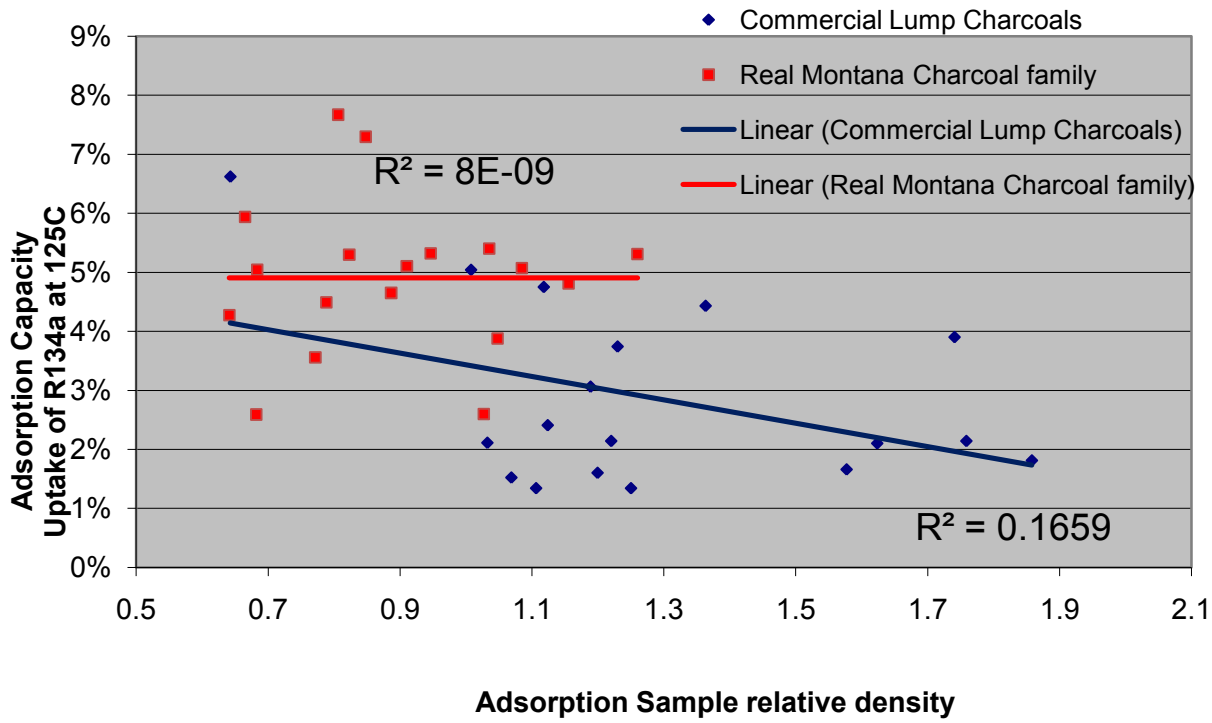


FIGURE 11: REAL MONTANA CHARCOAL ADSORPTION CAPACITIES



6.3. Charcoals from Small Retorts [anoxic]

Pyrolysis of biomass is caused by heat, and does not require a flame. So "anoxic pyrolysis" [without oxygen] can occur and is the basis for charcoal/biochar creation via retorts that essentially bake the raw biomass to drive off volatiles and tarry gases. Many variations of small charcoal-making retorts appropriate for personal experimentation are discussed on the Internet, including:

http://www.holon.se/folke/carbon/simplechar/simplechar.shtml
http://www.youtube.com/watch?v=ahIX54facp0&feature=related
http://www.biochar-international.org/technology/production
http://www.biochar.info/biochar.biochar-production-methods.cfml

In these anoxic procedures, there must be some external heat source that will elevate the temperature of the raw biomass without flame contact. Several of these retorts cited above utilize the external burning of the pyrolysis gases, created and emitted from the inner retort chamber, as fuel to sustain the carbonization process. Each anoxic approach can make a variety of biochars and the biochar properties can vary from batch to batch and even within individual batches due to variations in local conditions. For example, temperatures differences between the walls and the center can yield different amounts of mobile matter remaining in the individual pieces of char. Similarly, a thick piece of wood in the center will require longer to carbonize than would smaller pieces closer to the heat sources, possibly leaving some torrified or even raw wood at the end of the process.

Biochars created via anoxic small-retort processes have not been specifically tested for this paper, but their characteristics would probably be quite similar to those of commercial lump charcoal, implying significant variations depending on many operational variables. Although the small retort chars can be quite different from each other, one advantage is the char producer is typically also the field-tester. This creates the opportunity for correlating the operational variables and qualities of each batch of biochar with the desired soil performance.

6.4. Charcoal from Gasifiers (background note)

Gasifiers are devices in which dry biomass is transformed into combustible gases and charcoal in a zone that is ***distinctly and controllably separate*** from where the volatile gases are combusted.

An important note on terminology: To the general public and most biochar enthusiasts, the word "gasification" denotes both the creation of gases via pyrolysis of the biomass and the subsequent oxidation of solid hot charcoal/carbon to yield CO_2 and CO gases. This latter char-consuming process is called "char-gasification" in this paper to avoid confusion with the pyrolytic gasification of the biomass, "wood-gasification", which yields char and wood-gas.

There are several different types of "gasifiers" (referring to the devices, not the processes). In almost all of them, the raw biomass moves downward, first undergoing anoxic pyrolysis caused by heat rising from below and converting the biomass to char, and then experiencing char-gasification and the creation of the heat, leaving behind only ash. In those gasifiers, the making

of biochar generally requires the removal of the downward moving fuel at an appropriate time, place and temperature, depending on the desired charcoal characteristics. Because most gasifiers were created to consume the charcoal to maximize energy production, prior to the recent interest in biochar, the removal of any char is easier in some designs than in others, and the carbonization conditions that any surviving char experiences are not always the same.

