

Schenkel and Shenxue revisited

- implications on char production and biochar properties

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ABSTRACT

Charcoal and Biochar are similar, but not the same. They share raw materials and production techniques, but they have different end uses and those end uses utilize different properties in the chars. Furthermore, by using a straightforward set of readily available lab techniques, a matrix of core properties of biochars can be measured and those properties used to assess the suitability of a given biochar in a given growing application.

A homologous series of slow pyrolysis chars was made under tightly controlled conditions, where the only significant variable was the HTT (Heat Treatment Temperature, referring to the highest temperature the char experiences during carbonization). The experimental procedures are documented (see Appendices) to allow replication of this study and utilization of the methods by others.

This paper looks at hardwood pellets under easily accessible carbonization conditions over a wide range of HTTs, analyzes the trends and discusses the implications on biochar properties and biochar production processes.

1. INTRODUCTION

Biochar is a term used to designate charcoal or biocarbon destined for addition to soils. Because biochar is a new utilization for an existing material, charcoal, many relevant insights may be found in past literature devoted to charcoal properties. Indeed, only recently are the properties of biochars and charcoals being studied with a focus on the differing demands of agriculture over cooking and other historic charcoal applications.

The esoteric title refers to past research on charcoal that provides preludes to the current understanding of biochar properties. "Schenkel" is a reference to Figure 3 of Antal and Gronli, "The Art, Science, and Technology of Charcoal Production", *Ind. Eng. Chem. Res.* 2003, 42, 1619-1640. This figure provides one of the few depictions of the evolution of char yield and elemental composition over a wide range of temperatures. In addition, the entire paper provides multiple relevant insights derived from historic charcoal technologies. "Shenxue" refers to Chapter 5.7 of the Training Manual of Bamboo Charcoal for Producers and Consumers, available at (http://terrapreta.bioenergylists.org/files/Training_Manual.pdf). Shenxue presents the insight that char surface area and related adsorption capacity is strongly influenced by the pyrolysis temperature.

Since charcoal is made from biomass, typically wood, there is significant variability in the starting raw material. Furthermore, as discussed in Antal and Gronli, the conditions during the pyrolysis of the biomass also influence both yield and charcoal properties. As such, precisely reproducing experimental results on charcoal can be challenging. To make matters worse, neither Antal and Gronli nor Shenxue provide significant details of the experimental procedures to allow replication of the charcoals created in the original research.

2. CREATING A HOMOLOGOUS SERIES OF CHARS

In order to capture a set of reproducible experimental procedures and generate a set of samples for additional characterization, a sequence of chars were carbonized under carefully controlled laboratory conditions. A single bag (18.8 kg, 40 pounds) of hardwood pellets, a widely available residential heating fuel, was used to create a homologous series of chars where the only significant variable was the highest temperature of the carbonization cycle.

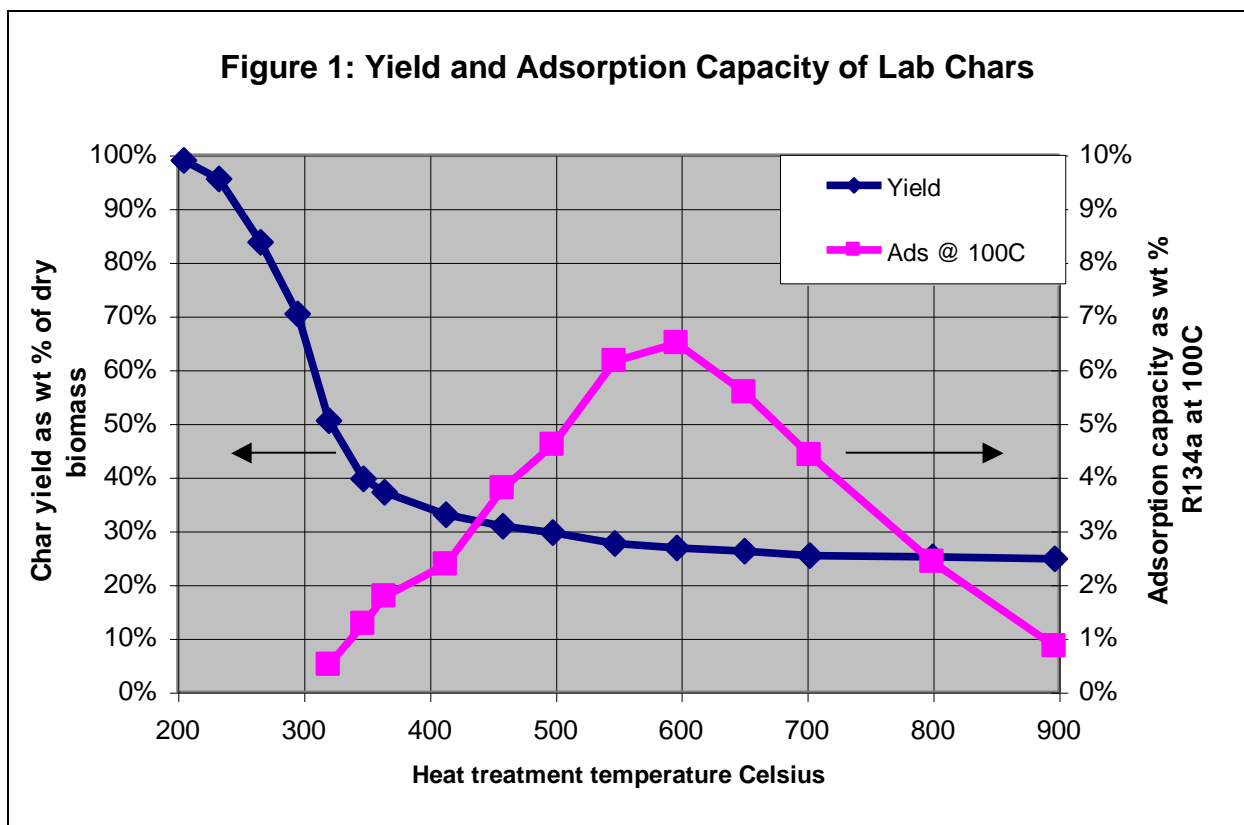
In summary, moisture-free hundred gram quantities of wood pellets were carbonized under nitrogen sweep (approximately one empty bed volume per minute) in a programmable temperature controlled 3.5 centimeter ID fixed bed reactor. The temperature ramp to the HTT was 200 degrees Centigrade per hour and the HTT was held for one half hour at the end of each temperature ramp. Chars were created over the range of HTTs of 200 Celsius to 900 Celsius. The specific experimental procedures are detailed in Appendix A.

Figure 1 shows two important trends; the yield of carbonized material as a weight percent of the moisture-free starting biomass and the "Adsorption Capacity" of the resulting chars. While the importance of yield is apparent, the role of Adsorption Capacity is less obvious. Adsorption Capacity is the extent that the individual char has activated carbon-like properties of retaining non-polar organic compounds and water vapor. Biochar efficacy is attributed in part to the ability of biochar to improve soil moisture retention under desiccating conditions, buffer soluble soil organic carbon and reduce soil levels of plant phytotoxins, including naturally occurring inhibitory allelochemicals and man-made herbicides. As such, Adsorption Capacity emerges as an important distinguishing property between biochars produced under varying conditions.

Unfortunately, measuring the adsorption capacity of a biochar is a fairly new and difficult assay to perform. Adsorption capacity is related to a more common and historically measured property called BET surface area. BET is named after the scientists who first wrote about the theory behind the assay in 1938, Stephen Brunauer, Paul Hugh Emmett, and Edward Teller. As such, it

is a well established, but dated, analytical method with identified and specific shortcomings when applied to microporous materials such as activated carbons and chars.

