NextChar @Biochar 2018

Biochar Standards and Characterization Schemes:

How and What is being measured, and What is it actually telling you

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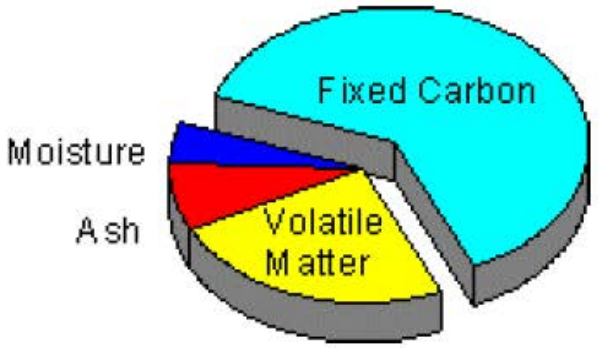
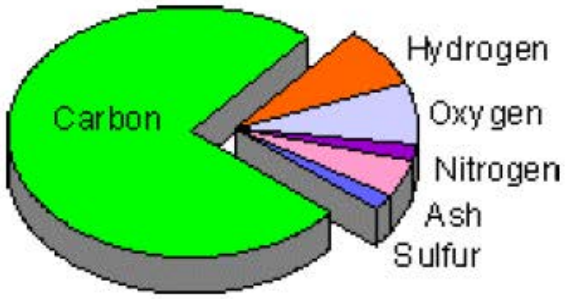
FIGURE 4: PROXIMATE AND ULTIMATE ANALYSES OF COALS

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.

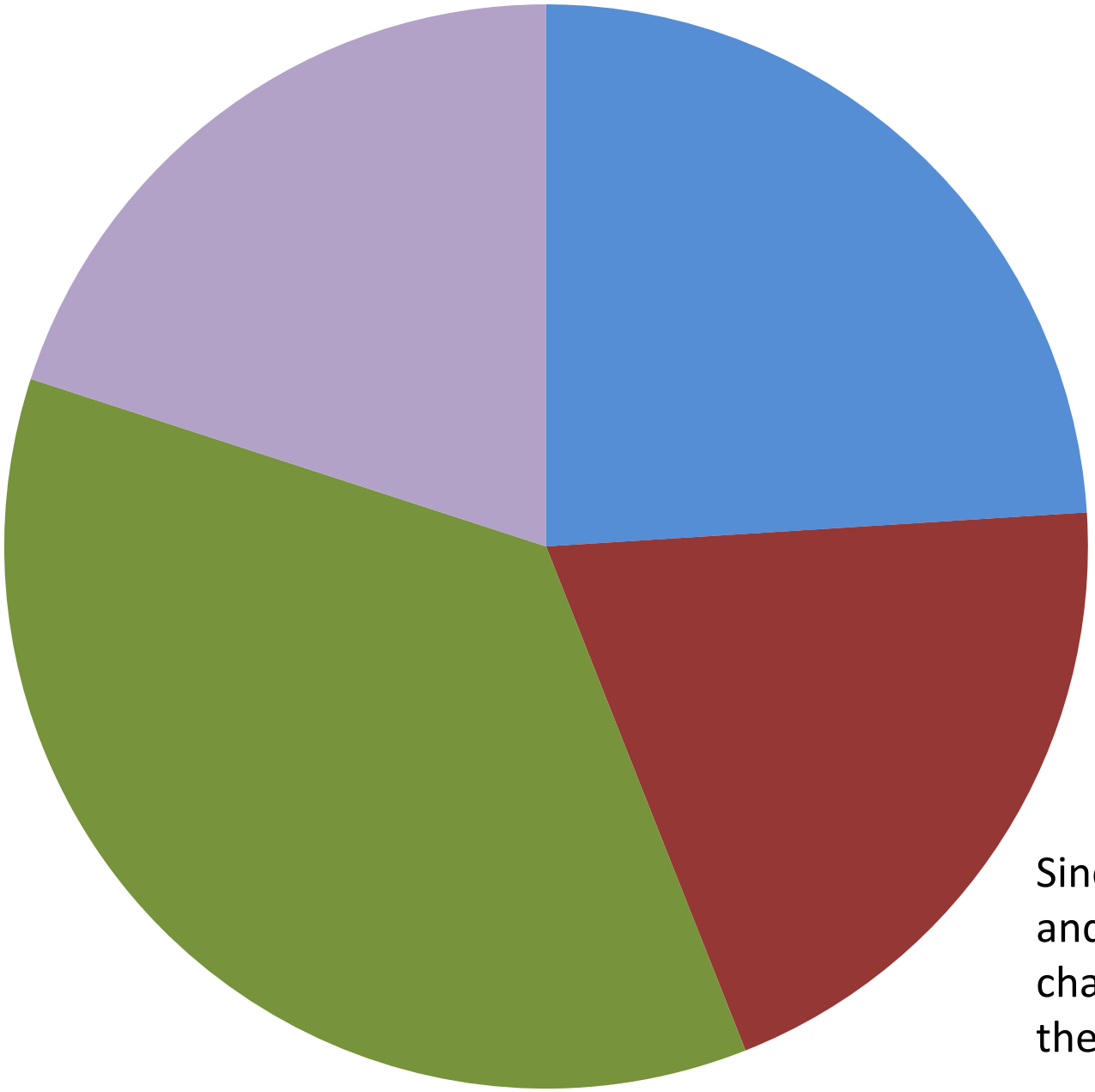
Ultimate Analysis

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 All Biochars Paper, V2, Oct 2009

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



Since this is Biochar, and not Coal, we will change the titles of the groups of materials

Each group is actually made up or two, or more , types of materials – which behave differently…

Let’s start with Ash

If anything is going to be well behaved, it is Ash.

It is conserved under virtually all conditions of the plants life and under the conditions of most pyrolysis – so let’s just design a method of seeing how much ash is there and be done with it.

Ash is not typically volatile nor reactive, so just remove the water and organics and weigh what is left…..

ASH: EBC vs IBI vs BBM Sanity check

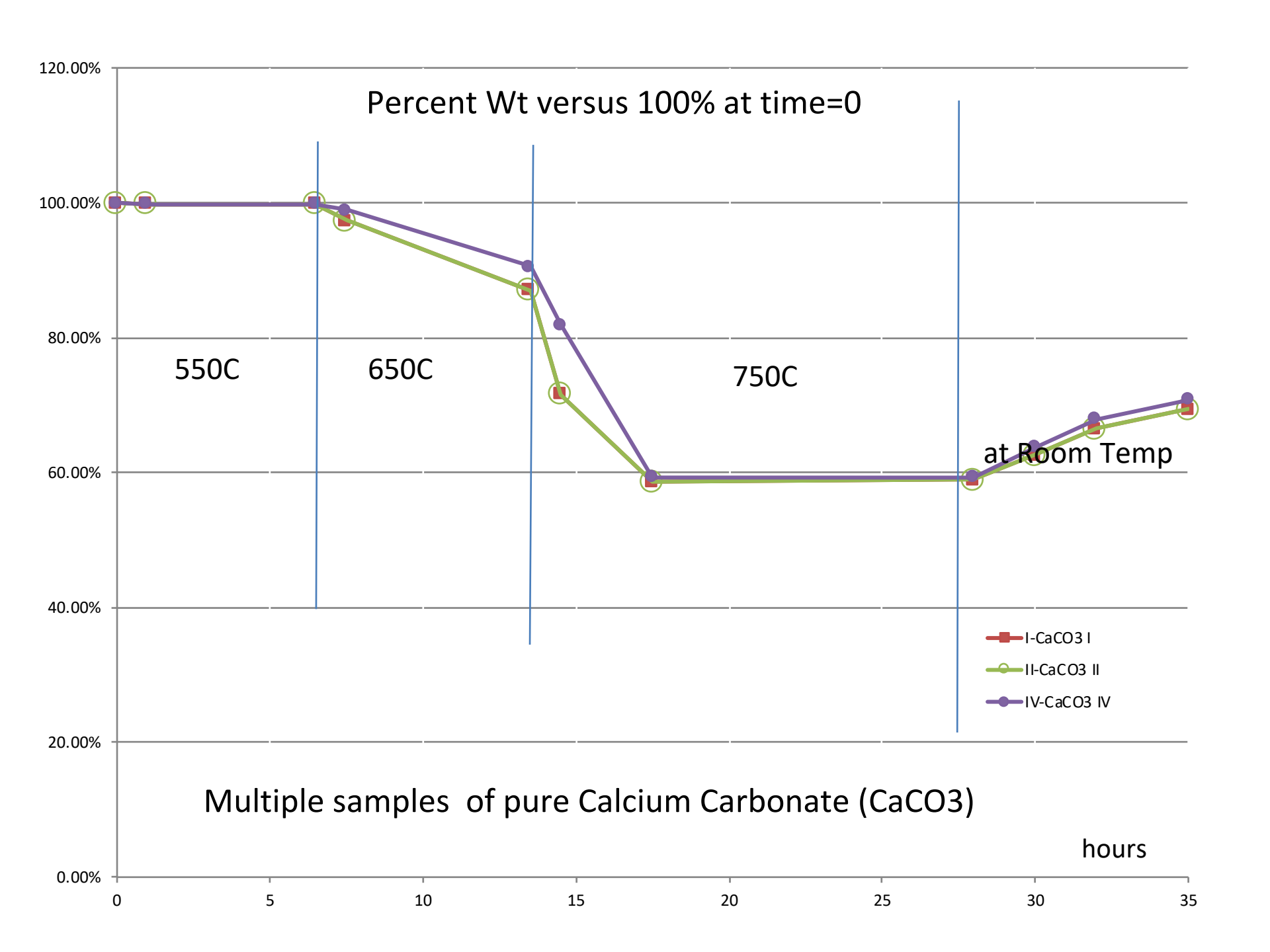
European Biochar Certificate V4.8 – Required - Declaration
DIN 51719, ISO 1171 or EN 14775 – **ashing at 550°C**
heating at 5 K/min to 106°C under nitrogen atmosphere
then at 5 K/min to 550 ° C under oxygen, hold for 1h