6.5. Biochars from oxic Top-Lit UpDraft (TLUD) Pyrolytic Gasifiers

One convenient gasifier source of biochar is the Top-Lit UpDraft (TLUD, pronounced "Tee-lud") pyrolytic stoves and biochar makers. They can be easily constructed and operated for small-scale production of biochar.

Originated in 1985 by Dr. Thomas B. Reed, and with almost simultaneous independent development by Paal Wendelbo, the TLUD devices have always been intended as biomass-burning cook stoves. Therefore, by intention, Top-Lit UpDraft gasification has been demonstrated primarily at a small scale. The TLUD devices feature flaming pyrolysis, a unique combustion process that produces char at the same time as the pyrolytic wood gas is released from the biomass. Cooking is accomplished by secondary combustion of the pyrolytic gases. The value of the TLUD char has been largely ignored (except by Dr. Ronal Larson, whose prominent advocacy of char-from-TLUDs enabled subsequent development efforts) until the recent surge of interest in biochar. Recent efforts are focused on making larger TLUDs with the emphasis on biochar production, leaving the utilization of the heat as a secondary feature and the subject of ongoing development efforts.

In the TLUD gasifiers, the fuel does not move (except by shrinkage when pyrolyzed). Instead, a "pyrolysis front" moves downward through the mass of fuel, converting the biomass to char. The name "Top-Lit UpDraft" denotes two key characteristics: The fire is ignited at the top of the column of biomass and the primary combustion air is coming upward through the fuel from the bottom of the biomass. The primary combustion air sustains the pyrolysis reactions occurring within the pyrolysis front. This mode of combustion is called "flaming pyrolysis", where biomass is converted to char and releases combustible volatiles, in contrast with "glowing pyrolysis" that is characteristic of the combustion of char.

The tiny "flames" within the descending pyrolysis front are due to the combustion of a portion of the created pyrolysis gases, thereby generating the heat needed for propagating the pyrolysis front downward. Since the rate of heat generation is determined by the amount of available oxygen, the progression of the pyrolysis front is controllable by regulating the primary airflow. In a typical TLUD, the pyrolysis front moves downward 5 to 20 mm per minute, depending on the nature of the fuel and the amount of available primary air.

Above the pyrolysis front, the created char accumulates and the oxygen-depleted air (mainly nitrogen, carbon dioxide, carbon monoxide and water vapor) sweeps the created pyrolytic gases to the secondary combustion zone. There, additional air is provided and the pyrolytic gases are burnt in a separate and very clean flame. These pyrolytic gases are tarry and long-chain hydrocarbons that, if not burned, would form a thick smoke.

Unique among the gasifiers, TLUDs operate in an oxic batch mode and do virtually all of the biomass pyrolysis or wood-gasification before doing appreciable char-gasification. The transition between the two phases is quite distinct, changing from a characteristic yellow-orange flame (from burning tarry gases) to a smaller bluish flame that denotes the burning of carbon monoxide.

There are numerous variations of the TLUD technology. Each variation has its own unique history and intended application. Most of them are do not facilitate the creation and salvaging of the char, because they promote the burning of the char by providing char-gasification within the TLUD device.

Almost unique among the TLUD gasifiers, the version named "Champion" (because it won a clean combustion award at Stove Camp 2005) is designed for easy removal of the fuel canister after the pyrolysis is completed, facilitating the collection of the char into a simple container to extinguish the hot char. Such a "snuffer box" could be as simple as a clay pot with a plate to cover it or any other airtight vessel that will smother the residual combustion.

Figure 12 shows a vertical cross-section of the "Champion" TLUD stove. Information about and construction details for the Champion TLUD gasifier and the Wendelbo Peko Pe TLUD gasifier are on the Internet at:

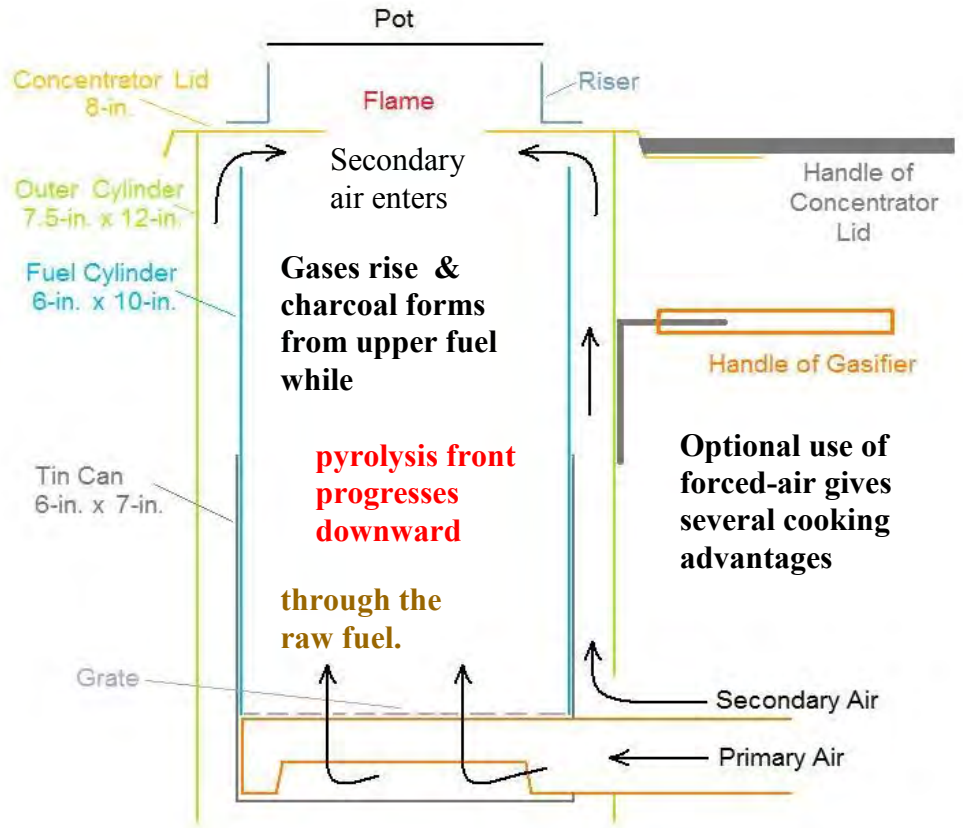
www.bioenergylists.org/andersontludconstruction and
www.bioenergylists.org/wendelbopekope.