The current Adsorption Capacity assay is derived from more recent practices used within the activated carbon manufacturing industry, known by a number of acronyms (GRPD, GAED, GACS = Gravimetric Adsorption Capacity Scan). The specific metric used in this discussion is the equilibrium uptake of R134a (1,1,1,2 tetra-fluoro ethane) vapor by the solid adsorbent at 100 Celsius, as measured in weight percent R134a per unit weight of dry char. The specifics of the assay are discussed in detail in Appendix B.



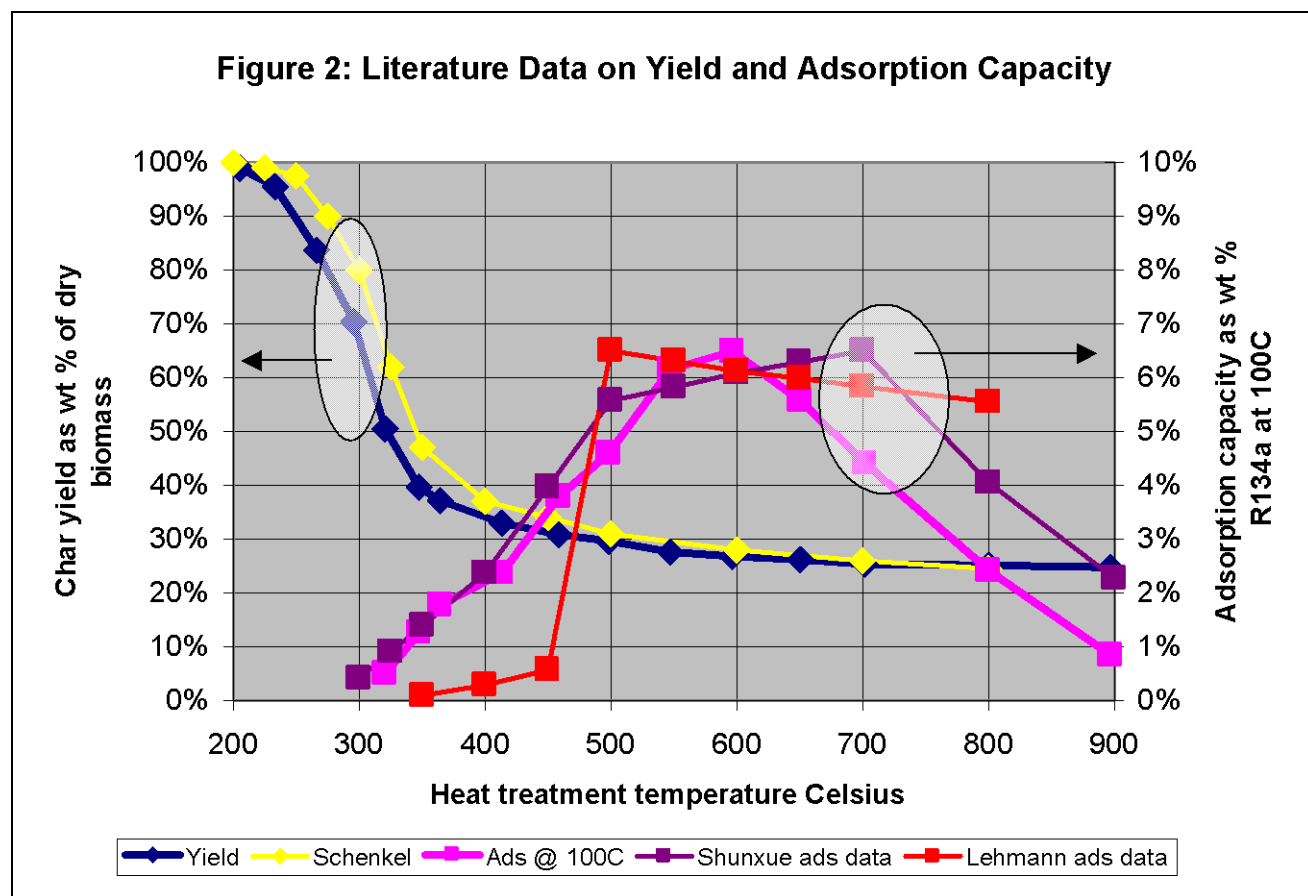
In Figure 1, the well-documented decrease in char yield with increasing HTT is apparent, with a dramatic weight loss between 200C and 400C. In general, 220 Celsius to 280 Celsius is the range of “Torrefaction”, producing a spectrum of increasingly darker brown torrefied materials. Above 300C is considered “Carbonized”, and the color of the pyrolyzed product is black. Notably, the incremental weight loss above 400 Celsius is more gradual, but still significant in terms of overall yield, with the 400C char losing an additional 25 weight percent of mass if pyrolyzed to 900C.

Unlike yield, which decreases progressively with increasing HTT, the Adsorption Capacity undergoes a pronounced and distinctive rise and fall between 300C and 900C. Adsorption Capacity is associated with surface interactions between internal graphitic complexes in the carbonized char and the adsorbate (in this case, the R134a vapor). Logically, the adsorption phenomenon is not observed in torrefied chars because insufficient graphitic domains are formed

under torrefaction conditions, as evidenced by the characteristically brown coloration of such materials. Additional discussion of the role of graphitic domains in adsorption is provided in Appendix C.

3. COMPARING THE LAB CHARS TO LITERATURE TRENDS

While the trends shown in Figure 1 appear to be qualitatively in agreement with previously reported phenomenon in Schenkel and Shenxue, it is useful to confirm how closely the trends compare. Figure 2 shows a collection of data from the literature, including additional data from Lehman (from Figure 5 of “Bio-energy in the black”, appearing in *Front Ecol Environ* 2007; 5(7): 381–387). The adsorption data from Shenxue and Lehmann have been scaled in Figure 2 to match the maximum values of the BET measured surface areas to the maximum adsorption capacity, quantified as the weight percent uptake of R134a at 100C, in the Lab Chars.

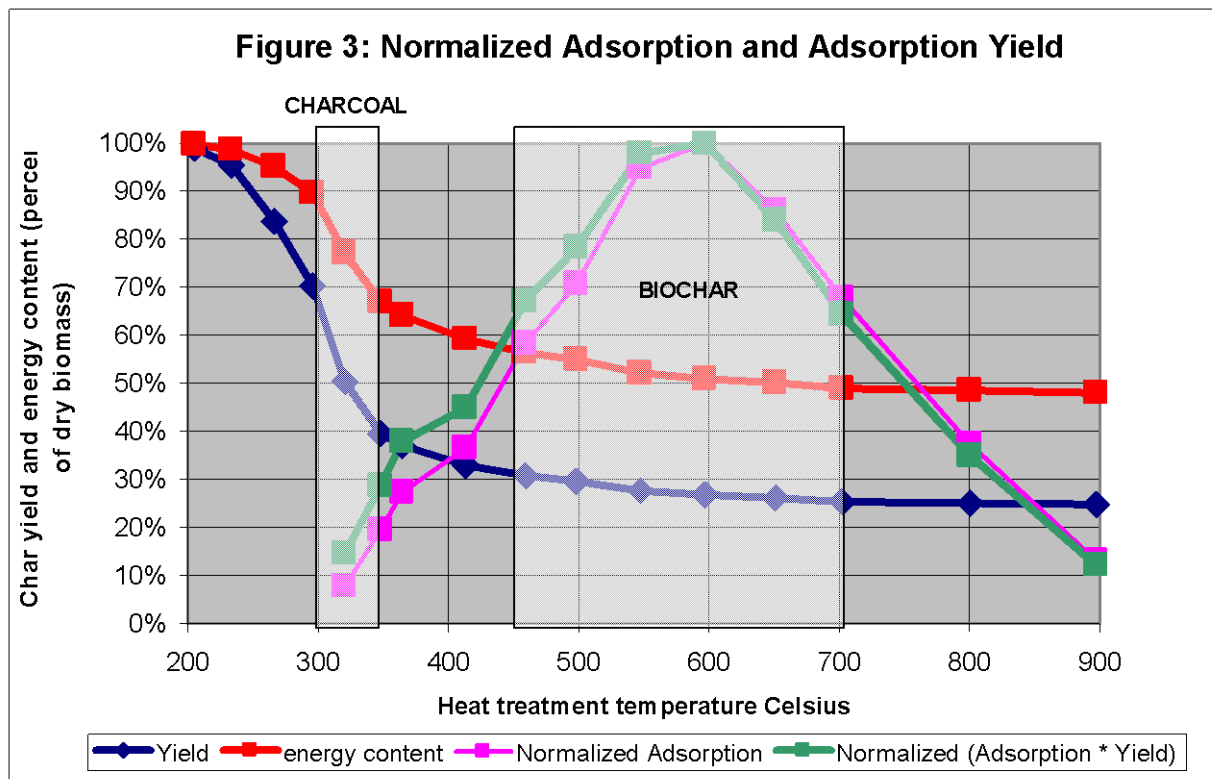


As can be seen in Figure 2, the various data sources overlay reasonably well and are qualitatively in agreement. While the decreasing yield with increasing HTT seems intuitive, it is unexpected to see the intermediate maximum for adsorption capacity and to further find it in historic literature on the subject.