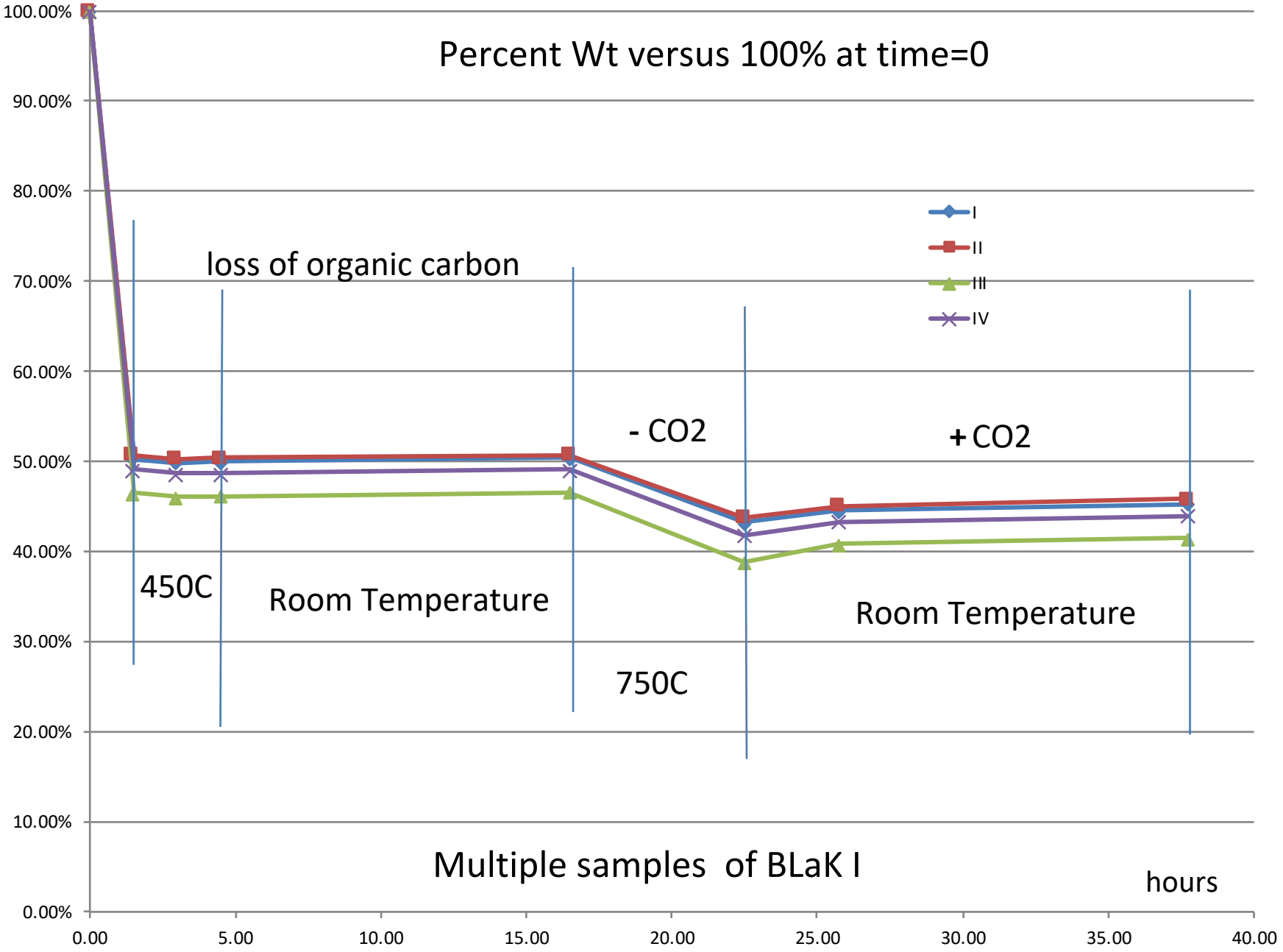
IBI Test Method – Required – Declaration - (% of total mass, dry basis)
ASTM D1762-84 'Standard Test Method for Chemical Analysis of Wood Charcoal'. **Ash at 750 °C for 6 hours.**
Air dried and ground sample, dry at 105C for two hours, covered volatile matter to 950C, then ash at 750C for 6 hrs uncovered

BBM Test Method - Required in "Dry Biochar" Procedure
Dry at 145C to 155C as per ASTM D2867 "Standard Test Methods for Moisture in Activated Carbon" then **Open crucible ashing at 550C in air for two hours** - *similar to EBC Method*

Assumptions need to be confirmed

- "The majority of carbonates in biochar, specifically calcium and potassium carbonates, resist decomposition at 750 C (Dean, 1999), the temperature prescribed by ASTM for quantification of the ash content."
- Bioresource Technology 114 (2012) 644–653, "Characterization of biochars to evaluate recalcitrance and agronomic performance", by Akio Enders, Kelly Hanley, Thea Whitman, **Stephen Joseph, Johannes Lehmann**


Percent Wt versus 100% at time=0
120.00%
100.00%
80.00%
60.00%
40.00%
20.00%
0.00%
550C
650C
750C
at Room Temp
I-CaCO3 I
II-CaCO3 II
IV-CaCO3 IV
Multiple samples of pure Calcium Carbonate (CaCO3)
hours
0
5
10
15
20
25
30
35


Percent Wt versus 100% at time=0
100.00%
90.00%
80.00%
70.00%
60.00%
50.00%
40.00%
30.00%
20.00%
10.00%
0.00%
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
I
II
III
IV
loss of organic carbon
- CO2
+ CO2
450C
Room Temperature
750C
Room Temperature
Multiple samples of BLaK I
hours

And the winner is …..

