2024 NORTH AMERICAN BIOCHAR CONFERENCE

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CALIFORNIA, USA

Methods for measuring biochar properties *and* how they determine value and performance

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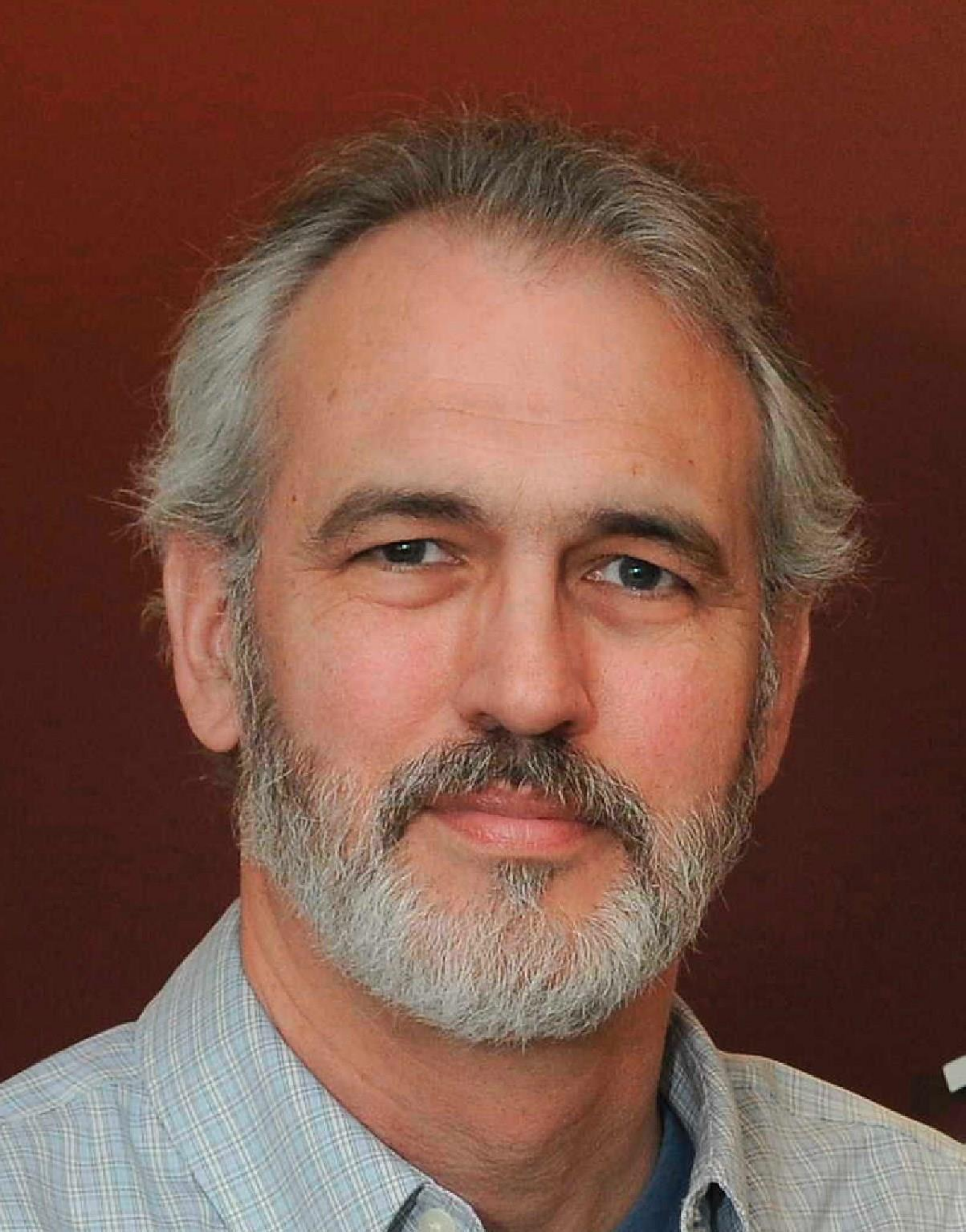


I have been doing biochar since 2008.

It shows.

It was a mystery.

Now it is well under-stood.

par·a·digm

- a paradigm is **a standard, perspective, or set of ideas**

par·a·digm shift

- a **fundamental change** in approach or underlying assumptions

THE STATE OF Carbon Dioxide Removal

A global, independent scientific assessment of Carbon Dioxide Removal

1st EDITION

A collaboration led by Stephen M Smith (University of Oxford), Oliver Geden (German Institute for International and Security Affairs, SWP), Jan C Minx (Mercator Research Institute on Global Commons and Climate Change, MCC) and Gregory F Nemet (University of Wisconsin-Madison)