4. IMPLICATIONS FOR CHARCOAL AND BIOCHAR PRODUCTION

Since charcoal is principally used as a cooking fuel and biochar is used in agriculture, it is logical that different properties would influence the valuation of the char depending on the end use. Figure 3 shows some additional metrics to facilitate the prediction of relative performance.

Since charcoal is a fuel, the dominant measure of value is energy content, represented by the product of the yield times the energy density per unit weight of the char. As Figure 3 shows in red, the “energy content” of charcoal drops over the same temperature range that the yield decreases, although to a less severe extent than yield. This is because the energy density of charcoal increases during carbonization, since the char is more carbon-rich than the starting biomass. The exact quantitative relationship is dependent on the specific method of estimating the energy density, with the trend in Figure 3 based on Lower or Net Heating Values of the chars. The same trends derived from Higher or Gross Heating Values would show a less pronounced difference because of how the two methods treat the energy content of the water vapor generated.



As Figure 3 clearly shows, for someone producing charcoal and selling it by weight or energy content, the lowest possible HTT that produces a charcoal of acceptable quality (typically based on a maximum volatile matter content) is the most profitable operating regime.

In contrast, if biochar is valued on the basis of adsorption capacity, then the optimal conditions for production are located at HTTs between 450C and 700C. The two curves shown in Figure 3

for “BIOCHAR” are normalized by the maximum measured value, at 600C. The green curve is the “Adsorption Yield”, which is the product of the weight yield of biochar times the adsorption capacity of the biochar per unit of product. Thus, for the case of optimizing the creation of adsorption capacity from a given amount of biomass, adsorption yield is the appropriate metric to maximize.

In summary, charcoal and biochar are different, and far removed from each other in processing conditions. The optimal operating conditions are separated by roughly 250 degrees Centigrade or 450 degrees Fahrenheit, which is a huge separation of operating conditions. Furthermore, there is really no overlap of the conditions, so the concept of one process making a combination of the two products implies that neither product will be made anywhere near optimal. Such a strategy would appear to be a case of, as the Native American proverb goes, “If you chase two rabbits, you will lose them both”.

5. MOBILE AND RESIDENT MATTER TRENDS IN THE LAB CHARs

Having created a homologous series of chars, additional properties were measured in an effort to further understand what is causing the variation in adsorption capacity and other distinctions between charcoals and biochars. The chars were characterized by a strategy known as the “McShields Biochar Characterization Procedure”. In this characterization scheme, the char is partitioned into four basic constituents: moisture, ash, mobile matter and resident matter. The ash can further be partitioned into acid-soluble and acid-insoluble fractions and the mobile and resident matter further divided into carbon (C) content and the hydrogen + oxygen (HO) portion.

The McShields Procedure evolved from the historical methods used to characterize coals and charcoals, such as ASTM D 1792, with various temperature set points modified to generate information more relevant to evaluating biochars and to maximize the cost-effectiveness of the data collection effort. The “method to the madness” is discussed in detail in Appendix D.

The McShields Procedure initially dries the char sample to 200C and the weight loss is referred to as “moisture”, but does include low boiling volatiles such as acetic acid and methanol. The oven-dried char is then pyrolyzed at 450C for four hours in a vented but anoxic ampoule, which drives off a portion of the char demarcated as the “mobile matter”. A sample of the mobile matter-free sample is ashed at 550C in air to determine the ash content and generate an ash sample for further characterization, if desired. The original oven-dried material and the mobile matter-free sample can be further characterized by a CN elemental analyzer, which is a readily available assay in soil characterization labs.

Figure 4 shows the trends in mobile and resident matter, in addition to the partition of the carbon (C) and the total of the hydrogen + oxygen (HO) in each “matter”, where $\text{Sum} = \text{C} + \text{HO}$. The data shown in Figure 4 has been smoothed to clarify the trends and the minor constituents (ash and nitrogen measurements), present at very low levels due to the high purity of the starting biomass, have been omitted and the data normalized for the remaining organic portion. The raw data is provided and the data smoothing is discussed in Appendix E.

The mobile matter is postulated to represent that portion of the biochar that is unstable over time in the soil. The principal mechanism for loss of the mobile matter in the soil is believed to be the

migration from the biochar into the soil pore water and subsequent metabolization by soil microbes. At this point, and pending further research by the soil scientists and vetting this assay against other available analytical options such as Soxhlet Extraction with a water miscible solvent, the mobile-resident partition is just a practical and convenient analytical procedure that generates a metric for comparing chars. At this juncture, perhaps it should be treated as a premise, awaiting validation by others and based on future research results.