- **Do not go to 750C** for extended periods of time – the carbonates decompose and then reabsorb atmospheric CO2 upon cooling
- BBM procedure uses the tops of the crucibles to present char for ashing in air purged M/F
- Ash until uniform color of residual material
- Grind sample (mortar & pestle) and pass through window screen or finer
- Typical time: 2 hours at 450C to 550C
  - additional holding time does not hurt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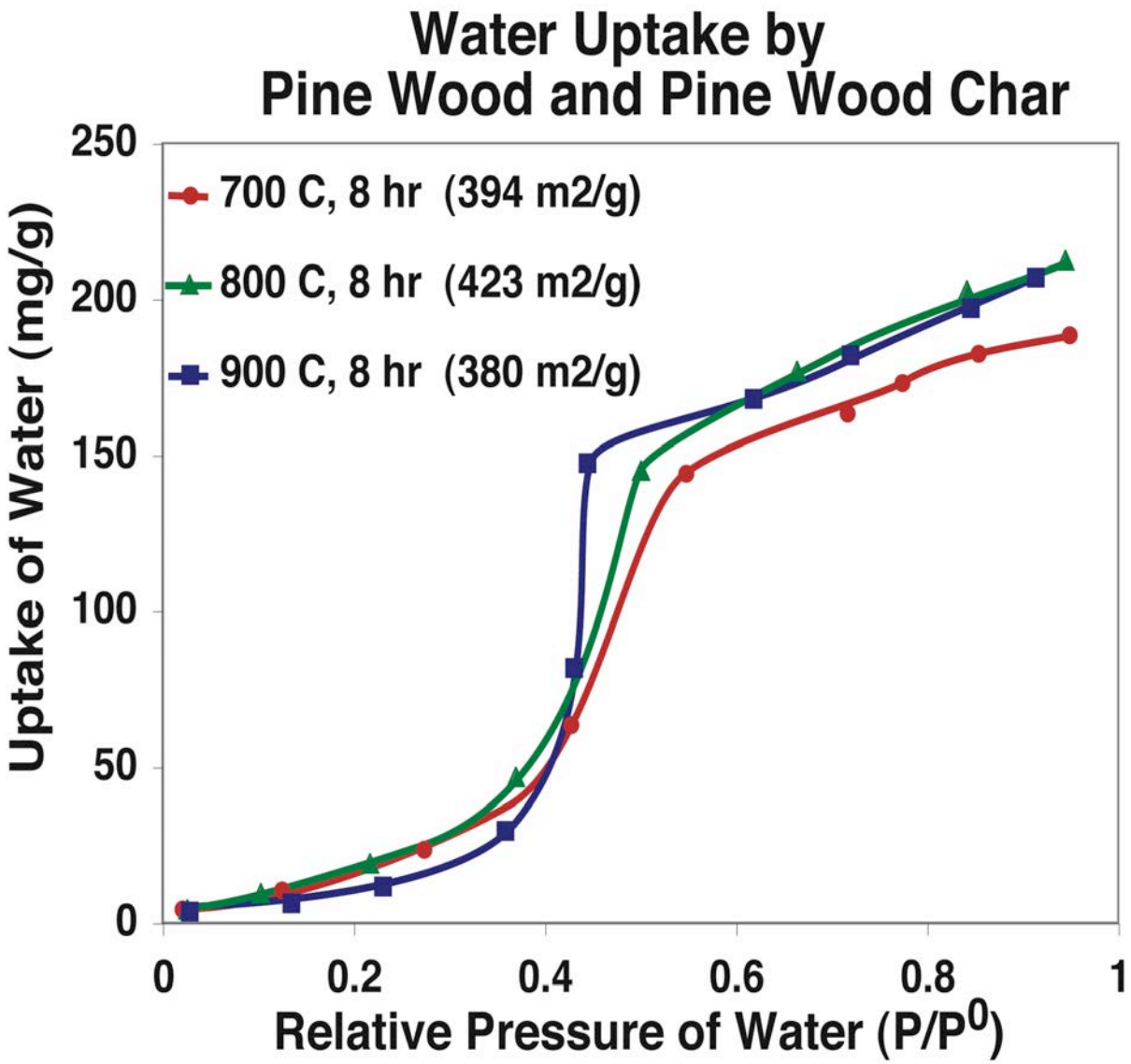
Next, let's try to dry biochar

Moisture levels in biochars range from none (as produced) to 500+% of char weight – if flooded and drained. It is often adjusted during handling for dust suppression and responds to ambient conditions – both gives and takes atmospheric moisture

Many biochars adsorb water vapor at >60%RH, and give it back at <40%RH, and the amount of involved is significant (>10wt%)

The conditions that remove water, especially adsorbed water, also remove Volatile Organic Compounds (VOCs), which we intend to account for as part of the Mobile Matter weight fraction ……