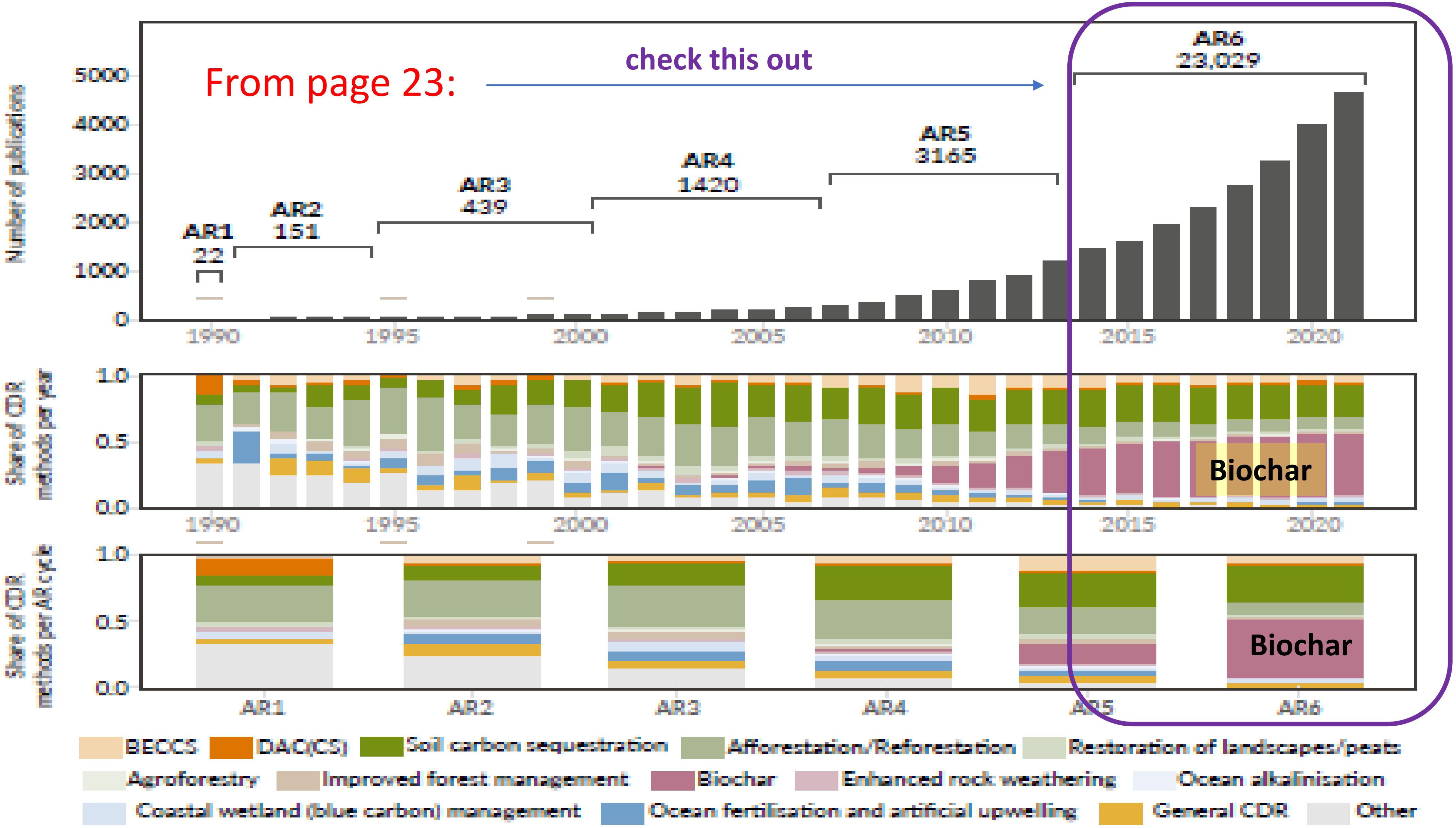


Figure 2.1. *Exponential growth in the scientific literature on Carbon Dioxide Removal (CDR) over time. Total*

Research on biochar is growing faster than that of any other CDR method, accounting for about 40% of the coverage on CDR methods in the scientific literature overall and about 50% of the studies published in 2021.

Based on first author affiliation, 32% of scientific studies on CDR are written in China, 9% in the United States and 4% in Australia. This is particularly driven by a strong dominance of biochar research in China.

Dear Biochar World: ***YOU ROCK!***

- You have nailed the research on Biochar. Furthermore, biochar is the CDR method that is safe, shovel ready, scalable – and, apparently, researched so exhaustively that there is, effectively, an extinction of uncertainty.

- We know how to make it, how to use it, how to value it, and now we get to sit back and watch the world use biochar to avoid impending doom. ***or NOT***

Organic Carbon (C_{org})	10% Minimum *Class 1*: ≥60% *Class 2*: ≥30% and <60% *Class 3*: ≥10% and <30%
$H:C_{org}$	0.7 Maximum

Beyond *Declarations*, here's what you know

ar Initiative

Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil

After you pass all the tests ONE TIME, and if the check don't bounce, you get to tell the world that your biochar is

IBI certified biochar ™

Type of Document:	Product Definition and Specification Standards
Status of Document:	Final
Version Number:	2.1
Version Date:	23 November 2015
Document Reference Code:	IBI-STD-2.1

Table 1. Test Category A Parameters, Criteria, and Test Methods.

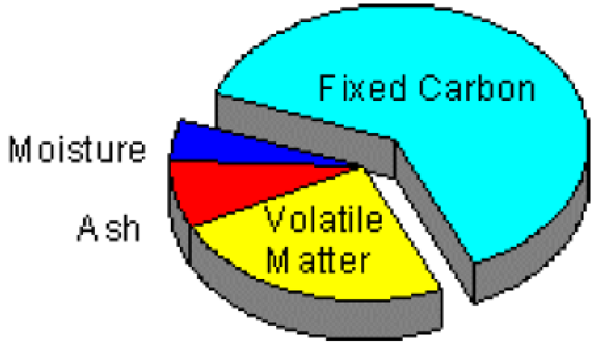
Test Category A: Basic Utility Properties (Required for All Biochars)			
Parameter	**Criteria**[1]	**Unit**	**Test Method**[2]
Moisture	Declaration	% of total mass, dry basis	ASTM D1762-84 Standard Test Method for Chemical Analysis of Wood Charcoal (specify measurement date with respect to time from production)
Organic Carbon (C_{org})	10% Minimum *Class 1*: ≥60% *Class 2*: ≥30% and <60% *Class 3*: ≥10% and <30%	% of total mass, dry basis	Total C and H analysis by dry combustion-elemental analyzer. Inorganic C analysis by determination of CO_2-C content with 1N HCl, as outlined in ASTM D4373 Standard Test Method for Rapid Determination of Carbonate Content of Soils. Organic C calculated as Total C – Inorganic C. See Appendix 7 for $H:C_{org}$ discussion.
$H:C_{org}$	0.7 Maximum	Molar ratio	
Total Ash	Declaration	% of total mass, dry basis	ASTM D1762-84 Standard Test Method for Chemical Analysis of Wood Charcoal
Total Nitrogen	Declaration	% of total mass, dry basis	Dry combustion-elemental analyzer following the same procedure for total C and H above.
pH	Declaration	pH	pH analysis procedures as outlined in section 04.11 of TMECC (2001) using modified dilution of 1:20 biochar:deionized H_2O (w:v) and equilibration at 90 minutes on the shaker, according to Rajkovich et al. (2011). See Appendix 5 for further information.
Electrical Conductivity	Declaration	dS/m	EC analysis procedures as outlined in section 04.10 of TMECC (2001) using modified dilution of 1:20 biochar:deionized H_2O (w:v) and equilibration at 90 minutes on the shaker, according to Rajkovich et al. (2011). See Appendix 5 for further information.
Liming (if pH is above 7)	Declaration	% $CaCO_3$	AOAC 955.01 potentiometric titration on "as received" (i.e., wet) samples. Use dry weight to calculate % $CaCO_3$ and report "per dry sample weight".
Particle size distribution	Declaration	% <0.5 mm; % 0.5-1 mm; % 1-2 mm; % 2-4 mm; % 4-8 mm; % 8-16 mm; % 16-25 mm; % 25-50 mm; % >50 mm	Progressive dry sieving with 50 mm, 25 mm, 16 mm, 8mm, 4mm, 2 mm, 1 mm, and 0.5 mm sieves.