Additional references are:

www.bioenergylists.org/andersontludcopm (Summary of emissions testing of TLUDs)
www.bioenergylists.org/stovesdoc/Anderson/GasifierLAMNET.pdf (the "big picture")
www.hedon.info/docs/BP53-Anderson-14.pdf (A paper entitled "Micro-gasification: What it is and why it works")
www.woodgas.com (Website of Dr. Tom Reed and the Biomass Energy Foundation - BEF)
www.bioenergylists.org (An extremely good website dealing will all types of cookstoves.)

Also, conducting Internet searches on the names and topics associate with TLUDs will reveal substantial additional information.

FIGURE 12: Vertical section of the "Champion" TLUD Gasifier (2008)



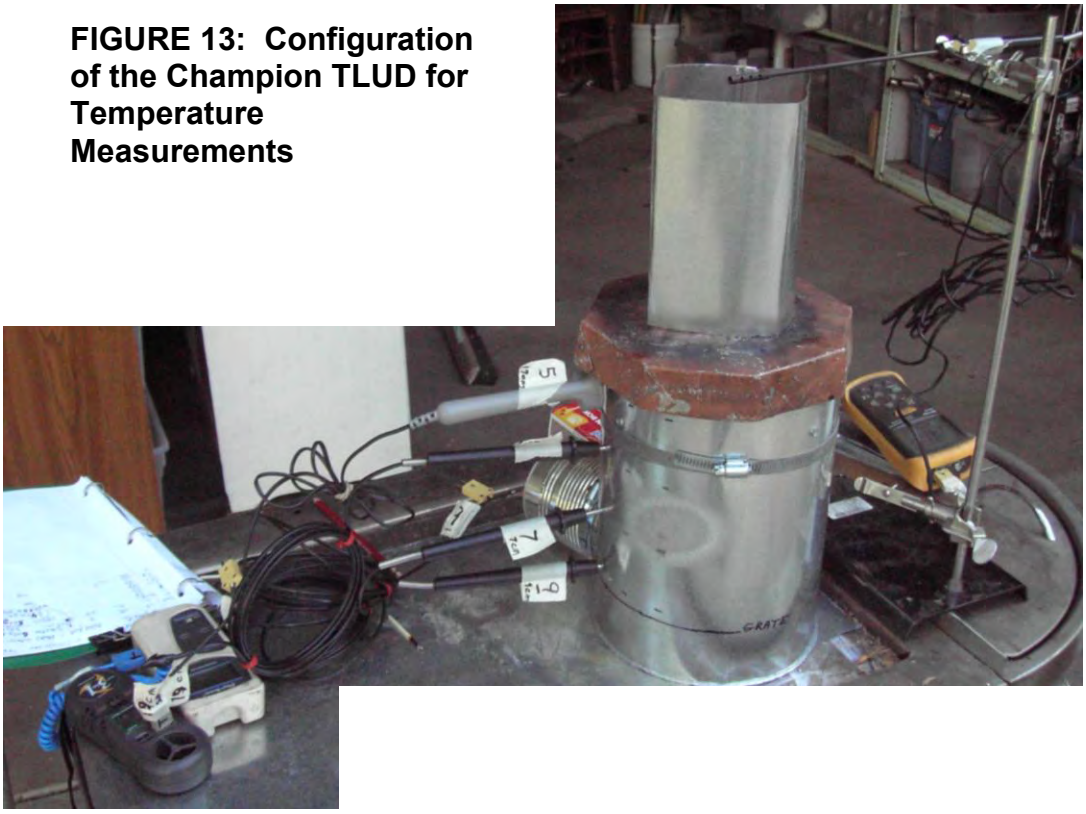
6.6. Analyses of TLUD Biochars

6.6.1. Background and Procedures

Research about biochars is barely beginning and structured studies of carbonization conditions and resulting char properties are rare. This Section 6.5 examines data from one biochar maker (a Champion TLUD cookstove) using one fuel (wood pellets) and operated only one time in each of two settings for the primary air supply. The findings, summarized from unpublished records, are still singular observations and offer potential generalizations similar to those of earlier Sections. Any apparently meaningful observations should be replicated before acceptance and usage in further studies. The purpose of this section is to utilize some of the proposed biochar analyses, report some very preliminary results, and suggest some hypotheses for the underlying causes of the observed trends about characteristics of biochar. Individuals using TLUD technology can easily replicate these studies.

A standard-size Champion TLUD (15 cm or 6 inch diameter of the fuel chamber) was modified to take temperature readings at five locations, as shown in Figure 13. Four K-type thermocouples were inserted into the center of the 22-cm tall fuel pile at heights of 1, 7, 13, and 19 cm above the grate. The fifth one recorded temperatures of the secondary combustion flame at the top of an 18 cm riser; no cooking pot was in place. The fuel both times was 2500 grams of standard woodstove pellets.