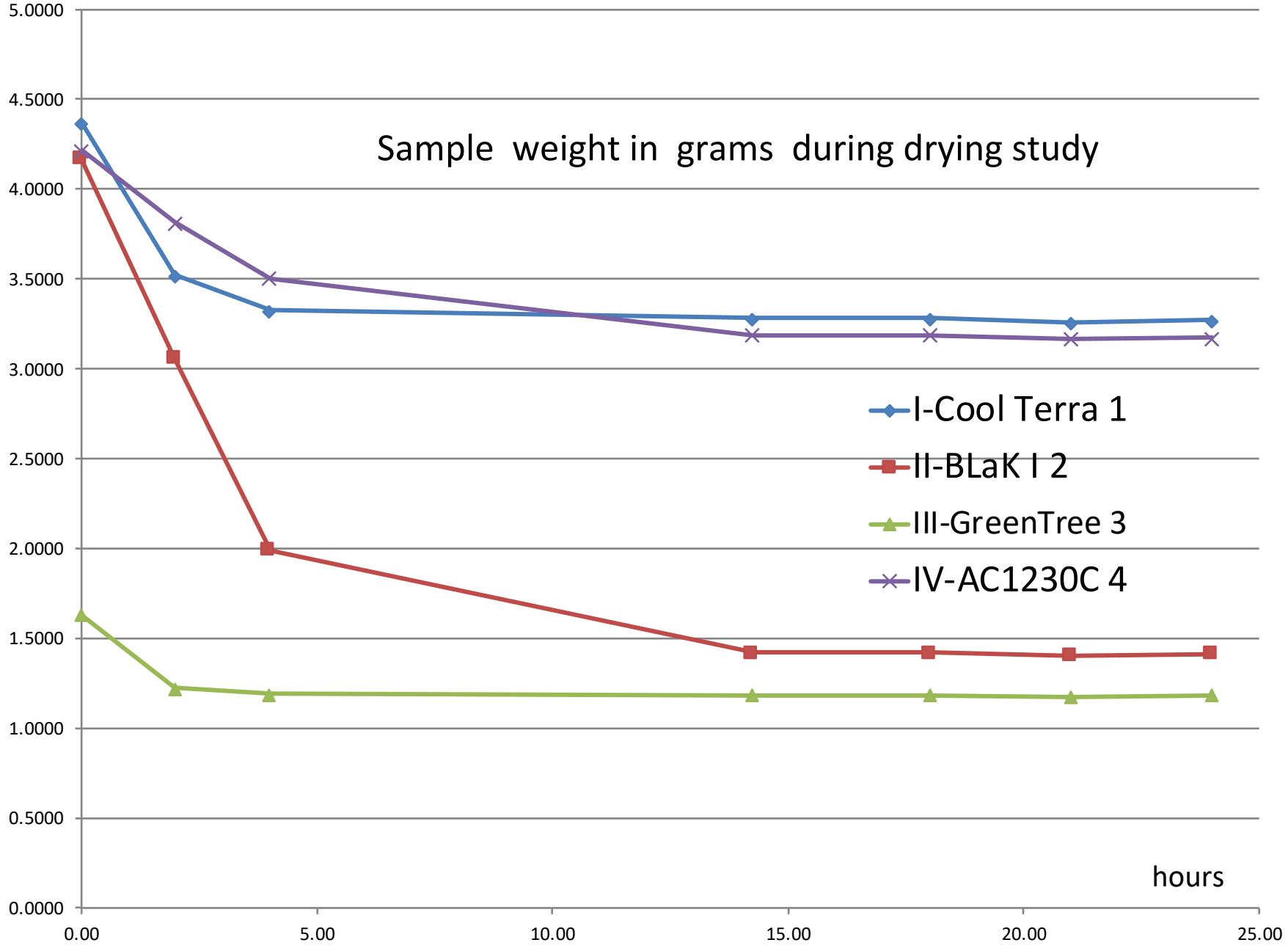
USGS
science for a changing world

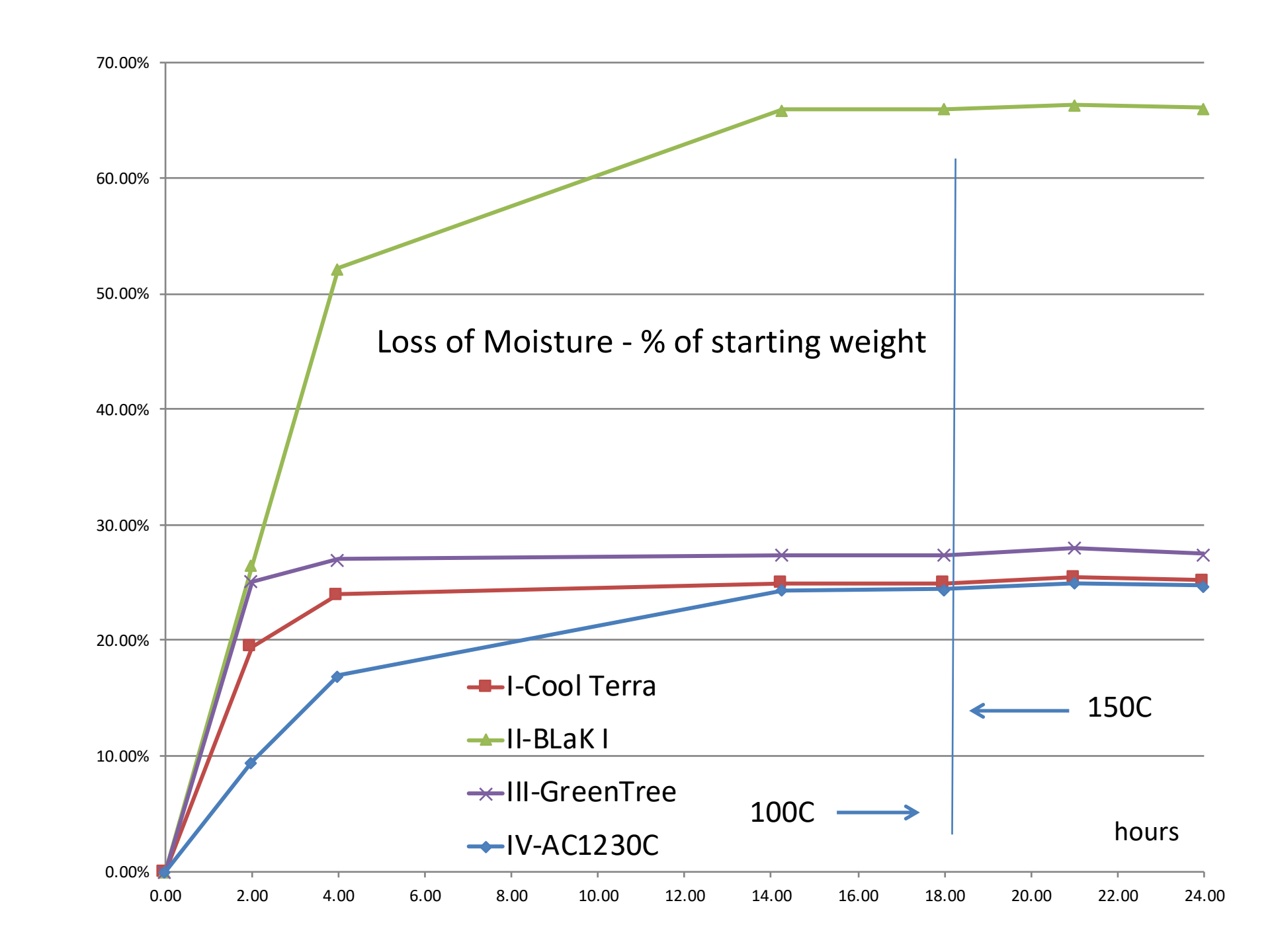
WATER: EBC vs IBI vs BBM Sanity check

European Biochar Certificate V4.8 – Required (Water content) - DIN 51718 method A Two step: raw moisture at (40 ± 2)°C until constant mass; hygroscopic moisture in TGA crucible and nitrogen atmosphere **at (106 ± 2) ° C to constant mass**.

IBI Test Method – Required (Moisture content) ASTM D1762-84 'Standard Test Method for Chemical Analysis of Wood Charcoal' Moisture content **at 105 °C for 2 hours**. 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.

BBM Test Method - Required in "Dry Biochar" Procedure **Dry at 145C to 155C** as per ASTM D2867 "Standard Test Methods for Moisture in Activated Carbon" - 3 hrs normally sufficient


Sample weight in grams during drying study
I-Cool Terra 1
II-BLaK I 2
III-GreenTree 3
IV-AC1230C 4
hours
5.0000
4.5000
4.0000
3.5000
3.0000
2.5000
2.0000
1.5000
1.0000
0.5000
0.0000
0.00
5.00
10.00
15.00
20.00
25.00


70.00%
60.00%
50.00%
40.00%
30.00%
20.00%
10.00%
0.00%
0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
Loss of Moisture - % of starting weight
I-Cool Terra
II-BLaK I
III-GreenTree
IV-AC1230C
150C
100C
hours

And the winner is …..

- Do not go by the expectation in the method – they were not written for something as variable as biochars.
- Many conditions will work: 18 hrs at 105C, 3 hours at 150C, 1 to 2 hour at 200C (not higher). Wet and wetted chars take longer and have higher error due to volatile stripping. **This cannot be avoided, so live with it.**
- Cover samples to avoid stripping volatiles and, if possible, don't dry samples in ovens with circulating fans. BBM methods provide simple way to minimize error, but nothing prevents the simultaneous loss of VOCs when removing water vapor – they leave together because that is the Law (of Thermodynamics).

Finally, let's do MM vs RM

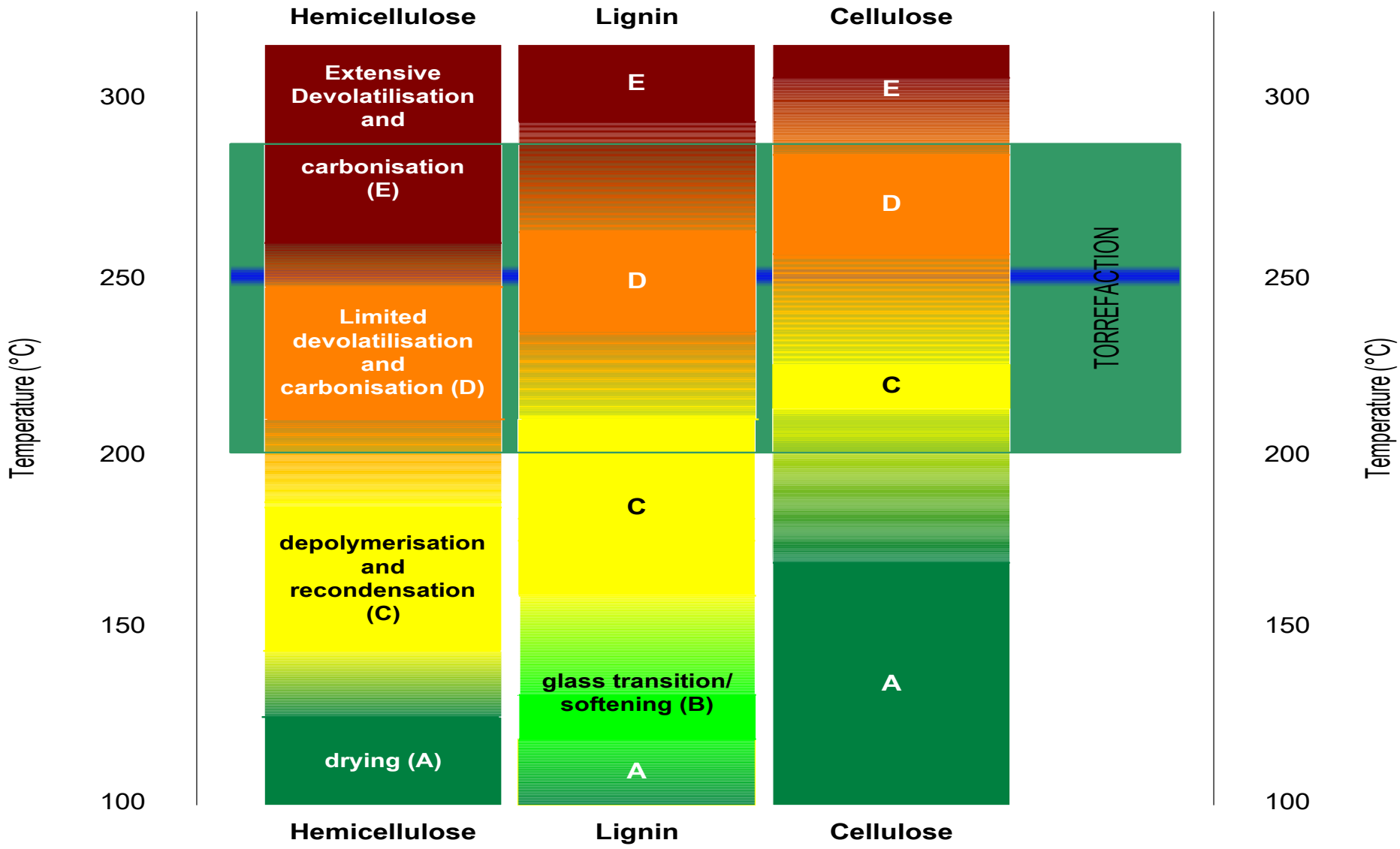
Volatiles, aka Volatile Matter, aka Labile Matter, aka Mobile Matter, is a class of materials defined by what it is not – it is not stable carbon that will not break down in the soil. It is also defined by being vapors that are generated in and released by the coexisting solid phase throughout the pyrolysis process.