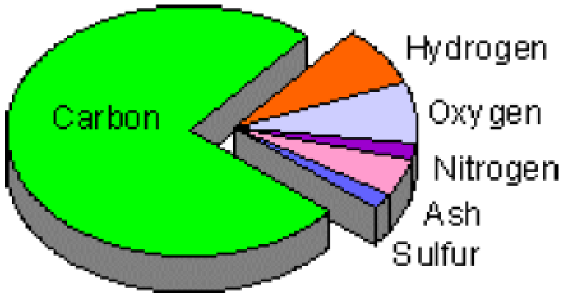
FIGURE 4: PROXIMATE AND ULTIMATE ANALYSES OF COALS

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 page 8 of "All Biochars are not created equal and how to tell them apart", V2, Oct 2009

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

Drying: par·a·digm

par·a·digm shift

D1762 – 84 (2021)

Standard Test Method for Chemical Analysis of Wood Charcoal[1]

7. Procedure

7.1 Make duplicate determinations.

7.2 *Moisture*—Heat the muffle furnace to 750°C and place previously ignited porcelain crucibles (Note 1) and covers in the furnace for 10 min. Cool the crucibles in a desiccator for 1 h. Weigh the crucibles and add to each approximately 1 g, weighed to the nearest 0.1 mg, of the ground sample. Place the samples in the oven at 105°C for 2 h. Place the dried samples in a desiccator for 1 h and weigh (Note 2).

Note 1—In practice, a crucible from a previous determination is used.

Note 2—The sample shall be considered oven-dry when the decrease in weight of consecutive weighings is 0.0005 g or less. Succeeding drying periods shall be not less than 1 h.

D2867 – 09

Standard Test Methods for Moisture in Activated Carbon[1]

7.2 Remove the cover and place the capsule and cover in a preheated forced circulation oven (at 145 to 155°C). Close the oven and dry to constant weight (3 h normally sufficient). Open the oven and cover the capsules quickly. Cool in a desiccator to ambient temperature and weigh.

Takeaway: Dry at 150 degrees C

Volatile Matter & Ashing: par·a·digm

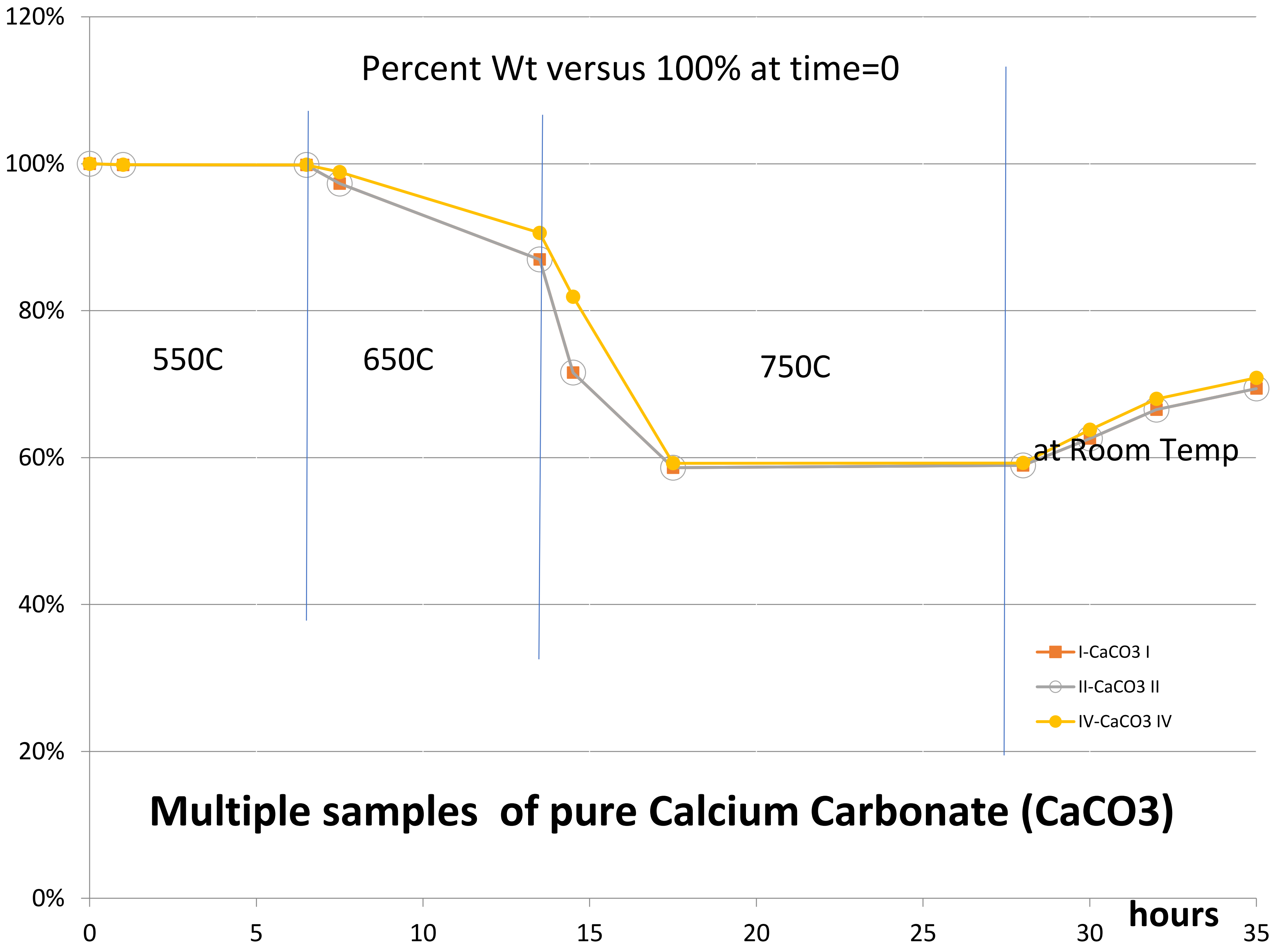
D1762 – 84 (2021)