FIGURE 13: Configuration of the Champion TLUD for Temperature Measurements



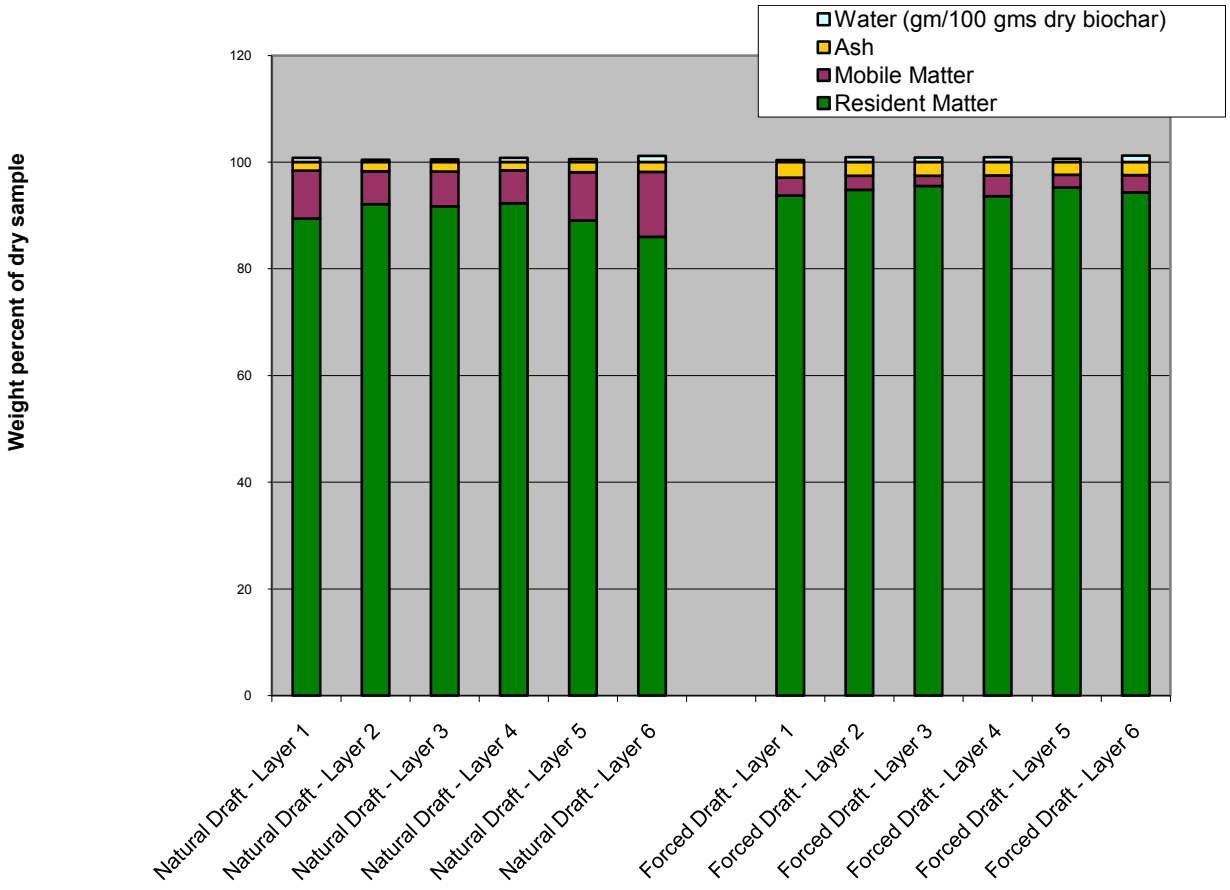
The first data set was with both primary and secondary air supplied by "Natural Draft", where the chimney effect of the rising hot combustion gases results in the air flows. The first TLUD run lasted 2 hrs 50 minutes functioned in pyrolysis mode, consistently produced 3 kW (~11 MJ/hr) of thermal energy, and produced 566 g of biochar, (22.6 wt % yield). The second data set, demarcated as "Forced Draft", featured the primary combustion air supply boosted by a small blower. This TLUD run pyrolyzed for 1 hr 25 minutes, doubled the energy output, and yielded 350 g of biochar (14 wt % yield). In both cases, the biochar was carefully removed in six approximately equal layers, extinguished without adding water, allowed to cool, and bagged for analyses. "Layer One" was from the top of the cooled char, and "Layer Six" was closest to the grate.

Summary of observations during the tests: No visible smoke was observed during either of the test runs. Temperature readings at one-minute intervals revealed the approach of the pyrolysis front to each thermocouple, but the temperatures did not decrease after its passage. Typical temperatures at and above the pyrolysis front were recorded as 600C to 700C in the first data set, and 800C to 1000C in the second, but initial efforts at thermocouple calibration on a 400 degree Celsius hotplate showed them to be reading 100Cto 200 degrees high, and the error probably increased at higher temperatures. In previous independent experiments with accurate thermocouples, temperatures in the flaming pyrolysis zone of similar TLUD devices have been measured from 490ºC to 700ºC, increasing with increasing gas flow and faster pyrolysis. Therefore, the reported temperature trends should be considered qualitative and requiring replication with better equipment.

6.6.2. Modified Proximate Analyses of the Experimental TLUD Chars

The modified proximate analyses of the six layers of each of the two data collections are presented in Figure 14.

FIGURE 14: MODIFIED PROXIMATE ANALYSES OF TLUD CHARS



Based on the trends shown in Figure 14, the following observations are noted:

a. Moisture was measurable in eight of the 12 samples, even though every sample was air-cooled and bagged within six hours of the completion of the data collection. The moisture levels were small, less than two weight percent, and were attributed to water vapor adsorbed from the ambient air during cooling.

b. The ash content of the chars created with higher heat forced draft run was approximately double that of those created with the lower heat natural draft study. This is compatible with the reduced yield of char by weight from the same amount of starting wood pellets. Unless ash is physically carried away within the flow of the gases, which was not the case in TLUDs, it will accumulate to the extent any gasification reduces the amount of remaining char.

c. It is interesting that both cases, Layer 6 (the lowest level, with visibly more loose ash in the collection tray) did not measure higher percentages of ash than the other five layers. One explanation is that only the pyrolyzed pellets were tested and any loose ash was not included in the testing. This practice was adopted because loose ash tends to migrate down within the bed of char and the each layer may contain ash descending from all the layers above it.

d. The mobile matter is roughly three-fold higher in the lower temperature natural draft chars than in the higher temperature forced draft data set. Considering the 38% reduction in total weight of char produced, the total mass of mobile matter are roughly five times greater in the first set than in the second set.

e. The impression is that the percentage of mobile matter is slightly lower in the middle levels than at Layers 1 and 6 in both data sets. This phenomenon, and the other observations above, deserves further replication studies before less conjecture-inspired explanations should be attempted.