Any time a char experiences a higher temperature (HTT) for the first time, it undergoes "incremental carbonization", where the solid phase further consolidates into more stable forms and a portion of the original solid is converted to vapors = volatiles.

Unfortunately, it is not possible to know the split of volatiles versus additional solid phase from the amount of volatiles generated – it depends on the properties of the starting material. So if 10wt% volatiles comes off at a higher temperature, we can't tell if it came from 40wt% wood or 20wt% medium weight tars, etc.

Pyrolysis & Carbonization Reactions of Wood

Below 288 C = Torrefied Wood Above 325 C = Biochar



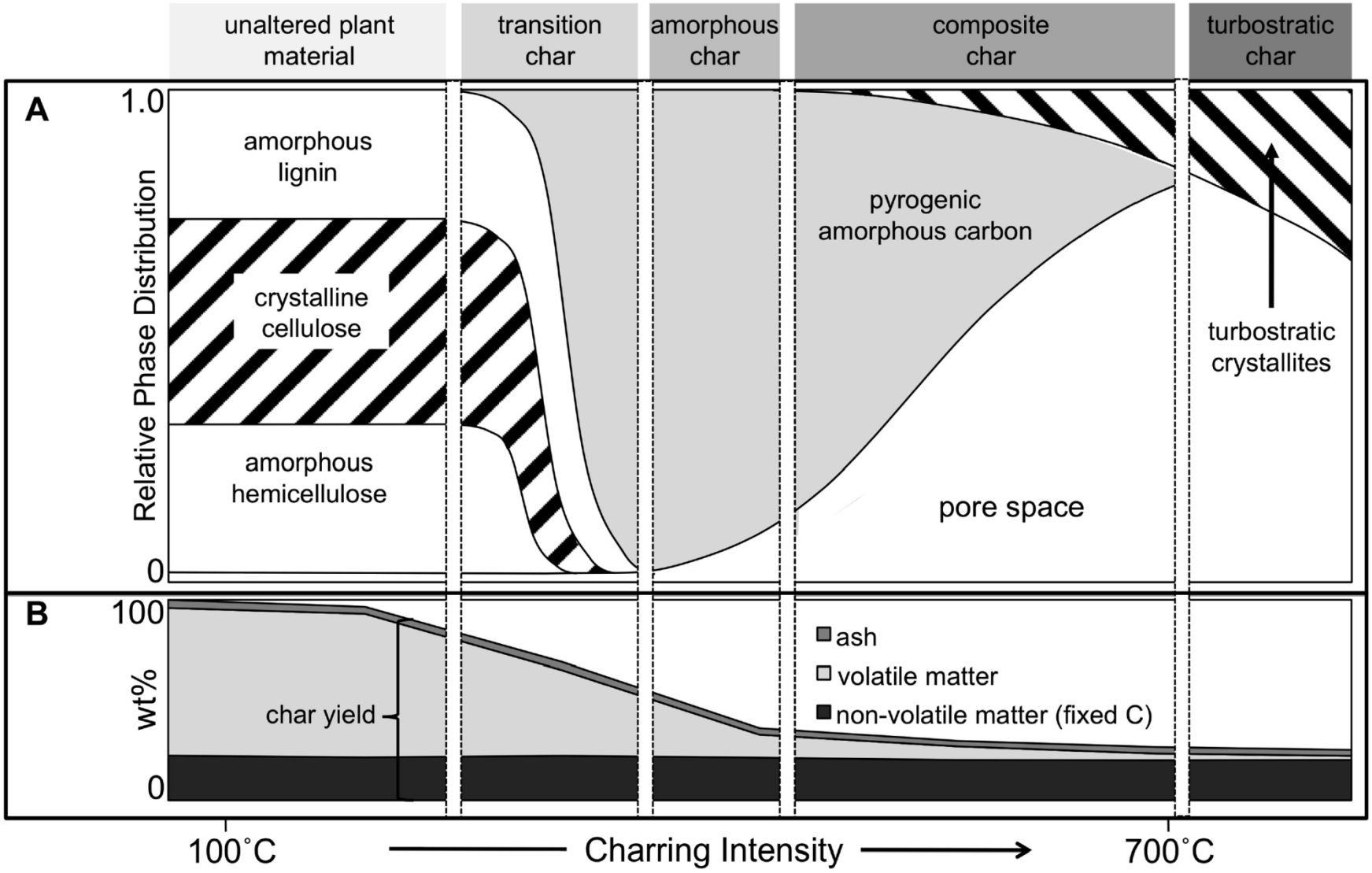
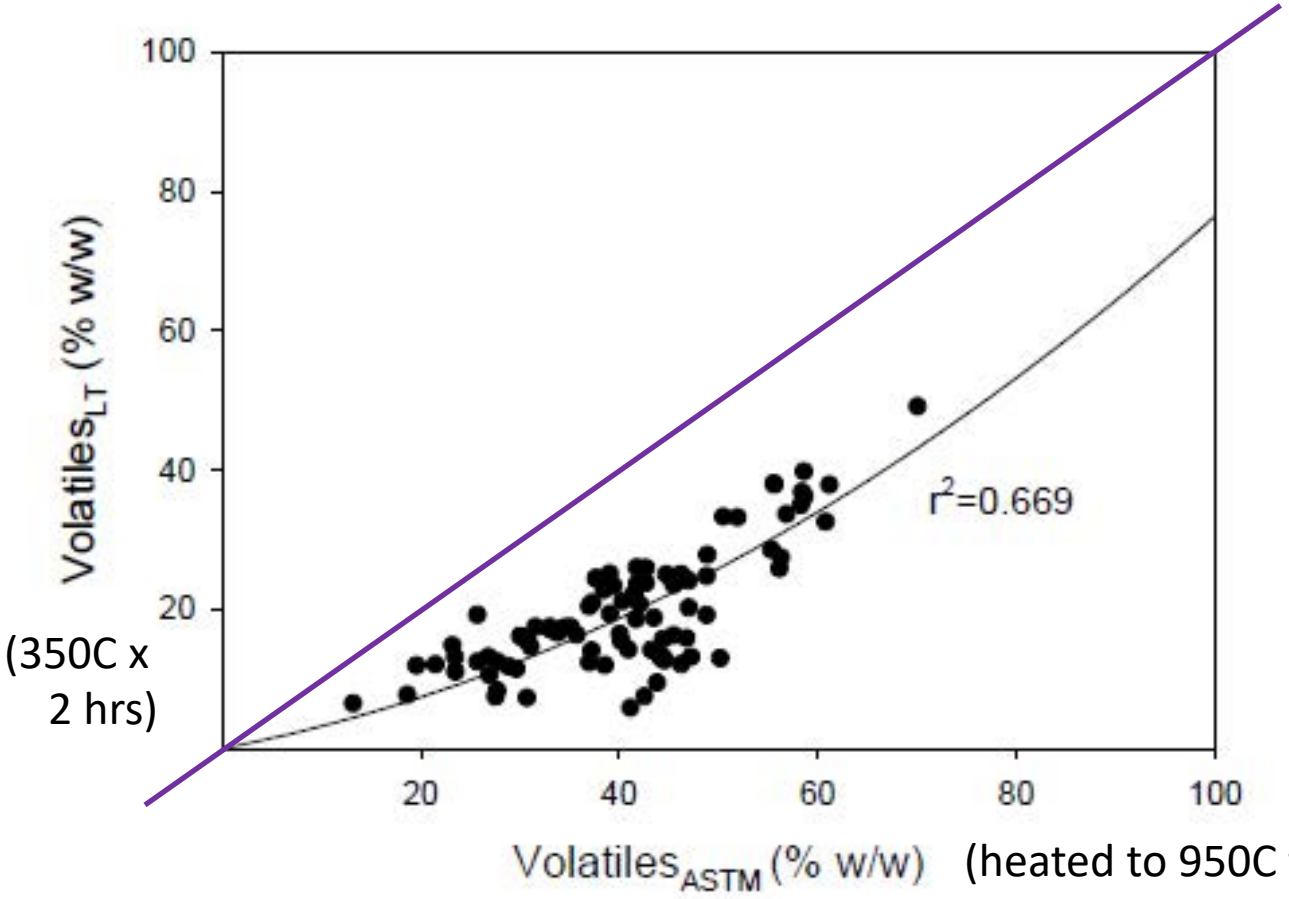


Figure 4 from *Environ. Sci. Technol.* ***2010, 44, 1247–1253***



Supplementary Fig. S1. Relationship between volatile contents determined by ASTM and the modified LT method (see text for description of methods; n=2).