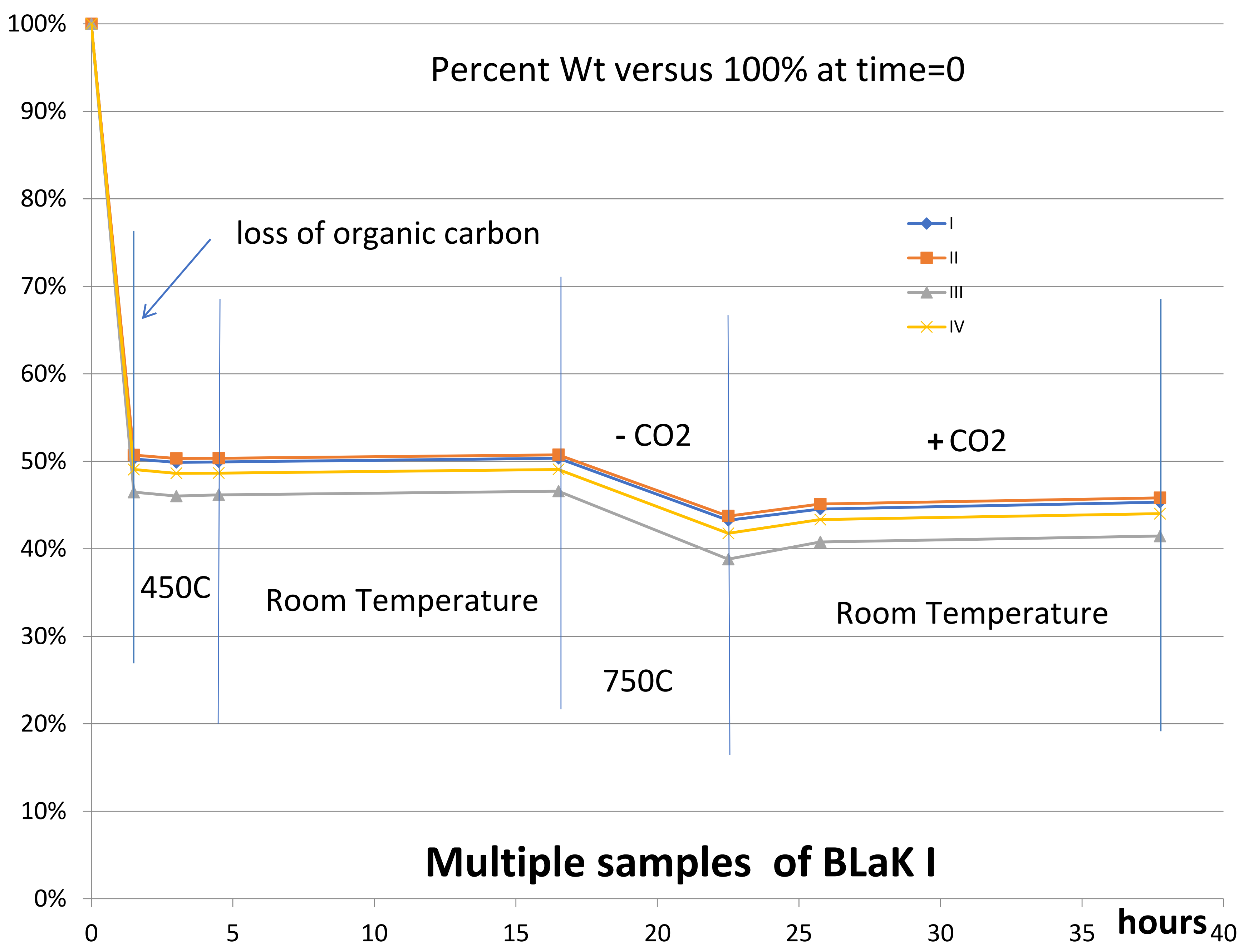
Standard Test Method for Chemical Analysis of Wood Charcoal[1]

7.4 *Ash*—Place the lids and the uncovered crucible used for the volatile matter determination, and containing the sample in the muffle furnace at 750°C for 6 h. Cool the crucibles with lids in place in a desiccator for 1 h and weigh. Repeat burning of the sample until a succeeding 1-h period of heating results in a loss of less than 0.0005 g.

7.3 *Volatile Matter*—Heat the muffle furnace to 950°C. Preheat the crucibles used for the moisture determination, with lids in place and containing the sample, as follows: with the furnace door open, for 2 min on the outer ledge of the furnace (300°C) and then for 3 min on the edge of the furnace (500°C) (Note 3). Then move the samples to the rear of the furnace for 6 min with the muffle door closed. Watch the samples through a small peep-hole in the muffle door. If sparking occurs, results will be in error (Note 4). Cool the samples in a desiccator for 1 h and weigh.

This is a Muffle Furnace at 950C when you open the door – good luck with that.