6.6.3. Modified Ultimate Analyses of TLUD Chars

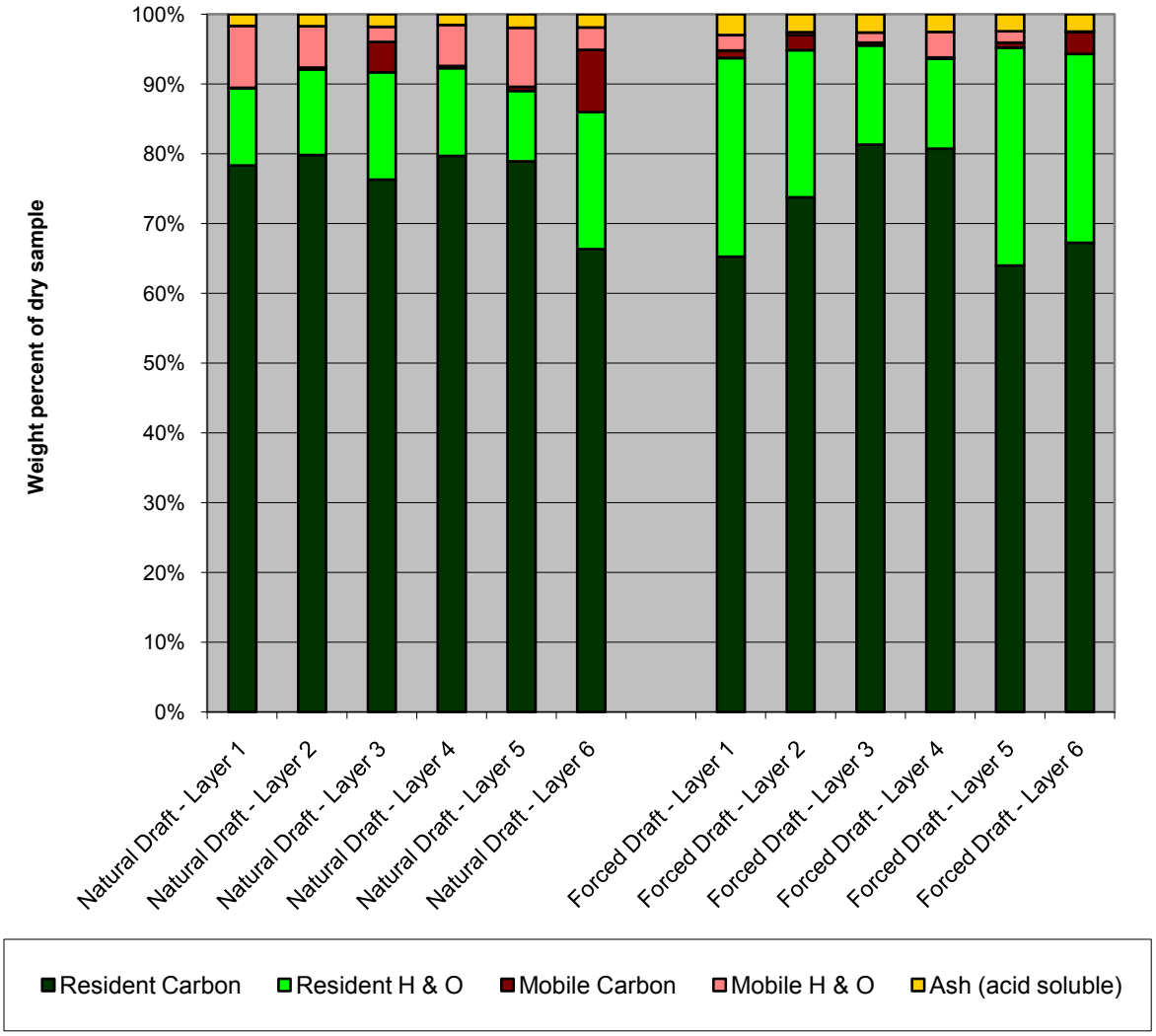
Except for the indication of the moisture content, all of the above observations can also be seen in the Modified Ultimate Analyses in Figure 15. (Future biochar studies could present reasons to omit the Proximate Analysis altogether because modern chemical analyses greatly facilitate the testing.)

Based on the trends shown in Figure 15, several observations are most evident:

a. Almost all of the ash is acid soluble; the non-soluble ash was barely detected. Furthermore, because of the purity of the wood pellets used as the biomass source, mobile and resident nitrogen were present at the analytical detection limit. All three trace compounds, non-soluble ash, mobile nitrogen and resident nitrogen, have been eliminated from Figure 15. The original data may be accessed by exploring the embedded spreadsheet on MS Word versions of this document.

b. The amount of mobile carbon is highly variable, being significant in only six of the twelve samples. This inconsistency merits further examination.

FIGURE 15: MODIFIED ULTIMATE ANALYSES OF TLUD CHARS



c. For the higher temperature forced draft pyrolysis, the percentages of Resident H & O are nearly double those of the lower temperature data sets. However, given the total weight production was 62%, it appears that the actual amounts (grams) of Resident H & O are not greatly changed by the higher temperatures