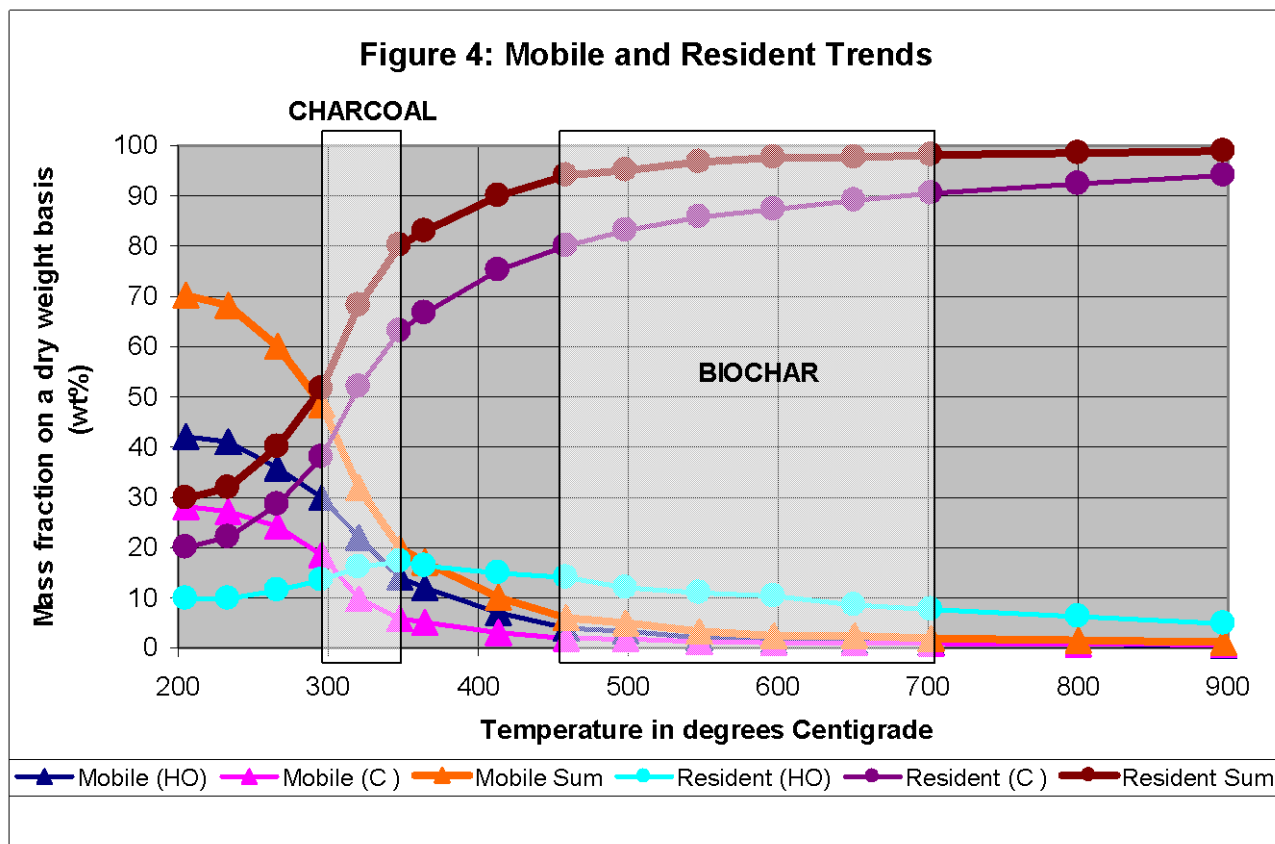
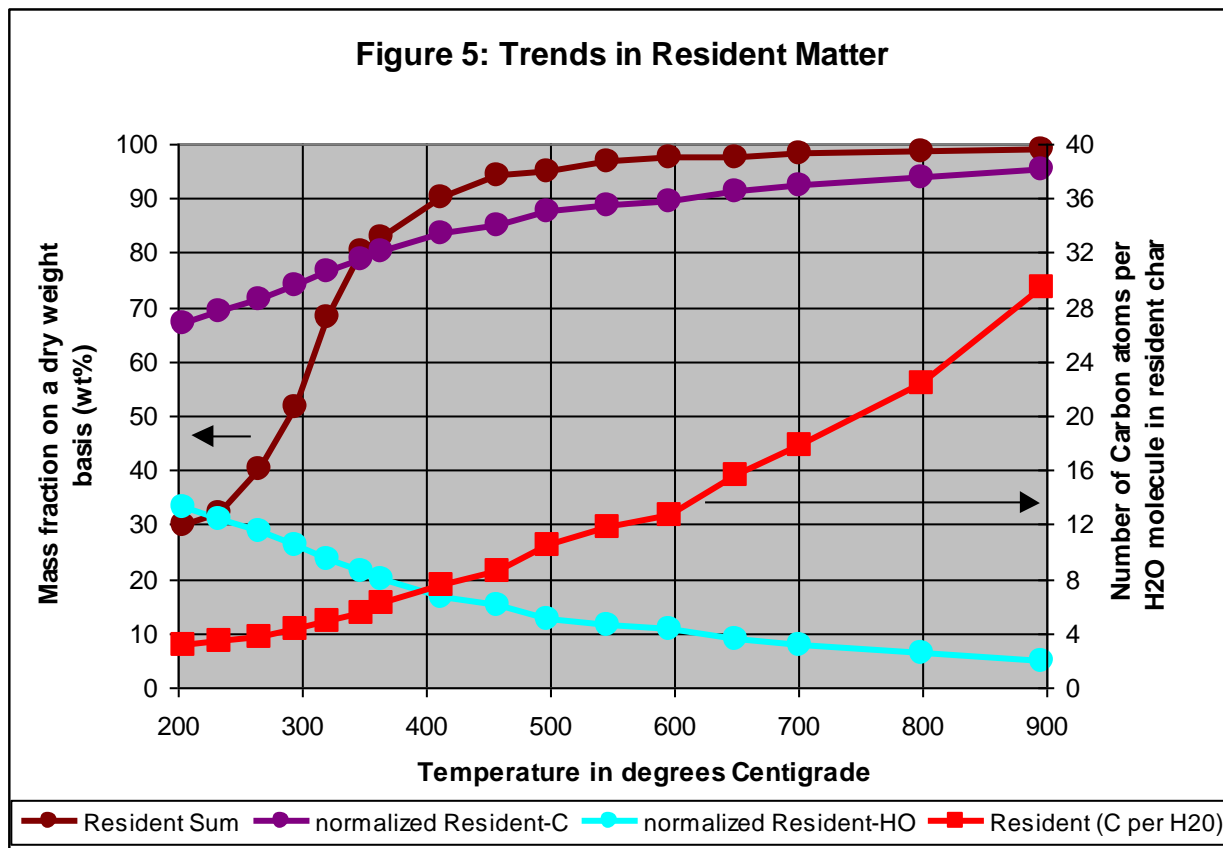


Figure 4 shows further distinctions of the distinction between charcoal and biochar. The variation of measured components is quite severe over a narrow temperature range large for the “charcoal” chars and considerably more consistent over the wider range of “biochar” chars.

6. ANALYZING TRENDS IN RESIDENT AND MOBILE MATTER

Figure 5 shows a detail of the trends in resident matter. The resident matter data from Figure 4 for the Resident Carbon and Resident HO portions have been normalized to add up to 100% before plotting in Figure 5. The resident matter represents that portion of the individual char that remains after the char is pyrolyzed in the absence of air at 450C for four hours. Thus, for samples that were made at HTTs lower than 450C, the chars are seeing a higher HTT for the first time and may undergo additional carbonization while losing additional volatiles at the higher temperatures. Samples that have seen HTTs higher than 450C also show a trend in the composition of the resident matter with increasing temperature, as shown in Figure 5. The specific explanation for this trend, as opposed to the “no change” for chars carbonized above

450C, is an area of current research and currently not adequately resolved within the biochar research community.



The normalized data in Figure 5 allow the calculation of the approximate ratio of carbon to non-carbon atoms in the resident matter fraction of the char. If one assumes that hydrogen and oxygen are present in a ratio of two hydrogen atoms for every oxygen atom, then the moles of non-carbon are proportional to the weight fraction divided by 18 (= 2 x H @ 1 + 1 x O @ 16). This assumption may not be exact, but because of the low molecular weight of hydrogen, the analysis is reasonable over a relatively wide range of hydrogen to oxygen ratios. Dividing the carbon weight fraction by 12 and the non-carbon portion by 18 allows a “Resident (C per H2O)” metric to be calculated. This metric is shown in Figure 5 as the red line and the calculated values refer to the alternate y-axis on the right of Figure 5.

A similar analysis was performed with the mobile matter fraction of the char and that data, analogous to the resident matter treatment, is shown in Figure 6. The differences between Figure 5 and Figure 6 are dramatic, as one might expect, since resident and mobile matter phases are segregating from each other and rapidly evolving with increasing HTT. The most pronounced difference is the behavior of the Mobile (C per H2O) trend, which varies over a minimum of 0.6 to a maximum of 2.1. This is in sharp contrast to the Resident (C per H2O), which monotonically increased from 3 to almost 30 for the range of HTT of 200C to 900C. One can conclude that, under slow pyrolysis conditions, the composite char is transforming into a highly carbonized resident phase, while continuously forming and volatilizing a different class of organic molecules characterized by much lower carbon to non-carbon ratios.