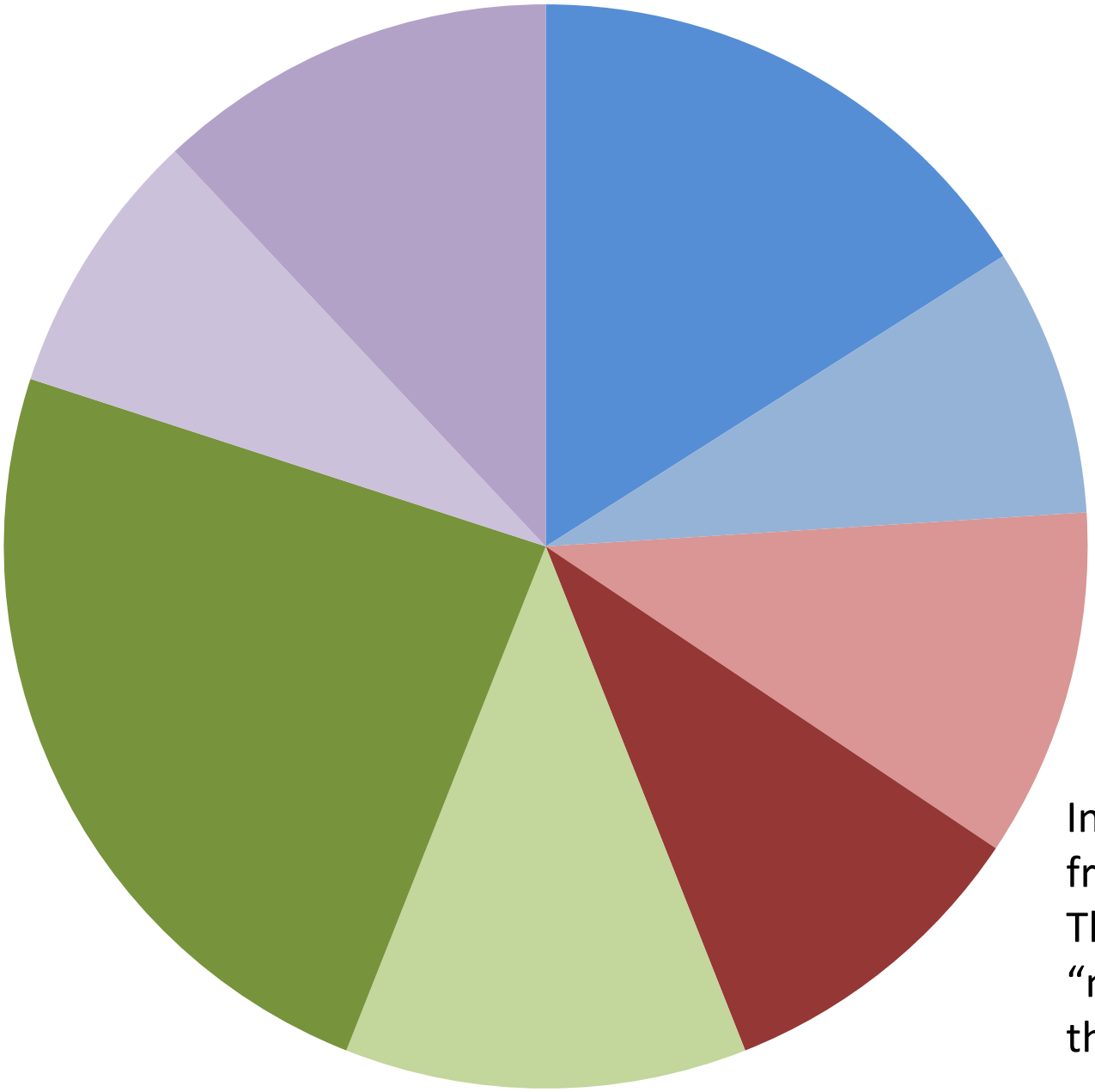
MM & RM: EBC vs IBI vs BBM Sanity check

European Biochar Certificate V4.8 – Required (Volatile Organic Compounds (VOCs)) - Thermal-Gravimetric-Analysis (TGA) using Leco TGA 701 ($38,000 instrument) – **mass loss at 950°C in N2**.

IBI Test Method – Optional (Volatile matter) ASTM D1762-84 'Standard Test Method for Chemical Analysis of Wood Charcoal'. **VM content at 950 °C for 10 minutes**. Muffle furnace, old school.

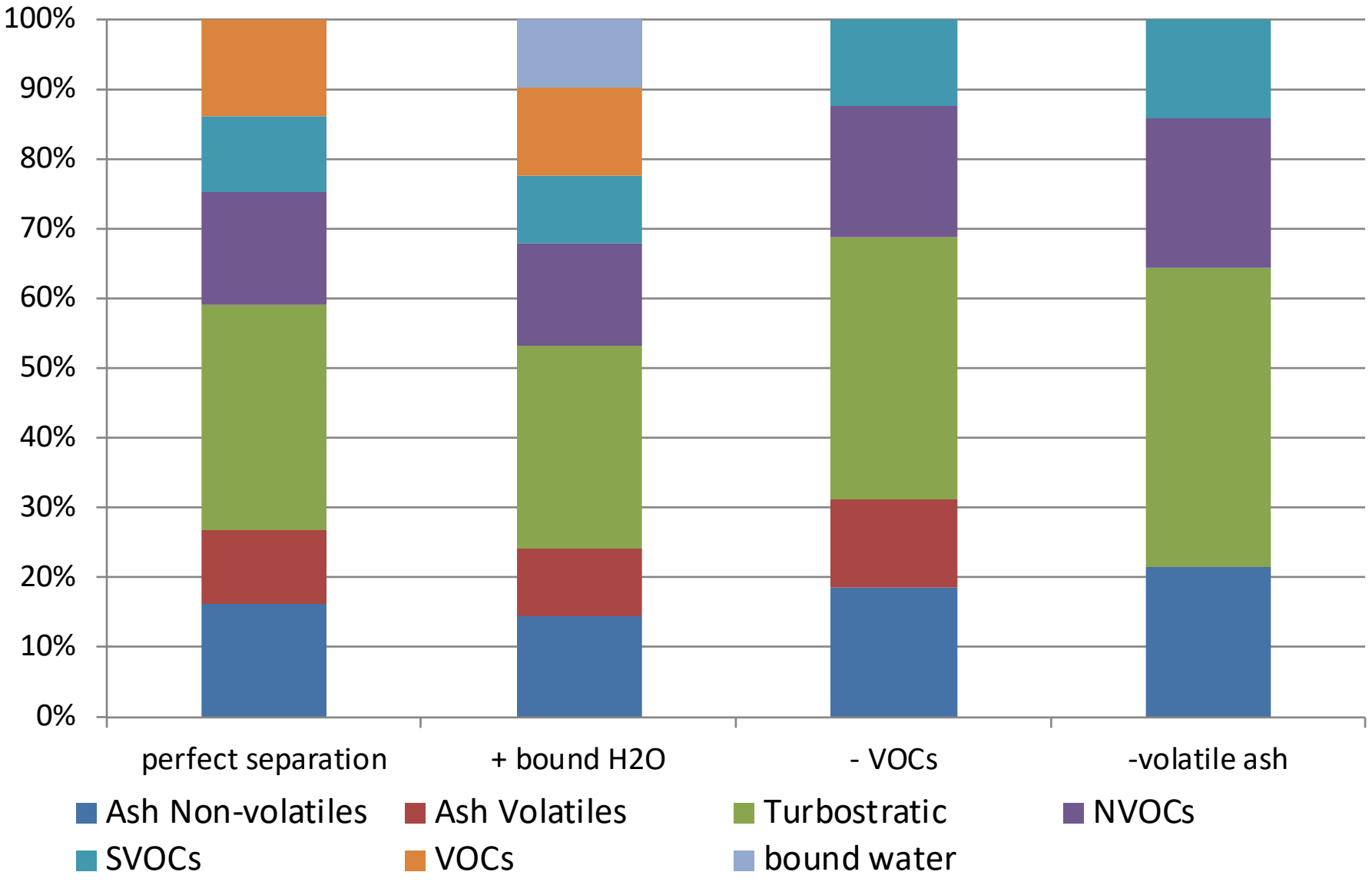
BBM Test Method - Required in "Dry Biochar" Procedure as "Volatile Dry Weight Fraction" Dry at 145C to 155C, then **vented covered crucible at 450C for two hours**. Custom procedure.