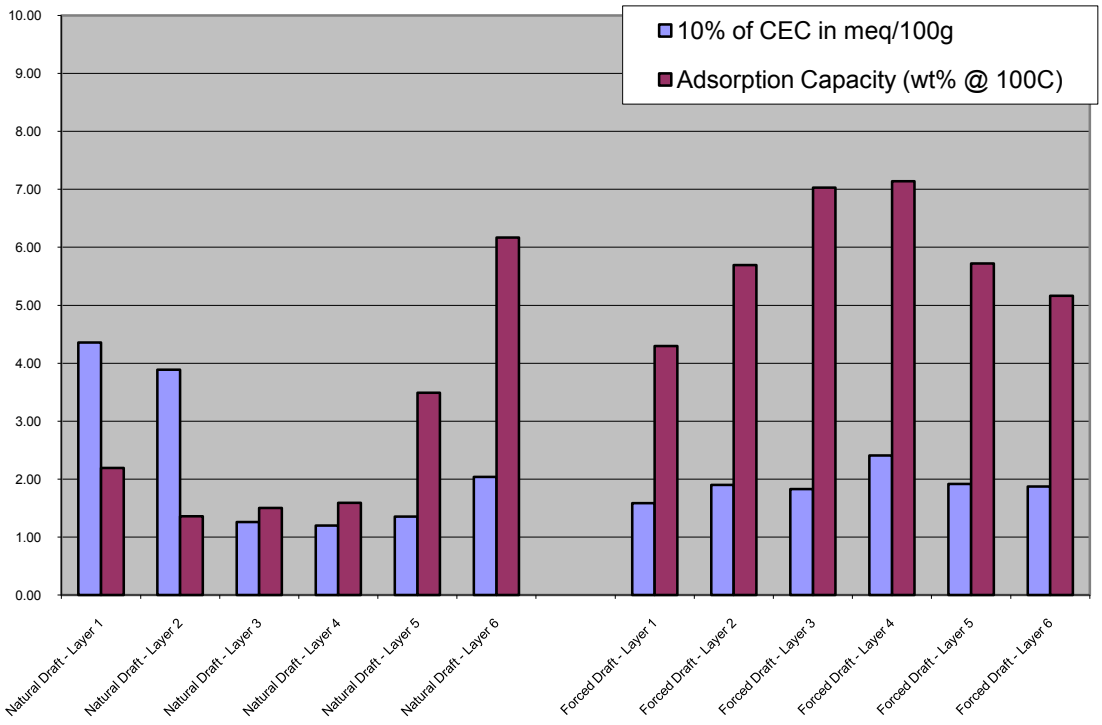
d. The greatest impacts of the higher temperatures on the percentages shown are on the amounts of Resident Carbon. Not only are the percentages 0% to 17% lower (between corresponding levels), but there is also the 62% weight factor to consider. In general, the absolute amount of Resident Carbon is perhaps only 50% of the Resident Carbon in the lower temperature biochar.

e. There is a noteworthy difference between the resident carbon content of TLUD chars and the other tested chars. The other chars (shown in Figure 6) have resident carbon amounts from 55 to 75 percent. The TLUD chars from the top five layers of the lower temperature natural-draft dataset have an average resident carbon reading of 77%. The percentages are more variable (from 63 to 81%) for the higher temperature forced-draft dataset.

6.6.4. The CEC and Adsorption Capacity of TLUD Chars

The higher temperatures associated with the forced draft appear to have dramatic impacts on the CEC and adsorption capacity of the two sets of TLUD biochars, as shown in Figure 16.

FIGURE 16: CEC AND ADSORPTION CAPACITY OF TLUD CHARS



Based on the trends shown in Figure 16, several observations are most evident:

a. The surprisingly high adsorption capacity in Layer 6 of the lower-temperature natural draft biochars caused a review of the methodology, and a probable explanation of the data. When the pyrolysis phase finished on that batch of fuel, the operator attempted to extinguish the processes by cutting off all of the air (with oxygen) that could enter the TLUD. However, 50 minutes later the biochar was still very hot, and then the 6 levels of samples were removed. One plausible interpretation is that some small amount of air managed to enter and sustain some char-gasification during the 50 minutes, resulting in the lowest level of the char being subjected to the

higher temperatures and perhaps other un-identified processes. This might have also influenced Layer 5 chars, but the impact is less dramatic. Referring to Figure 15, the higher amount of mobile carbon might also be attributed to this delay in removal of the biochar from the TLUD device. The delay did not occur with the second batch of data sets, since the operator learned how to (very carefully) scoop out the hot char.

b. The CEC readings of Layers 1 and 2 in the natural draft TLUD data are similar to the range of CEC readings reported in Figure 8 for the other tested biochars. The remaining TLUD chars had markedly lower CEC levels. Restated, ten of the twelve CEC readings on Figure 16 are lower than any of the readings on Figure 8. It is known that CEC levels can naturally increase in soils, so the long term consequences of these low values is not known and may not be of significance.

c. The adsorption capacities for the TLUD biochars in Figure 16 overlay the data reported in Figures 8 and 10, generally in the range of 1% to 7%. However, the TLUD data reveal that the adsorption capacities of the second set of six levels are substantially higher (average = 5.8 wt %) than for the first set (average = 2.0 wt %, with Layer 6 excluded because of the post combustion air leak discussed in *6.5.4.* a). The single difference in the TLUD runs was the forced air for the second set, resulting in higher pyrolysis temperatures. This near tripling of the adsorption capacity must be offset by the 62% weight yield. Combining these trends, per kilo of original raw biomass converted into biochar available to go to the soil, the second TLUD operation generated approximately double the total adsorption capacity.

A further observation based on *6.6.4.* b & c: Adsorption capacity and CEC comparisons within biochar production methods are not accurate without consideration of the char yields. Furthermore, when comparing the yields of charcoal produced by oxic processes (such as with TLUDs) and anoxic processes (such as by retorts), the external fuel utilized to sustain the anoxic pyrolysis needs to be taken into consideration and accounted for in the overall yield calculation.

6.6.5. Summary and Conclusions Concerning the Two TLUD Char Datasets

TLUD devices can be made and used at home and small commercial settings. They are easy and inexpensive to construct and operate in several sizes from very small (1-gallon) up to moderate (55-gallon) devices. Small quantities of biochar can be made quickly for research.

TLUDs can use a wide variety of feedstocks. The fuel pieces are generally smaller (being pellets, chips, briquettes, pucks, etc.). Well-dried feedstocks are recommended and TLUDs have less stable secondary combustion with wet fuels due to elevated moisture levels in the volatilized wood gases.