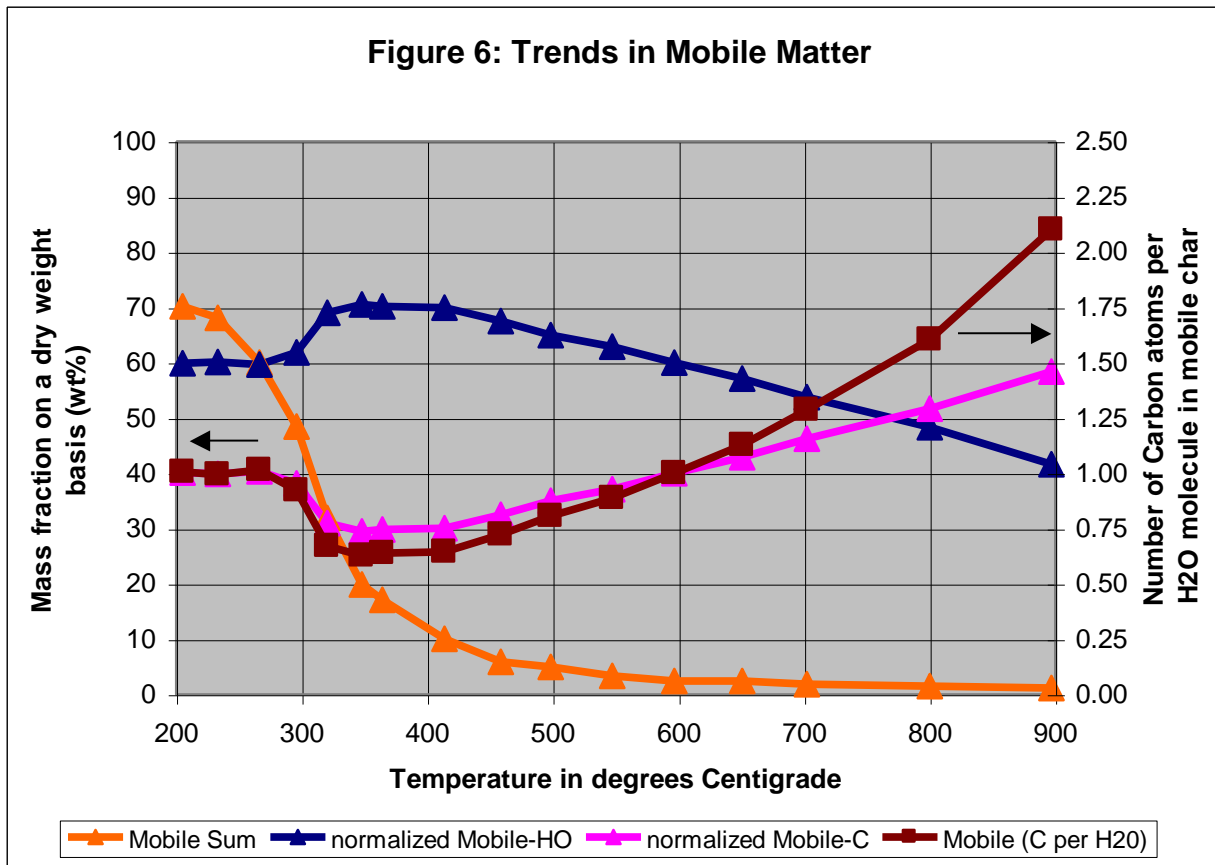


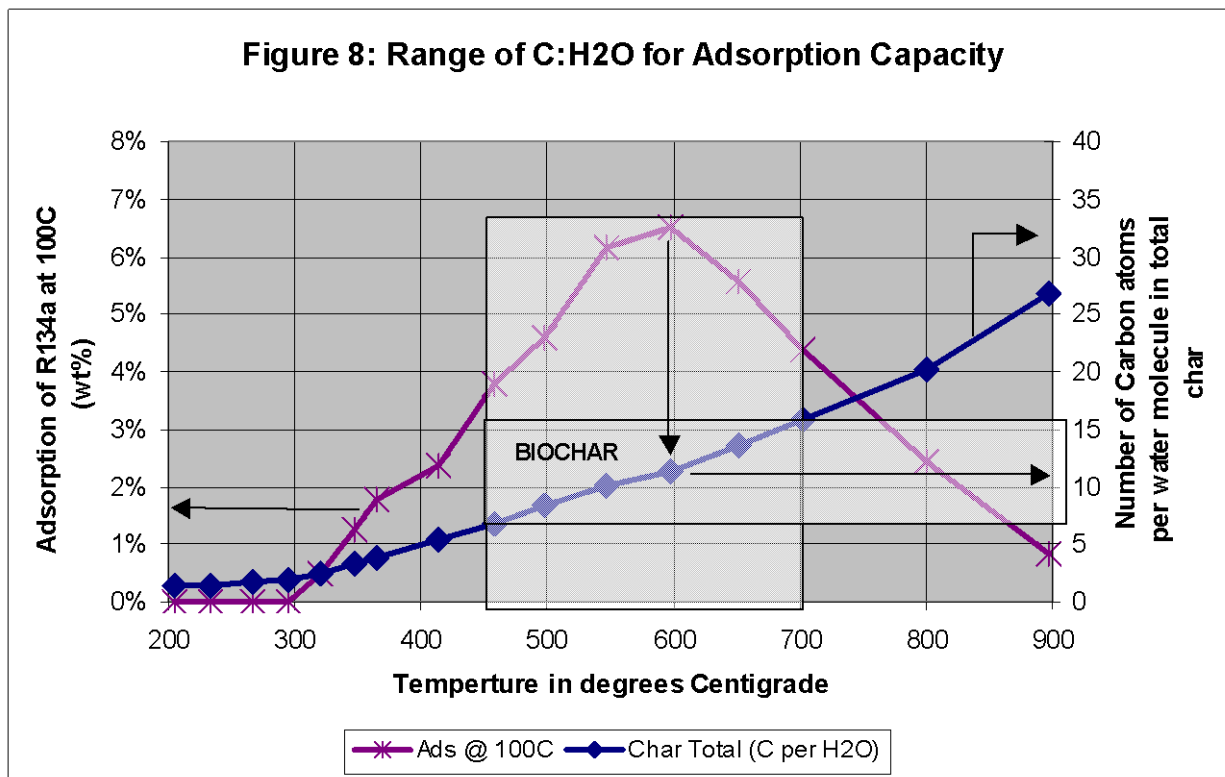
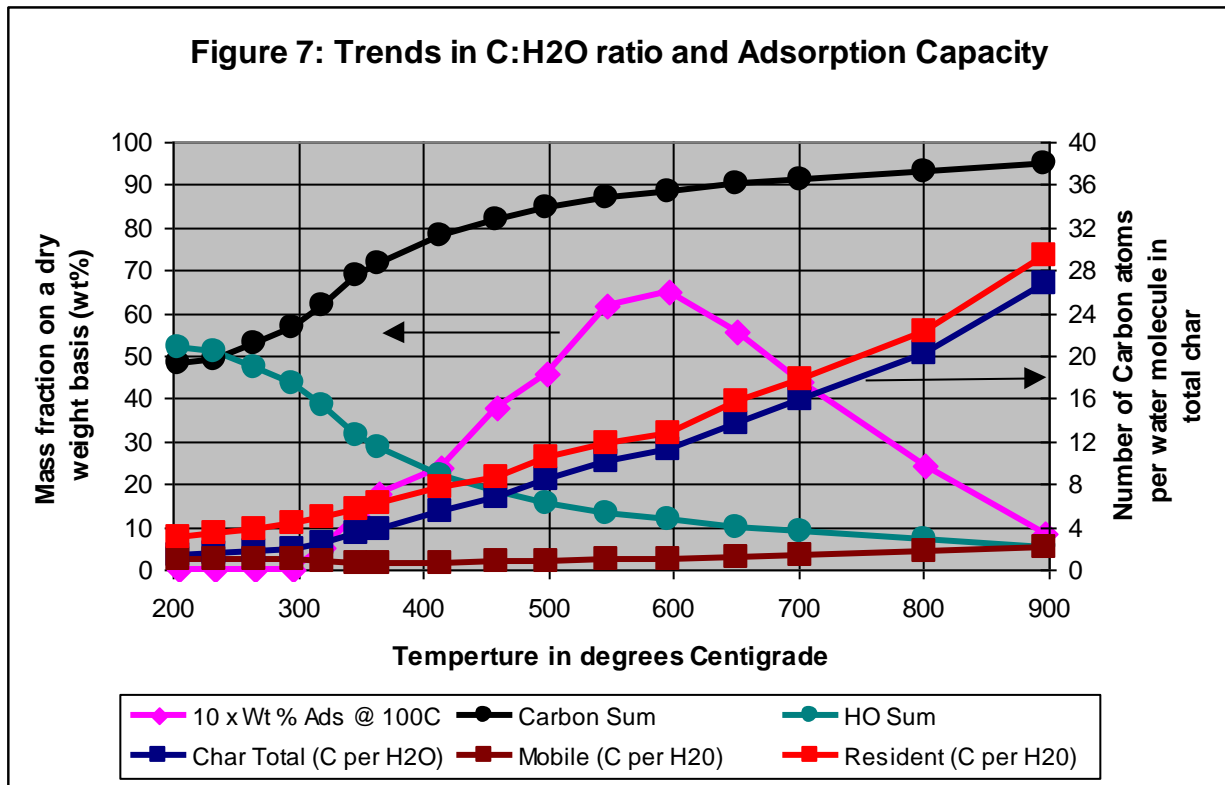
Figure 6 has some interesting and unusual trends for the normalized mobile C and HO fractions, where the properties over 200C to 300C differ from the 300C to 450C pattern, followed by another monotonic trend from 450C to 900C. Explanation of these phenomena awaits further experimental study and will likely require advanced analytical characterization of the specific chemical structures being formed and volatilized.