Percent Wt versus 100% at time=0
120%
100%
80%
60%
40%
20%
0%
550C
650C
750C
at Room Temp
I-CaCO3 I
II-CaCO3 II
IV-CaCO3 IV
Multiple samples of pure Calcium Carbonate (CaCO3)
0
5
10
15
20
25
30
35
hours



Percent Wt versus 100% at time=0
loss of organic carbon
I
II
III
IV
- CO2
+ CO2
450C
Room Temperature
750C
Room Temperature
Multiple samples of BLaK I
hours
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
0
5
10
15
20
25
30
35
40

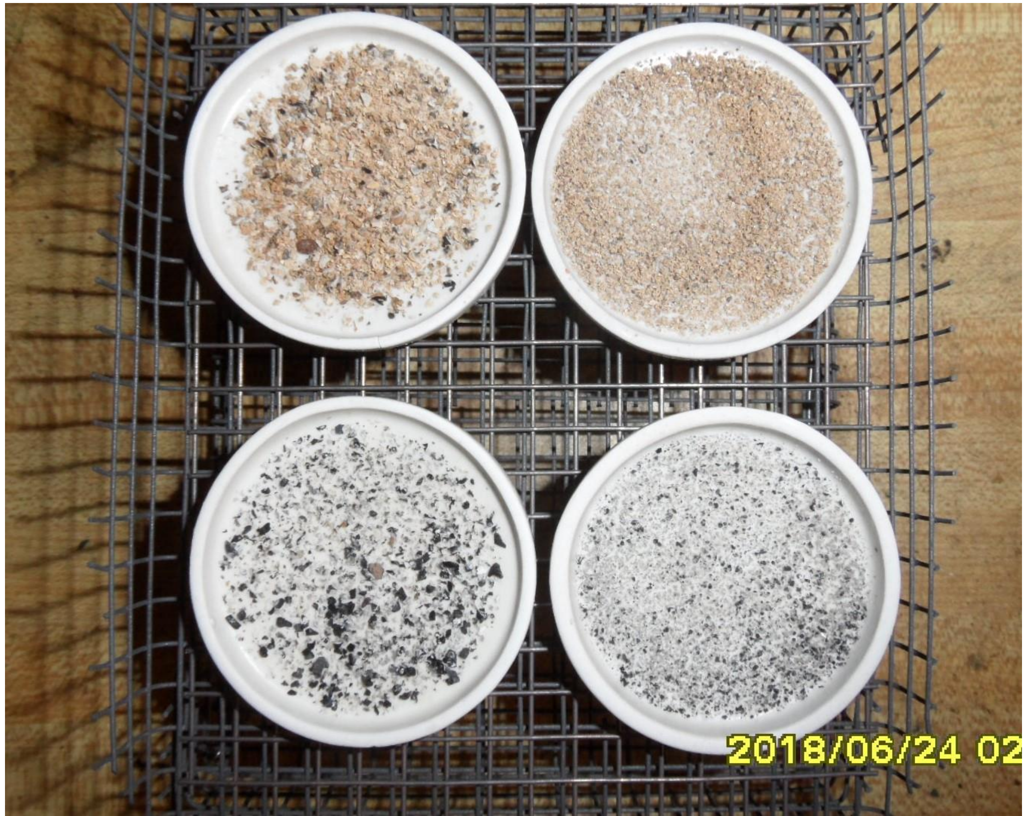
Ashing: par·a·digm shift

Takeaway:

Ash at 450 to 550 degrees C, 1 to 2 hr., check periodically

- lower ashing temp to below 600C to avoid decomposition of carbonates, such as:

$CaCO_3 \rightarrow CaO + CO_2$



Biochars at the molecular level.

Part 1 – Insights into the molecular structures within biochars.

So far, we have this sorted out

Rosie Wood[a], Ondřej Mašek[b], Valentina Erastova[a]*

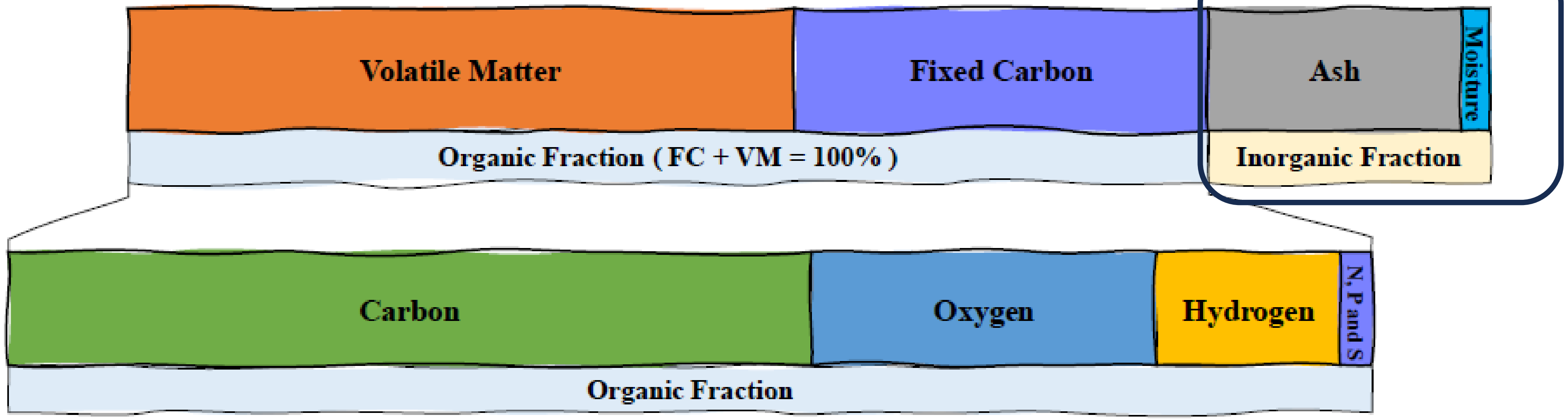


Figure 3. A schematic guide to the chemical composition of biochars. The upper band depicts the macromolecular composition, including both organic and inorganic fractions; the lower band depicts the elemental composition of the organic fraction only.

Proximate analysis has its roots in fuel chemistry, where it is used to determine the macromolecular composition of a substance at operational temperature (approximately 1000°C).[44] It has been translated into the study of biochars and is now one of the most commonly used characterisation techniques within biochar research.[13,16,21,27–

We need something that provides insights or measurements that correlate to the various organic compounds found in biochars. These organics can be grouped into VOCs, SVOCs and stable graphitic structures (via H/Corg correlation, inertinite, etc.)