Since the MM/RM split is indeterminate, it is a good thing we don't need it for calculating H/Corg, which is the metric that everyone (IBI, EBC, not BBM) hangs everything on, let's see what all these analytical challenges imply ….

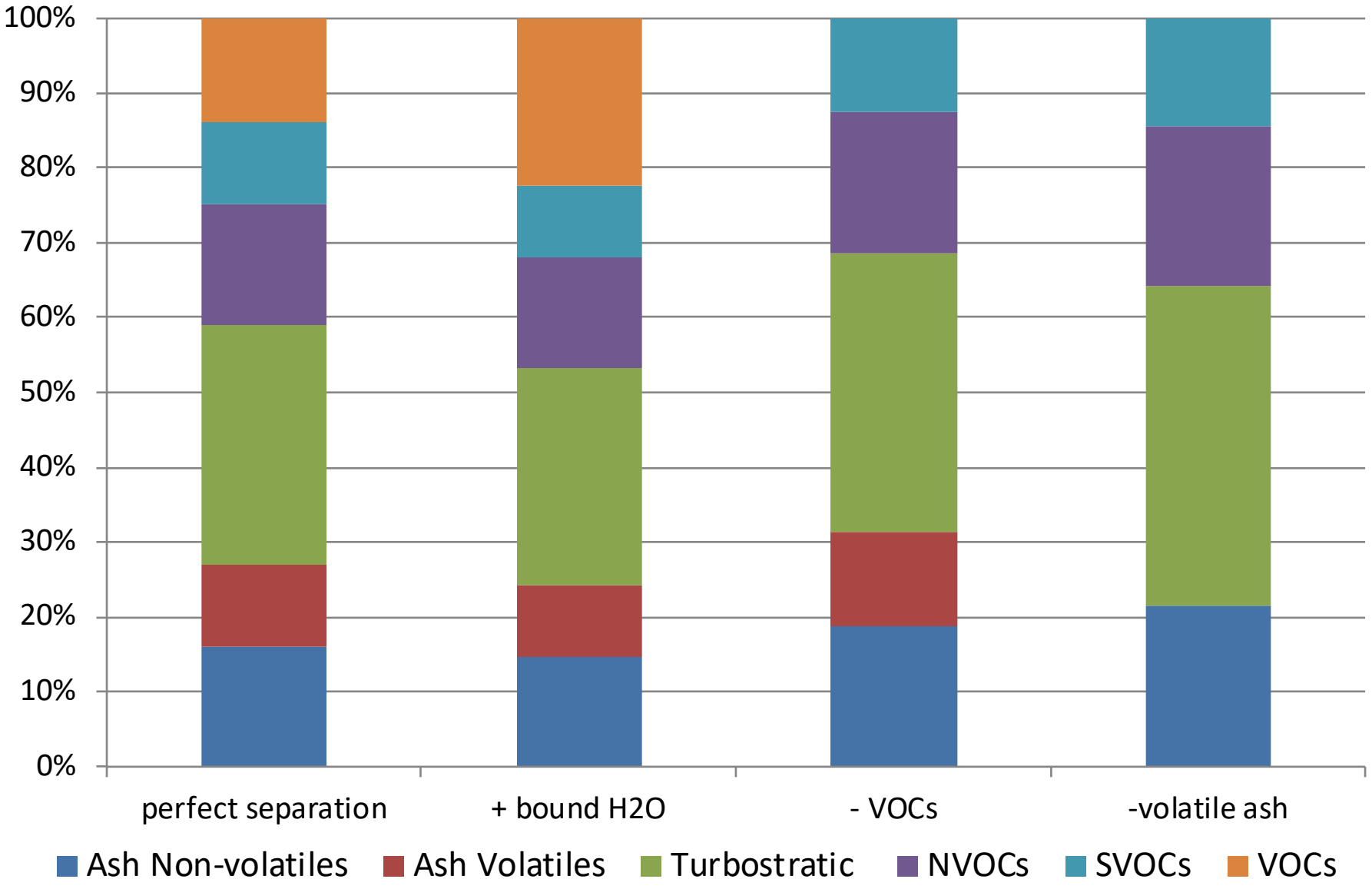


In this example, the free water is removed. The other classes get "melded" by errors in the analytical methods.

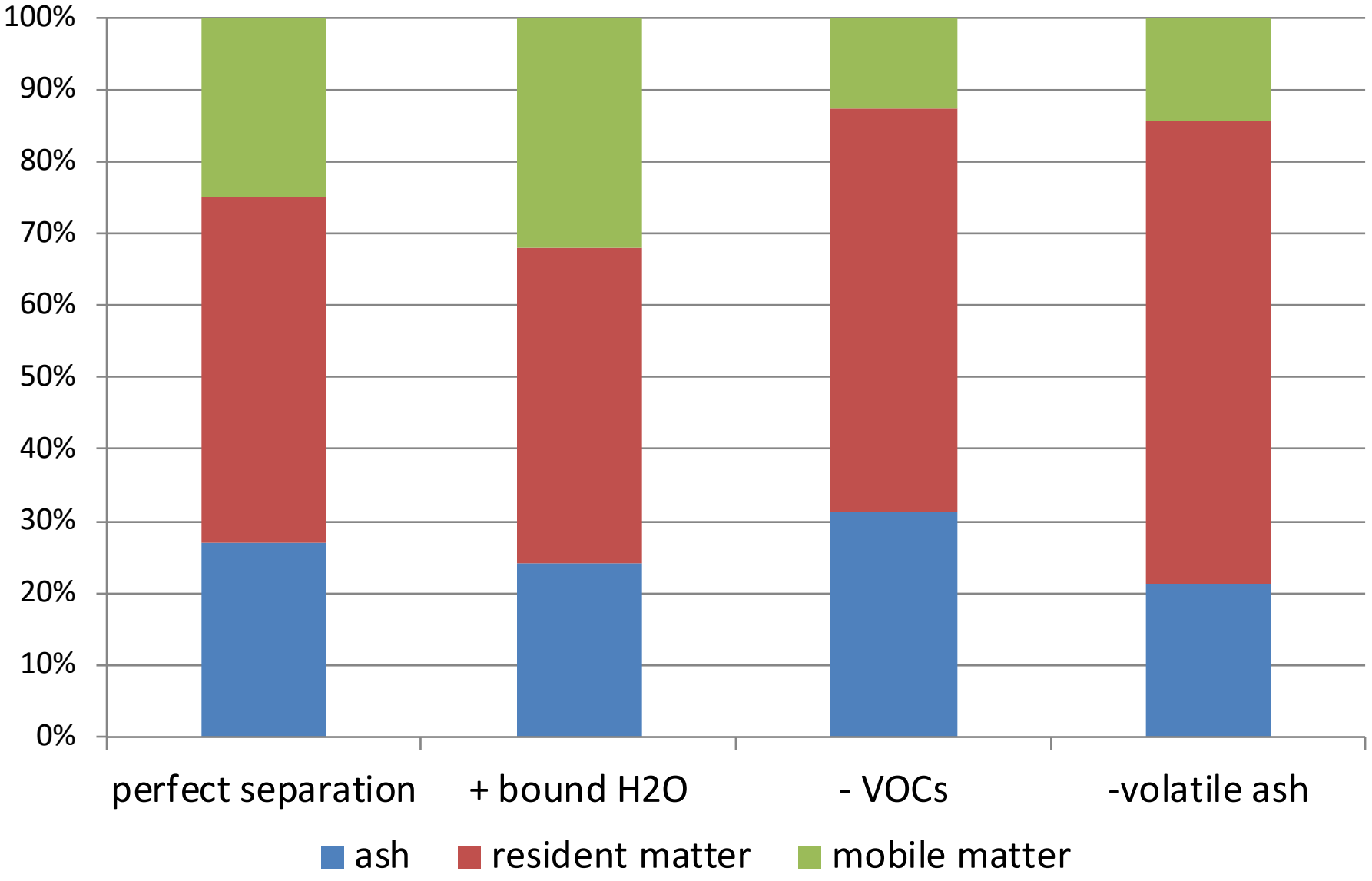
Let’s look at what errors in ash and water removal do to measured properties