7. IMPLICATIONS OF C:H₂O RATIO ON ADSORPTION CAPACITY

This analytical odyssey was intended to “further understand what is causing the variation in adsorption capacity and other distinctions between charcoals and biochars”. Having assembled a conceptual model of the formation of the chars with increasing HTT, where an evolving solid phase is consolidating, characterized by increasing C:H₂O ratios, and a relatively consistent supply of mobile phase is being created and volatilized, one can overlay the adsorption data and see if any insights emerge.

Figure 7 provides a summary of the relevant data, and the relationship between C:H₂O ratio and adsorption capacity is further highlighted in Figure 8. What Figure 8 seems to imply is that optimal adsorption capacity requires C:H₂O ratios of between 7 and 16, meaning that there are between 7 and 16 carbon atoms consolidated into the char matrix for each set of H₂O lattice defects. One is tempted to hypothesize that some phenomenon is resulting in the development of adsorption capacity as the C:H₂O ratio exceeds 7 and some additional phenomenon is

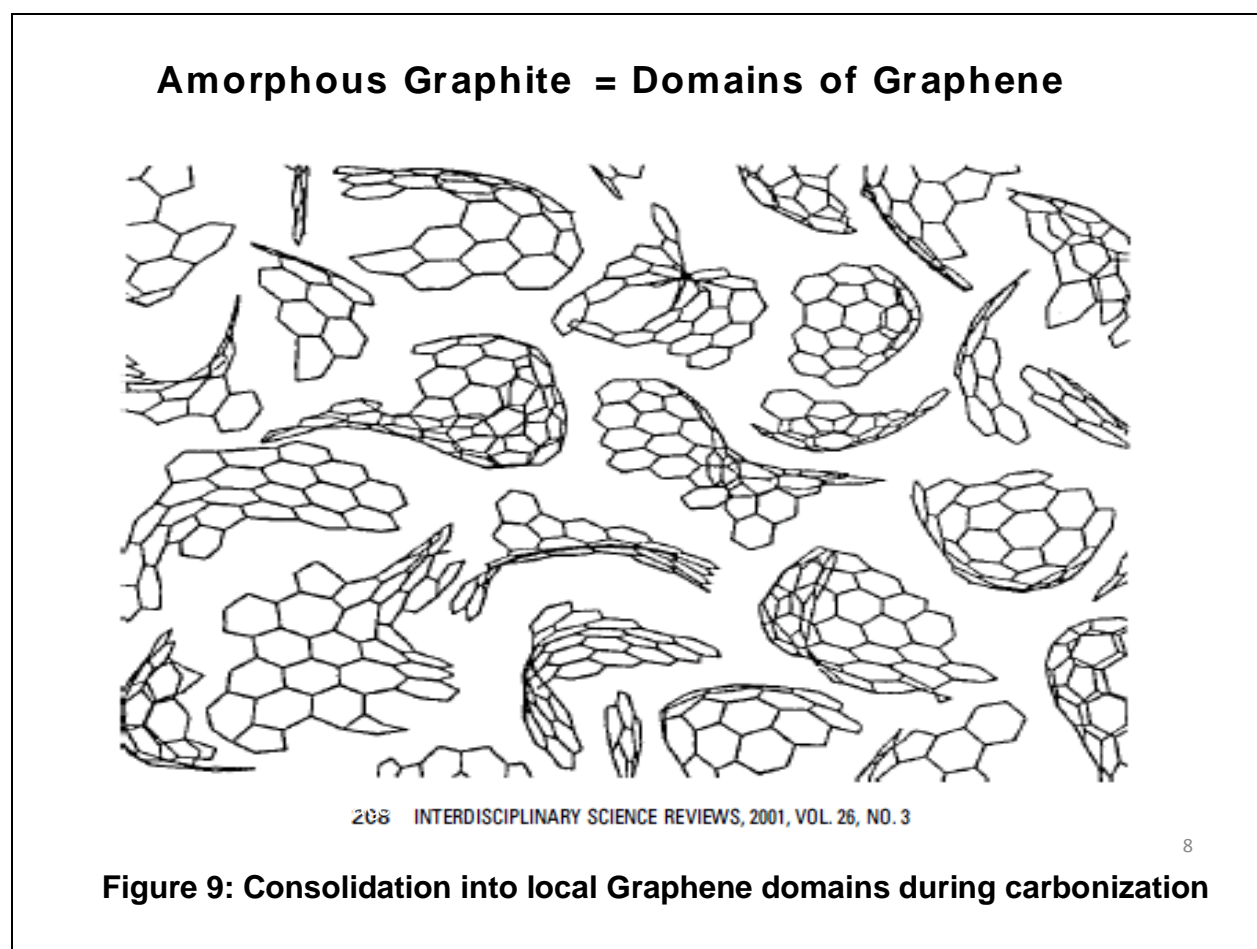
counteracting the development of additional adsorption capacity starting at C:H₂O ratios above 11 and dominating this char property at higher C:H₂O ratios.



8. INSIGHTS FROM ACTIVATED CARBON TECHNOLOGY

The manufacture of activated carbon from naturally occurring biomass, such as woods and nutshells, consists of two discrete chemical transformations; the formation of a carbon-rich char and the “activation” of that char to form an activated carbon. The formation of the char is basically a pure carbonization process, where heating the biomass to above 800C drives off the heteroatoms. During “activation”, an endothermic oxidizing gas (H₂O or CO₂) is reacted with the graphitic matrix to remove carbon atoms to create adsorption sites located in micro-pores.

The consolidation of carbon atoms into graphene sheets is depicted in Figure 9. Note that the individual graphene sheets are curved due to five and seven member rings and do not necessarily form multiple layers of consolidated graphene layers, which are typically referred to as graphitic domains. Graphitic domains are much more prevalent in chars that have been converted to activated carbons, as discussed in Appendix C.



The graphene sheets shown in Figure 9, represented by the individual “potato chip” shaped clusters of aromatic carbon atoms, contain many more carbon atoms than the range predicted for adsorption in chars. Other researchers have attempted to estimate the size of the graphene sheets and Figure 10 contains one such estimate that agrees well with the analysis provided here. While

the agreement between Figure 8 and Figure 10 may well be a case of “geniuses think alike and fools seldom differ”, it is still nice to not be in conflict with the predictions of others researchers in the biochar field. Additional support of the development and structure of graphene sheets is found within fundamental research focusing on carbon nanotubes, especially the work of Keith Gubbins at Cornell and NC State and Peter Harris at the University of Reading in the UK.