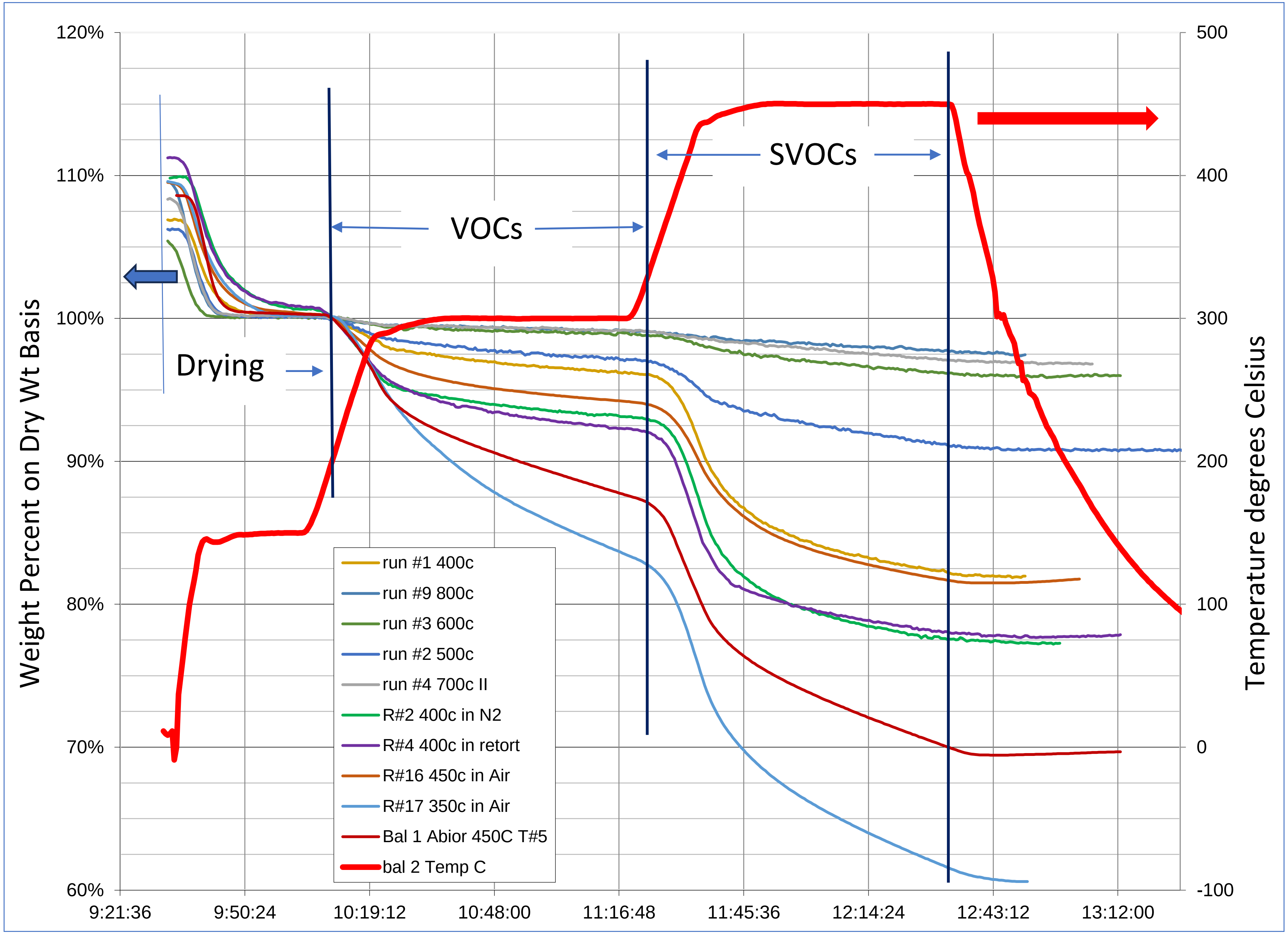
More modern techniques, based upon thermogravimetric analysis (TGA), are also used and measure mass loss in situ throughout the heating process.[18,27,30,32,33] TGA-based proximate analyses can be automated through use of a pre-set heating programme, making it more convenient and reliable than the traditional method. However, TGA is still susceptible to many of the same issues outlined above and, since very small sample sizes are often used, TGA-based analyses can be especially affected by sample inhomogeneity.[30] Averaging across multiple samples is, therefore, essential when using TGA.

Although useful for determining the proportions of inorganic to organic matter within biochars, proximate analyses give no absolute insights into their molecular structures. These molecular structures must, therefore, be characterised using other techniques. Nevertheless, knowing the ash and moisture content of a sample is critical