TLUD (Top-Lit UpDraft) pyrolytic gasifiers produce biochar with reasonable characteristics that merit further consideration. They utilize “oxic” (flame-present) pyrolysis. The conditions for operating the TLUD devices can influence biochar properties – especially adsorption capacity.

In the context of world cultures, the small sizes of TLUD cook stoves provide advantages for the poorest people to obtain household energy for cooking and space heating while also producing

biochar. By sheer numbers of possible users, large volumes of biochar are possible in developing countries, which would represent substantial soil benefits and carbon dioxide offsets.

7. OPTIONS FOR INFORMALLY TESTING CHARS

As has been seen, there is a significant amount of variability within virtually every measured property in chars that aspire to be good biochars. As such, it takes more than just the claim of the seller to make a quality biochar, which leads us to recommend, "Buyer beware".

This final section presents some fairly accessible tests that allow one to screen out highly undesirable biochar properties and, perhaps, assist in selecting the better biochar candidates.

Moisture and ash are two ingredients found in every bag of biochar, yet they add little value to the long-term biochar performance. Both are fairly straightforward to measure and any candidate char should be tested for both.

7.1. Moisture

Measuring moisture content is particularly straightforward and can be done even in a lowly toaster oven. A small sample of the char is placed into a closed but not sealed container, preferably metal, and heated to just above 100 Celsius in dry air for an extended period of time. The time is "until no additional weight loss is observed." (Heating overnight works great if your oven is appropriate for that many hours of use). A suitable container can be made out of a 4 oz tomato paste can, with the top removed using one of the newer-style can openers that slices the edge of the top lid so that it sets back in place on the rim and does not fall inside the can. The lid is to shield the char from the direct infrared heating of the toaster oven elements. An alternative is to cover the container with heavy-duty aluminum foil and poke a few slits in the cover. A standard oven thermometer, suitable for use inside the toaster oven, provides sufficiently accurate and reproducible temperature indications, since the thermostats of inexpensive toaster ovens are not actually precise.

An inexpensive scale, accurate to 0.01 grams, is needed to weigh the samples before and after heating. Acceptable units are available on "ebay" for less than $20 that read to 0.01 grams up to 200 grams – the principal target market application is likely the illegal drug trade at the retail level. Alternatively, a kitchen scale with nearest gram accuracy can be used if the sample of char is appropriately larger (also requiring longer drying times). The analytical techniques require a bit of practice to achieve consistency and reproducibility, but half a dozen attempts will turn you into a seasoned analytical practitioner for measuring moisture content.

In general, as produced, chars have less than 5% and never more than 10% residual moisture. If higher, you are being sold "char with water added". However, many biochars are highly hydroscopic, an important property in the soil, and will adsorb significant amounts of moisture if exposed to humid air.

If you are using homemade chars, this is really not an issue because you probably know when the char was made and if it has been wetted or exposed to humid air. Since the water is not harming

anything in the ultimate performance of the biochar, the issue is that water should not be a significant component of a commercial product sold on a weight basis or requiring transportation over a long distance.

7.2. Ash

Ash is also relatively straightforward to measure – this requires the same scale accuracy of 0.01 grams, a propane camping stove and a clean open top tuna fish or cat food "tin can" (avoid aluminum). The tin can needs to be heated once while empty to burn off any coatings on the container. Weigh the container after it cools. A half-centimeter layer of **dried** char is spread on the bottom of this clean dry tin can and the weight of the added char is noted. The open tin can is heated on the camping stove over an open flame that uniformly heats the entire bottom of the container. The contents are periodically stirred to facilitate ashing, taking care to not knock or blow away any of the ash. The process is continued until the tin can contains only gray to white ash residue. At no time should the contents of the tin can catch fire and burn with an open flame, since that carries ash away as particulates in the smoke. The ashed sample and tin can are weighed, then the ash removed and the weight of the tin can subtracted. The weight of ash on a dry char basis is calculated.

Most chars made from clean wood sources have less than 5 weight percent ash, while agricultural residues, such as corn stover, may have significantly higher levels. It is tempting to worry about the ash constituents in chars. This concern is legitimate if one does not know the origin of the biomass utilized to produce the char. In most cases, the starting material is new clean wood or agricultural residues, and concerns about ash constituent are generally not justified. However, whenever the origin of the biomass is unknown, or the ash levels are significantly higher than 10 weight percent, it may be worth testing the ash for soil pH impact and the presence of metals. The former can be estimated using pH paper and will indicate how much the ash will act like lime in the soil. For acidic soils, additional alkalinity is welcome, but for high pH soils, additional liming may lead to poor crop performance. Testing for metals should be conducted by a qualified laboratory that can also help interpret the analytical results.