When one manufactures activated carbon, one can create a series of activated products from one starting char, and this series of incrementally activated carbons is known as an “Activation Series”. The Activation Series represents the family of possible activated carbons that can be derived from a particular starting raw material, in this case the fully carbonized char. Within the Activation Series is the optimal activated carbon for a particular adsorption application, and the preferred activated carbon varies with the individual adsorption application – although typically not by much.

Figure 10: Literature estimate of Graphene Domain Size

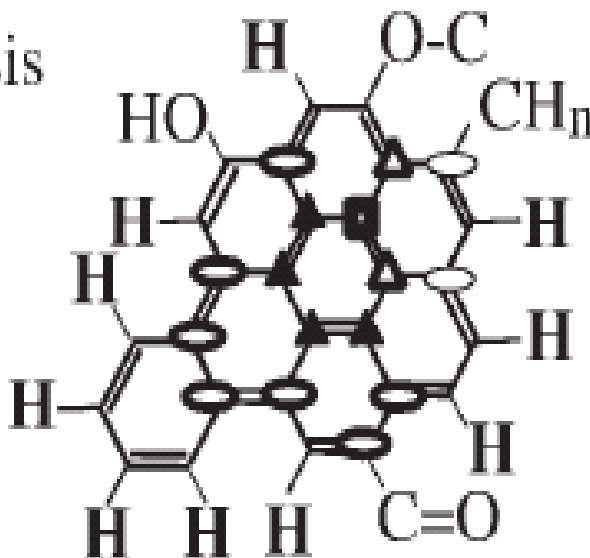
(a) Slow pyrolysis
(37% CH):

8 rings
28 C

C: 28 + 3

O: 3

H: 11 + n



500C Switchgrass “typical fused-ring system” from Brewer, et al.,
Env Progress & Sustainable Energy (Vol. 28, No.3, Oct 2009,
pp. 386-396). Reproduced from Figure 5a on page 393.

If one examines the entire GACS (Gravimetric Adsorption Capacity Scan) for the homologous series of lab chars, a very insightful trend is observed. As shown in Figure 11, the GACS trends for those chars in the series leading up to the maximum adsorption show a consistent development of adsorption across the entire range of adsorption temperatures, with the adsorption capacity being the value of the individual GACS at 100 Celsius. In contrast, as shown in Figure 12, the GACS trend past the adsorption maximum shows a decrease in adsorption, but principally at the lower adsorption temperatures and to a lesser extent at the higher temperatures.

Figure 11: GACS evolution with Increasing Adsorption over the temperature range of 300C to 600C

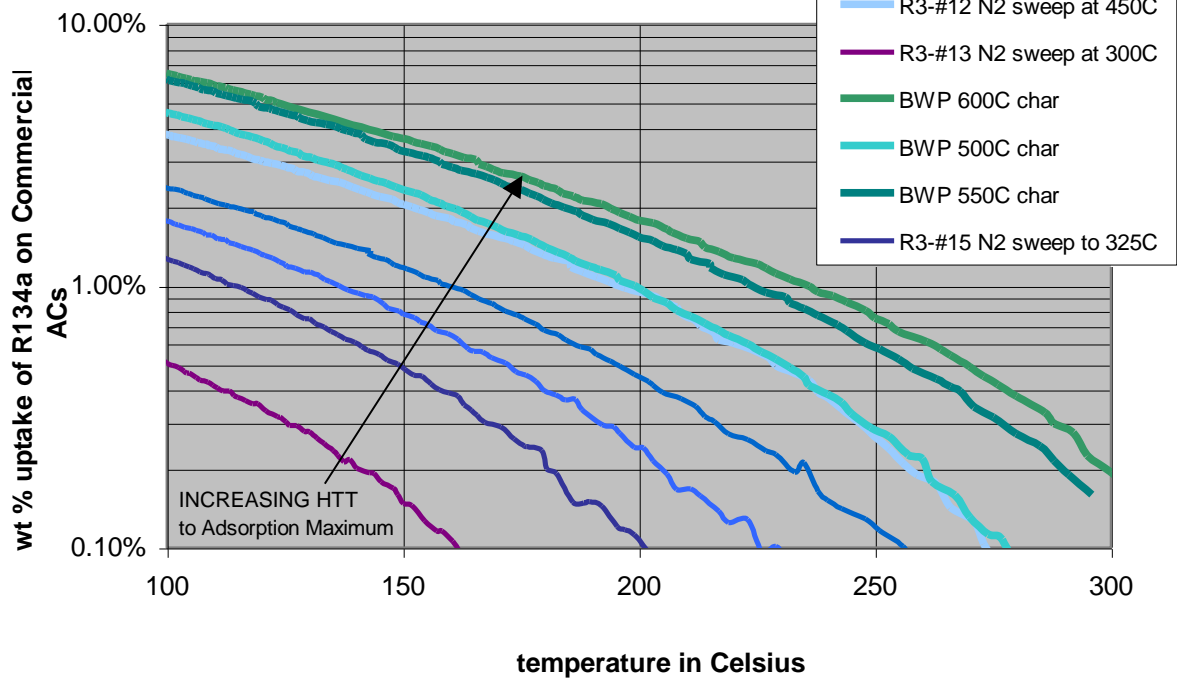
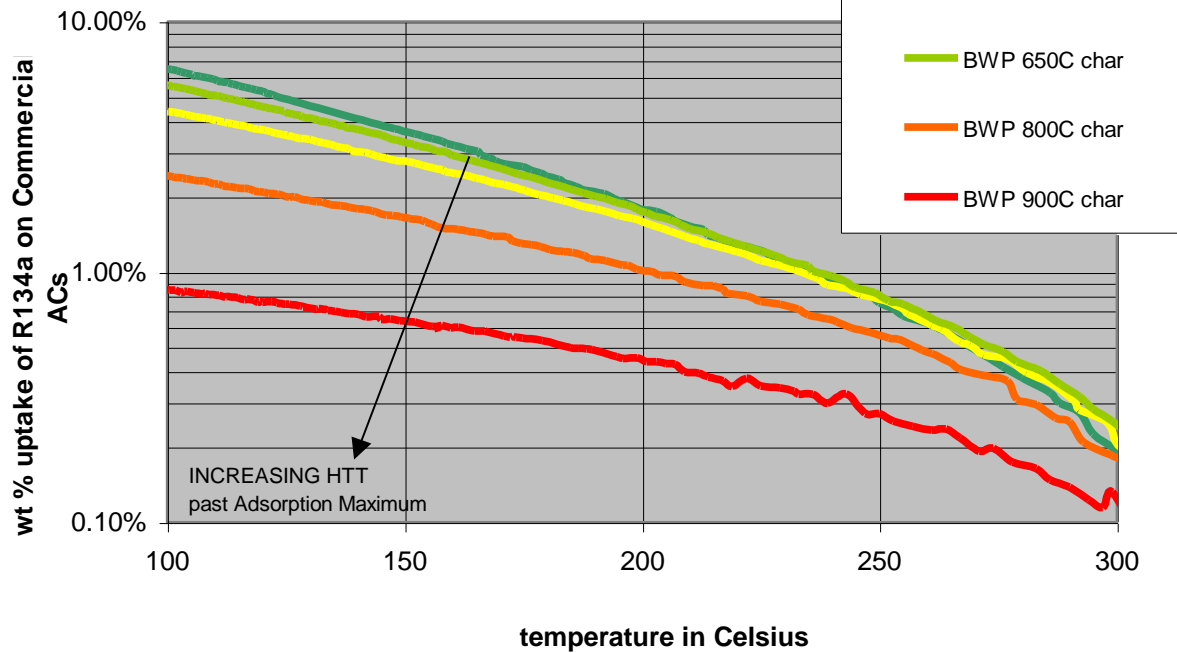


Figure 12: GACS evolution with Decreasing Adsorption over the temperature range of 600C to 900C



The trends of Figures 11 and 12 are combined in Figure 13, accentuating the difference in the GACS evolution of the lower adsorption temperatures, corresponding to lower adsorption energy, as compared to the trend at the higher adsorption temperatures and energies.