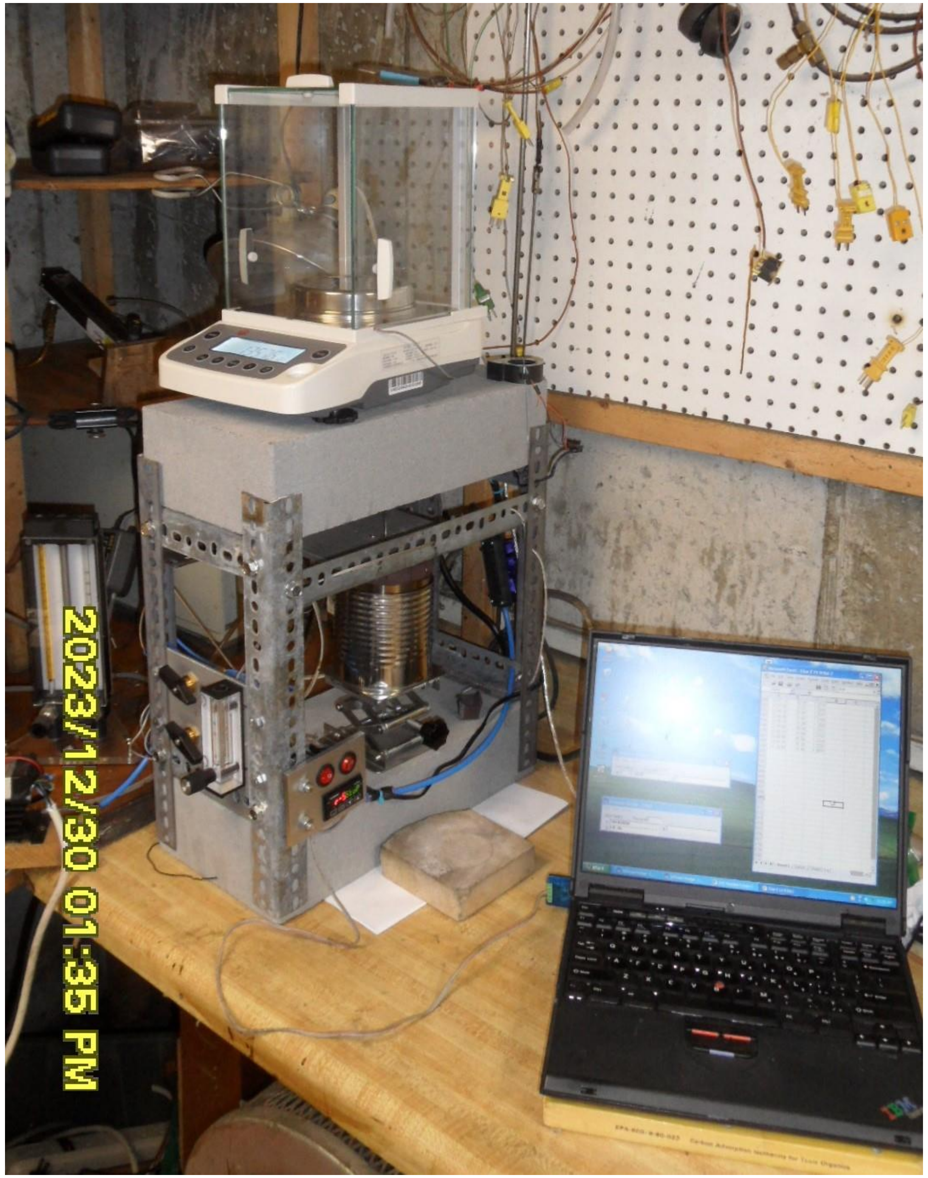
So, here we go: **Presenting the GACS+ Instrument**

The organic fraction of biochar is divided into **Moisture** that comes off below 200C, **VOCs** that come off between 200C and 325C, **SVOCs** that come off between 325C and 450C, and **Stable Carbon** – calculated by difference.

Ash is measured on a dry weight basis to make up all of the mass of the biochar.



Presenting the GACS+ Instrument: which is *easily* constructed for <$1500



Don’t worry, there are Alternatives to the GACS+ Instrument

For moisture only: starting at $22K
- Single sample devices are much more affordable, but so is a toaster oven and any ebay balance…..

TGM800 Moisture

- High precision, automated thermogravimetric moisture determination, which utilizes a direct method for replacing tedious manual loss-on-drying techniques
- Measure up to 16 samples at a time with drying time end-point recognition
- Intuitive *Cornerstone* brand software with flexible method settings and touch-screen operation
- Precise oven temperature ramping and set point control up to 150 °C
- Remote access through *Cornerstone* Mobile provides access to data, plots, and instrument status from smartphone, tablet, or desktop computer

For moisture, ash and desorption of volatiles: starting at $44K

TGA801 Thermogravimetric Analyzer

- Determines moisture and ash or other gravimetric methods
  in various organic samples
- Expanded temperature control (up to 1000 °C) with variable atmospheres and ramp rates
- Automated batch thermogravimetric analysis of up to 19 samples

Unparalleled Versatility

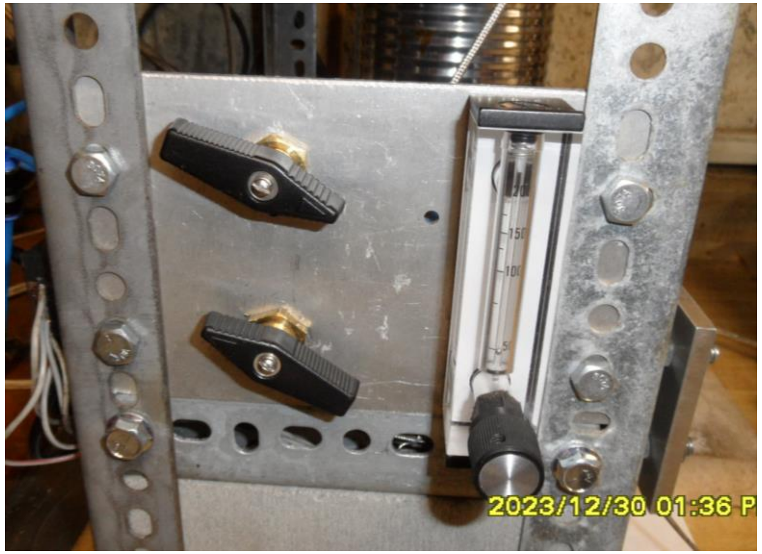
- Automated multi-sample analysis batch,up to 19 samples
- Macro sample mass capabilities, nominal 1 g
- Flexible method settings enable configuration of system to emulate classic gravimetric test method requirements
- Optimized analysis time with the automatic end point recognition using sample mass constancy