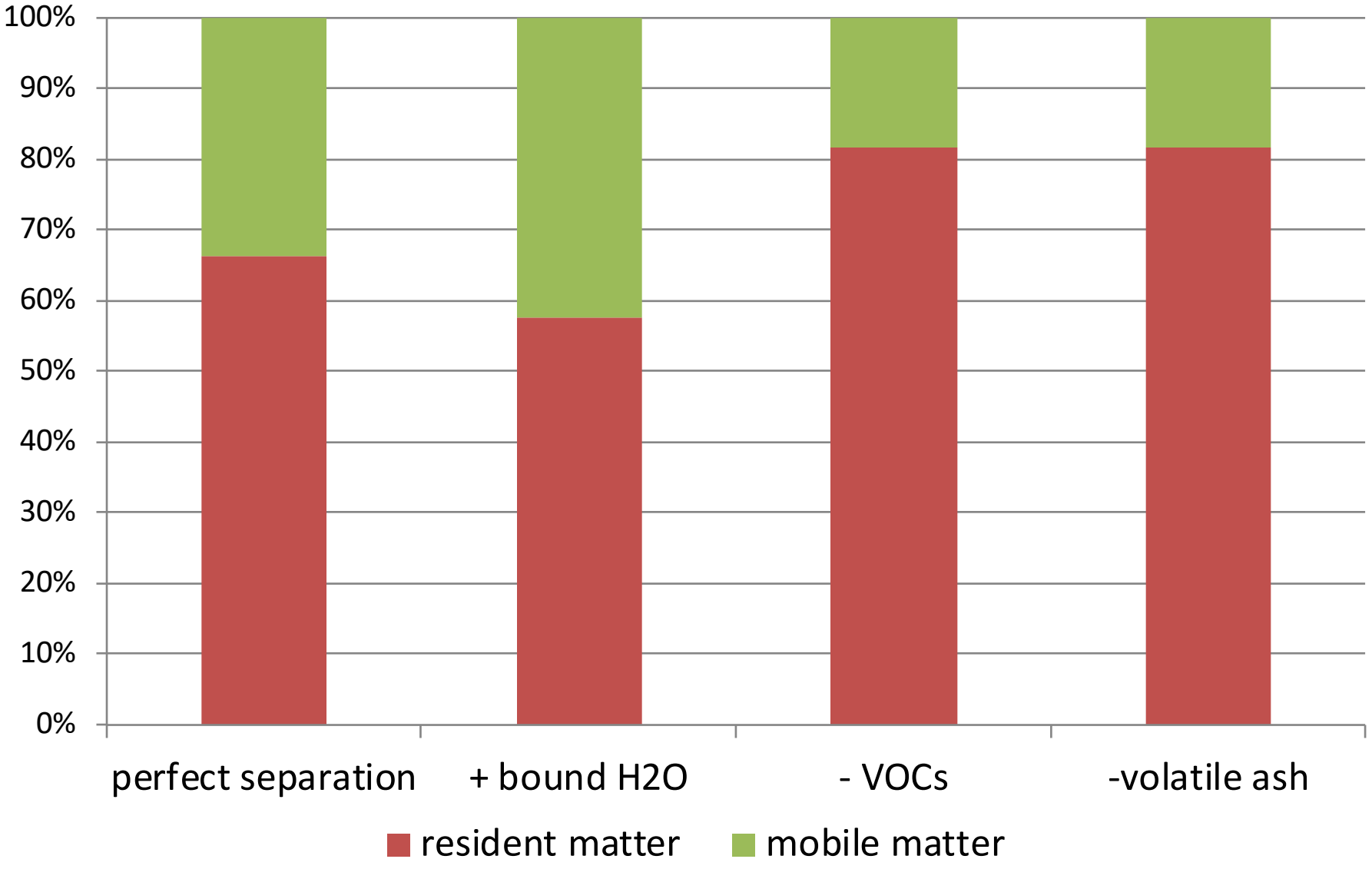
The residual water becomes Volatiles and the lost ash amplifies the other groups



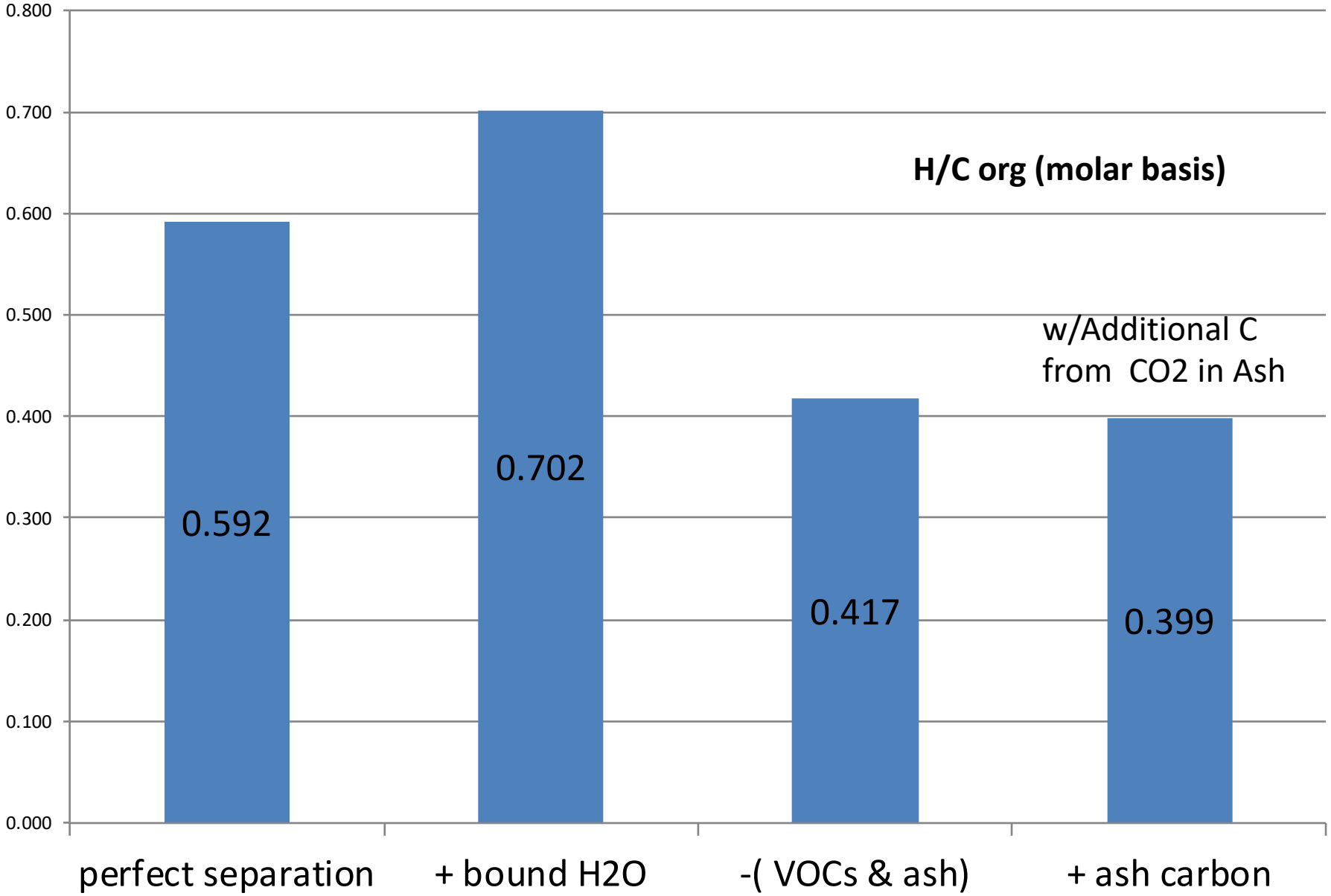
Clumping them back into the groups defined in the Proximate Analysis – less water



Normalizing by removing the ash portion, and assigning H & Corg to the organics



The errors introduced by inaccurate water and ash measurement bias the results



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