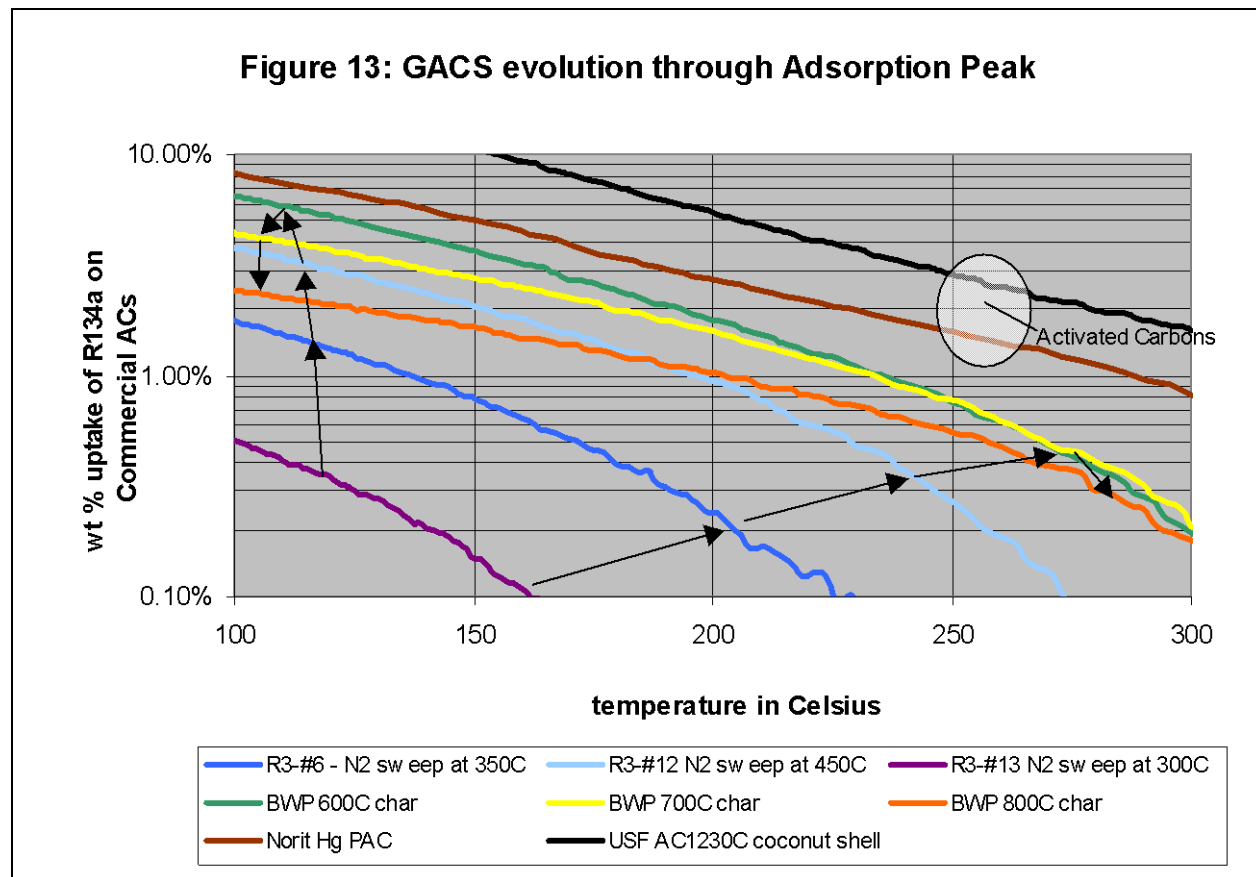


Figure 13 also includes two GACS data sets for fully activated carbons. Norit Hg PAC is a lower surface area powdered activated carbon, made from lignite, and USF AC1230C is a highly activated coconut shell granular activated carbon. What can be concluded from the comparison of the GACS trends is that the adsorption capacity for lower energy adsorption sites, as measured at lower adsorption temperatures, is rising and falling with HTT, whereas the higher energy adsorption capacity is continuing to build with HTT. These two trends are compatible with a mechanism where the individual graphene sheets are consolidating into multi-layer graphitic domains at HTTs above the HTT associated with maximum adsorption capacity.

In summary, the overall evolution of the char internal structure is consistent with a development of adsorption capacity by steadily enlarging graphene sheets with increasing HTT. At some intermediate HTT, the incremental loss of non-graphene carbons, either by volatilization or incorporation into expanding graphene sheets, weakens the local three-dimensional structure of the char such that individual graphene sheets can collapse on each other, in response to the same adsorption forces that impart adsorption capacity. This trend builds additional high-energy adsorption sites at the sacrifice of larger volumes of lower energy adsorption capacity. Additional background discussion of adsorption theory is provided in Appendix C.

9. DOES APPROPRIATE GRAPHENE CONTENT ASSURE ADSORPTION?

The above discussion leads one to conclude that a necessary degree of consolidation of the biomass into graphene sheets is a necessary requirement for the development of adsorption capacity. Furthermore, the consolidation of biomass into graphene sheets is fundamentally driven by the HTTs at which the individual char-forming biomass constituents, hemicellulose, cellulose and lignin thermally decompose and carbonize. Thus, individual biomass sources may build surface area at different HTTs, the differences are likely to be limited to the extent the biomass sources differ in hemicellulose, cellulose and lignin composition.

By similar logic, the decline of adsorption capacity with HTT, beyond the adsorption maximum, is likely to depend on the unique characteristics of the starting biomass with respect to resisting the consolidation of the graphene sheets into multi-layer graphitic domains, which will mainly depend on lignin content, since lignin pyrolyzes over a wide temperature range, and how the lignin is distributed within the original biomass. Hemicellulose and cellulose carbonize at temperatures below 500C, before the onset of the adsorption capacity decline, so their role in this phenomenon is expected to be less significant than that of lignin.

These dependencies on the properties of the starting biomass lead one to speculate if, given the right biomass and carbonized to the appropriate HTT, should appreciable adsorption capacity be expected. The answer is a rather disappointing “Maybe – if nothing else goes wrong”. Another critical consideration in the development of adsorption capacity is not destroying it by adsorbing pyrolytic vapors in the newly formed adsorption sites and having the vapors subsequently decompose into coke that effectively blocks the adsorption site.

This rather unfortunate phenomenon is poorly understood and often embraced as the mechanism for achieving higher char yields within a given pyrolysis process. As discussed in Antal and Gronli at the bottom of page 1627:

Although Klason established the key role of secondary (vapor-phase) pyrolytic reactions in the formation of charcoal 88 years ago; today, many researchers still assume that charcoal is solely a product of primary (solid-phase) pyrolytic reactions. In reality, charcoal contains both “primary” charcoal and “secondary” charcoal that is a coke derived from the decomposition of the organic vapors (“tars”) onto the solid carbonaceous solid.

10. CONCLUSIONS

It appears that adsorption capacity in an individual biochar depends on many things to go right. The char has to be formed at a sufficient HTT to pyrolyze the biomass, the biomass has to thermally decompose, and the remaining solid has to consolidate into graphene sheets. The HTT cannot be so high that the three-dimensional structure of the developing char weakens to an extent that the graphene sheets coalesce and deteriorate the lower energy adsorption capacity formed at lower temperatures. Finally, the vapors present in the pyrolysis reactor cannot excessively condense into the existing adsorption sites and block them with coke.

To the extent such conditions exist during char creation, one gets good biochar. To the extent such conditions are missing, which is virtually always the case, one does not get good biochar. As such, one should not assume that an existing processes that generates a char is producing good biochar, until that leap of faith is confirmed by measuring the actual char properties.

So, the phrase “I’d rather be lucky than good” does not apply to biochar production. Bummer.