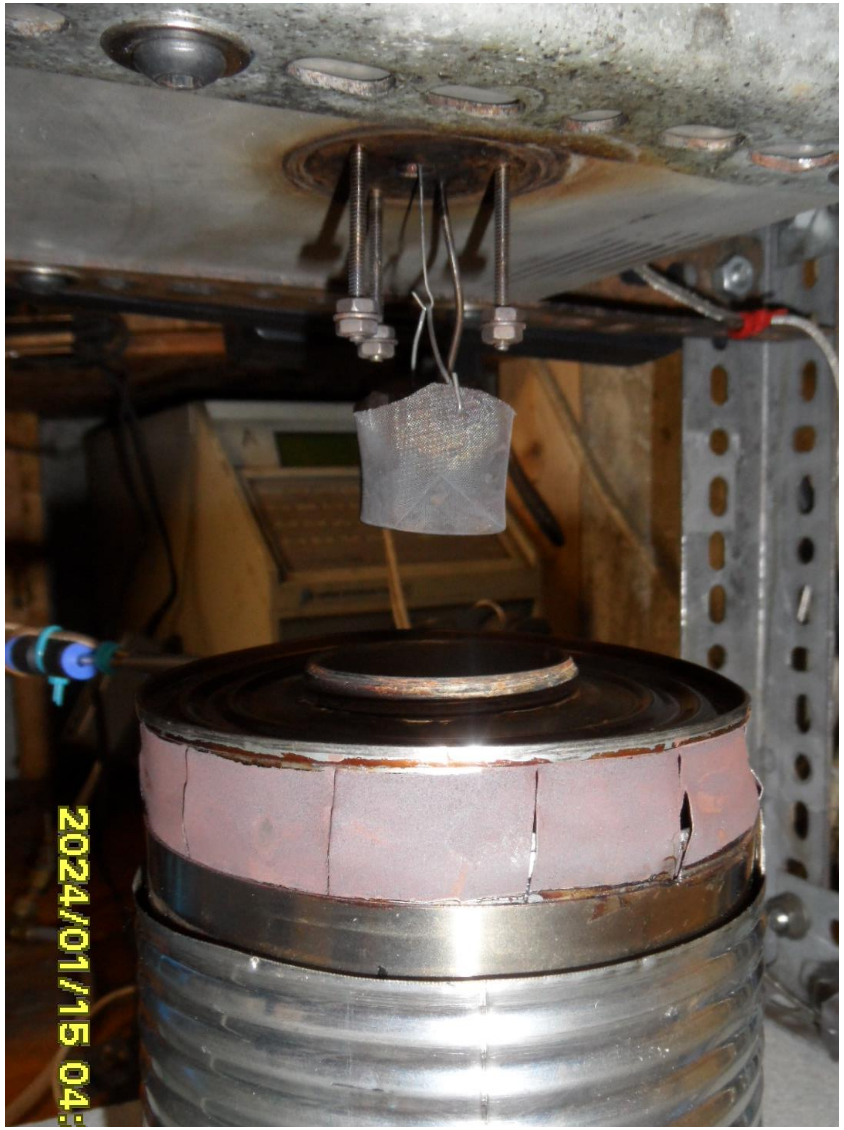
Now that I have your attention, the features of the GACS+ Instrument

Temperature ramp & soak
programmed into controller,
with local status lights & switches

Custom heated chamber with
vapor control and temperature
measurement, data to laptop

Choice of vapor and flowrate
manually selected and adjusted





Even the $44K TGA801 cannot do all the measurements that the GACS+ Instrument can, which include:

1) **Loss on drying of biochar samples at 150C** by controlled drying in air or nitrogen
   - the upward flow of dry vapor flowing through the sample allows <1 hr test time
2) **Ash content of dried biochar samples at 500C** by controlled oxidation in air
   - sample size is adjusted to allow sufficient ash for accuracy and reasonable cycle time
3) **Adsorption Capacity scan** using R134a or propane as the challenge gas
   - Gravimetric Adsorption Capacity Scan from 300C to 100C after drying sample at 150C
4) **Loss of VOCs from 200C to 325C** under controlled conditions
   - Programmed temperature ramp and soak, with data corrected to rate over 1 hour period
5) **Loss of SVOCs from 325C to 450C** under controlled conditions
   - Programmed temperature ramp and soak, with data corrected to rate over 1 hour period
6) **Adsorption Capacity scan** after removal of VOCs and SVOCs using R134a or propane
   - Gravimetric Adsorption Capacity Scan from 300C to 100C after removal of VOCs and SVOCs
7) **Self-heating tendency** by controlled oxidation of gram quantity of dried biochar at 140C
   - This is a screening test for shipment stability, same detection limits as UN Division 4.2 test for "Self-heating substances", but not an accepted alternate to the UN 4.2 test method.

Here an overview of how the properties determine value and performance

1) **Moisture:** relates to storage stability, especially is the biochar is susceptible to self-heating when exposed to air and/or dried out. Moisture also interferes in every other test so it is the first to go.
2) **Ash:** All biochars have ash at percent to majority levels, and that ash level directly impacts the market value of the biochar. If the ash constituents are needed by the crop, there is value, although biochar is a ***silly way*** to deliver plant nutrients unless is a high carbon wood ash and you need the liming capacity. Ash levels need to be considered together with pH impacts, especially out West. We never have enough calcium if we have rain.
3) **VOCs are a measure of the amount of degradable carbon** that will desorb during the first growing season(s). It is likely a correlation to the VOCs desorbed over the first hour at 300C. Degradable carbon is metabolized by soil microbes and they consume available nitrogen. This is a consideration in both the amount of biochar added, when it is added, and whether plant growth will be stunted after the first few rain events. ***Furthermore, the farmer may not actually want to pay for the VOCs.***
4) **SVOCs are a measure of the amount of biochar carbon that will be lost over the next century**, at a rate that will have little impact on crops, but may stabilize soil microbe populations between crops. Survival gets ***dicey*** when there are no plant exudates for the hard working soil microbes.
5) **Stable Carbon is the good stuff that lasts forever -** currently valued by H/Corg and market forces.
6) **Adsorption Capacity** is the property that biochar shares with activated carbon, and has multiple benefits like detoxification and desiccating moisture management. Unfortunately, surface area does not measure it.
7) **Self-heating tendency** tells you if the truck or ship will catch on fire ***because of your biochar***, and may be integral in your plea bargain or settlement of the lawsuit that will doubtless be coming. Any data will help.

In summation, minor corrections to current IBI protocols for moisture and ash determinations will remove systematic errors and get you the actual measurements you are claiming:

- **dry at 150C for a few hours, very wet samples may take overnight**
- **ash at 450C to 550C for a few hours, confirm completion by visual checks**

The GACS+ Instrument is not commercially available as of now, but can be assembled with *reasonable* skills and *affordable* components. It is a single sample instrument and requires operator interaction, but generates large amounts of data about the sample and facilitates tuning pyrolysis conditions.

Contact hsmclaughlin@verizon.net for instructions on *Construction* and *Programming* the temperature controller, PC data acquisition systems and subsequent data reduction and analysis. If this proves popular, it will show up on the web somewhere using **GACS+ Instrument** as the principal search term.

Questions - as time allows

TrinityBiocarbon

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