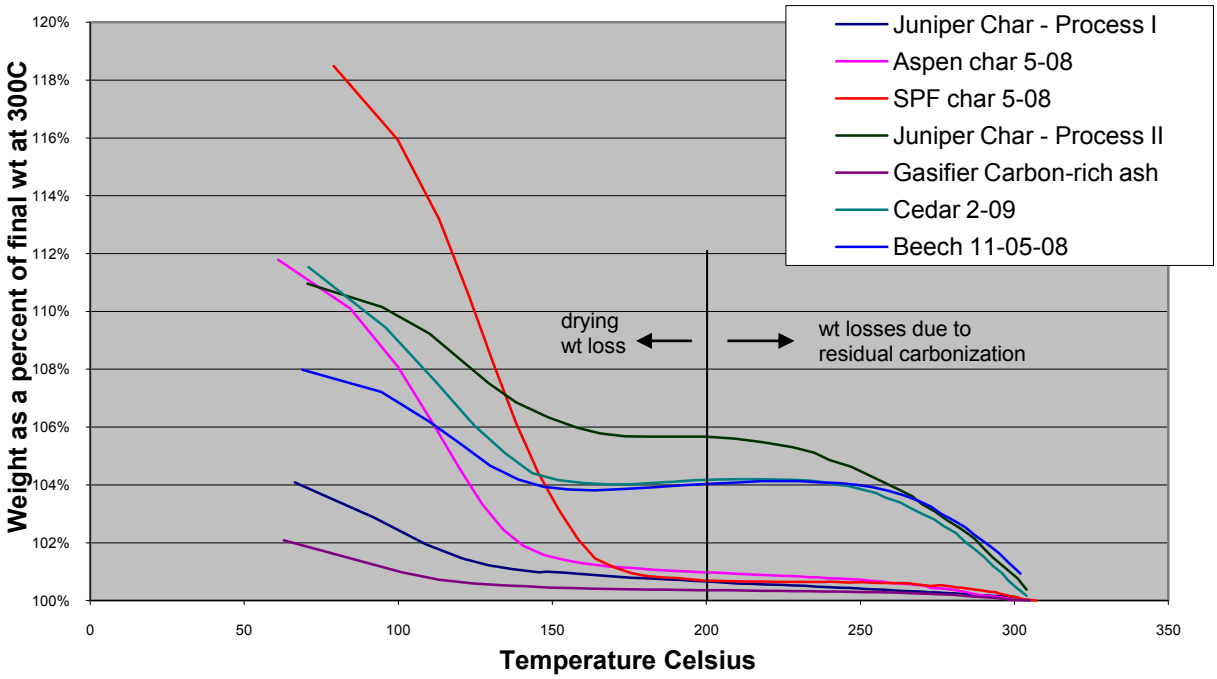
7.3. Adsorption Capacity

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. Furthermore, the adsorption test conducted on activated carbon should yield very high percentage increases in weight and a noticeable temperature rise during R134a addition. The differences become obvious with relatively little practice.

Note: The results obtained by this ambient-temperature method are not directly comparable with the reported GACS results obtained at 100 and 125 degrees Celsius, as discussed in conjunction with Figures 8, 10 and 11. Adsorption results at typical ambient temperatures are on the order of twice the levels observed at the 100-125 degree Celsius.

7.4. The "feel" of good char

Properly carbonized wood forms a rigid, easily crushed material that lacks pockets of under-carbonized material. This material differs from the partially burned logs that linger after the campfire goes out. In addition, fully carbonized chars are also not particularly "greasy" to the touch. They are dirty and make copious amounts of black dust, but that dust will wash off one's hands with just water. If it takes significant amounts of soap to remove the char powder from the pores of the skin, then the char has significant amounts of mobile matter, with the associated concerns discussed previously.

7.5. Other tests

Beyond these simple tests, it becomes difficult to accurately measure char properties outside a proper analytical lab. Attempting proximate and ultimate analyses without the proper analytical equipment is unlikely to yield any insightful results. It is expected that facilities that are currently testing soils for typical agricultural properties, such as fertilizer content, alkalinity, etc., will offer appropriate biochar characterization tests in the future as biochar becomes a more accepted soil component.

8. CONCLUSIONS and RECOMMENDATIONS FOR FUTURE EFFORTS

A discussion of this length does not lend itself to a comprehensive summary and one will not be attempted here. If but one conclusion is allowed, it would be that chars can be characterized sufficiently to discriminate between individual samples with a resolution adequate to predict subsequent effects when utilized as biochar, the soil amendment. Unfortunately, the research to relate char properties, measured by any means, to soil performance is at its infancy. However, when those cause and effect relationships are discerned, the composite path from measurable char properties to predictable soil performance will be in place.

In anticipation of the day when char properties can be projected onto soil performance, the following issues remain unresolved and deserve further investigation:

a. **Characterization of the "mobile matter" and "resident matter" and how it relates to the carbonization process that generates the biochar.** Pyrolysis processes produce a wide variety of carbonization conditions, both between commercial processes and even within individual operations. That variability manifests itself in the transformation of the organic portion of the biomass into biochar and, to a lesser extent, the modification of ash properties. Understanding how pyrolysis conditions influence the char properties (and how the formed chars impact soil performance) will create the hierarchy of carbonization processes for the production of biochar and guide the operation of individual processes to optimize biochar efficacy. For example, it is anticipated that anoxic retort processes will yield significantly different non-graphene organics than would be found in similar chars created under oxic conditions, with both the mobile matter and resident matter having different properties, impacts and fates in the soil.

b. **Identifying and standardizing unique analytical methods for biochars and establishing the appropriate interpretation of the results.** Biochar is a unique class of materials and its roles in carbon sequestration and influence on soil dynamics fall outside the capabilities of analytical methods developed for other materials, namely coal. This discussion has been very heavy-handed in the modification of traditional ASTM tests along with the wholesale advocacy of alternate analytical methods. We have proposed potentially insightful interpretations of the results, and have stated our rationale for those changes. Specifically, all components of the modified proximate and ultimate analyses methods, along with the standardization of the CEC assay and measurement of adsorption capacities, need to be subjected to a timely review, optimization, and adoption by the biochar research community.

c. **The science of biochar as a small but enabling aspect of the impact of biochar on society.** The improved soil productivity and carbon sequestration benefits of biochar achieve nothing unless implemented outside the ivory halls, and have little impact if restricted to the traditional pathways of technology development and distribution. TLUD technology represents one example of "distributed biochar production". Such "low tech – low capital" approaches, with implementation on a massive scale within existing non-affluent cultures, would yield immediate results and likely have more cumulative impact than the "patent-pending" improvements of centralized production. Clearly, the distributed programs need to be correctly orchestrated along with sustainable biomass procurement practices. But the programs actually do need to occur if biochar is to somehow make a difference to the plants, the farmers, the atmosphere, and the societies of this world. As such, the time for bickering, power plays, and haggling about the exact amount of carbon sequestration credits for a specific biochar addition should be pushed behind us. As Voltaire noted, "The perfect is the enemy of the good", but only if we let it.

In closing, biochar is at "the end of the beginning" and has the potential to play a dynamic role in the future of humanity and its societies. Hopefully, this discussion provides a small nudge in the right direction.