Analytical Options for Biochar Adsorption and Surface Area - Characterization of Biochar Materials

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Goal of Study and Presentation

- To provide comparison and guidance when trying to decide which technique(s) to use to characterize Biochar materials
- To support the recently released IBI Testing Guideline for Biochar
- Test same biochars using research and established commercial analytical methods
- Same raw material (wood pellets), two types of biochar, Retort and TLUD, over wide range of production conditions

Samples

- 4 TLUD Chars prepared at 0V, 3V, 6V, and 9V
- 4 Retort Chars prepared at 364, 500, 700, and 900 C
- Samples prepared by Alterna Biocarbon
- Homogenized, ground to a coarse powder, and split
- Characterization performed by Micromeritics Analytical Services, Control Labs, and Alterna

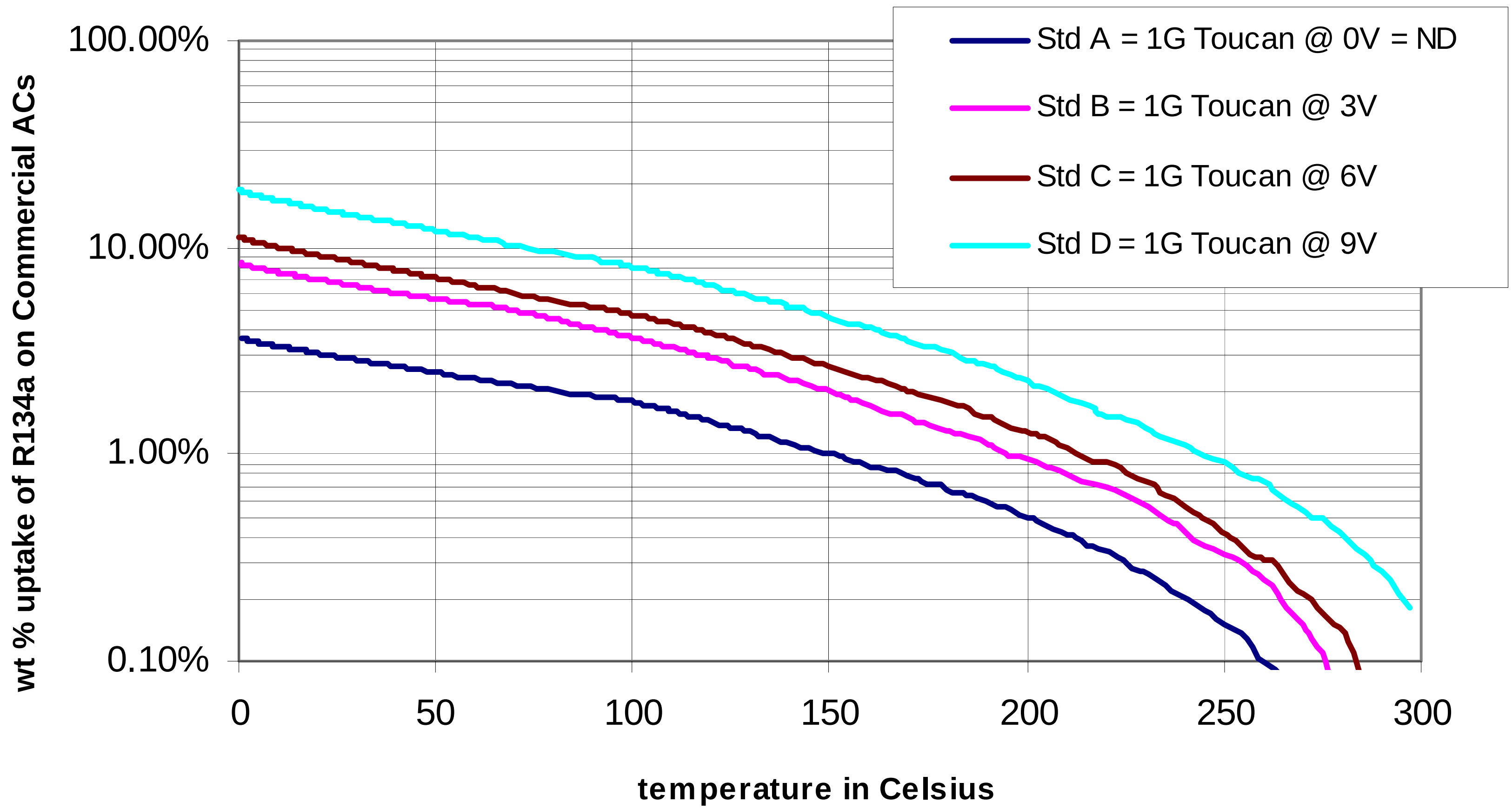
Analytical Techniques chosen

- R134a adsorption mapping using GACS analytical technique
- Butane working capacity
- N2 BET according to ASTM D6556
- CO2 adsorption capacity and micropore volume
- Water vapor adsorption isotherms

GACS – R134a adsorption test

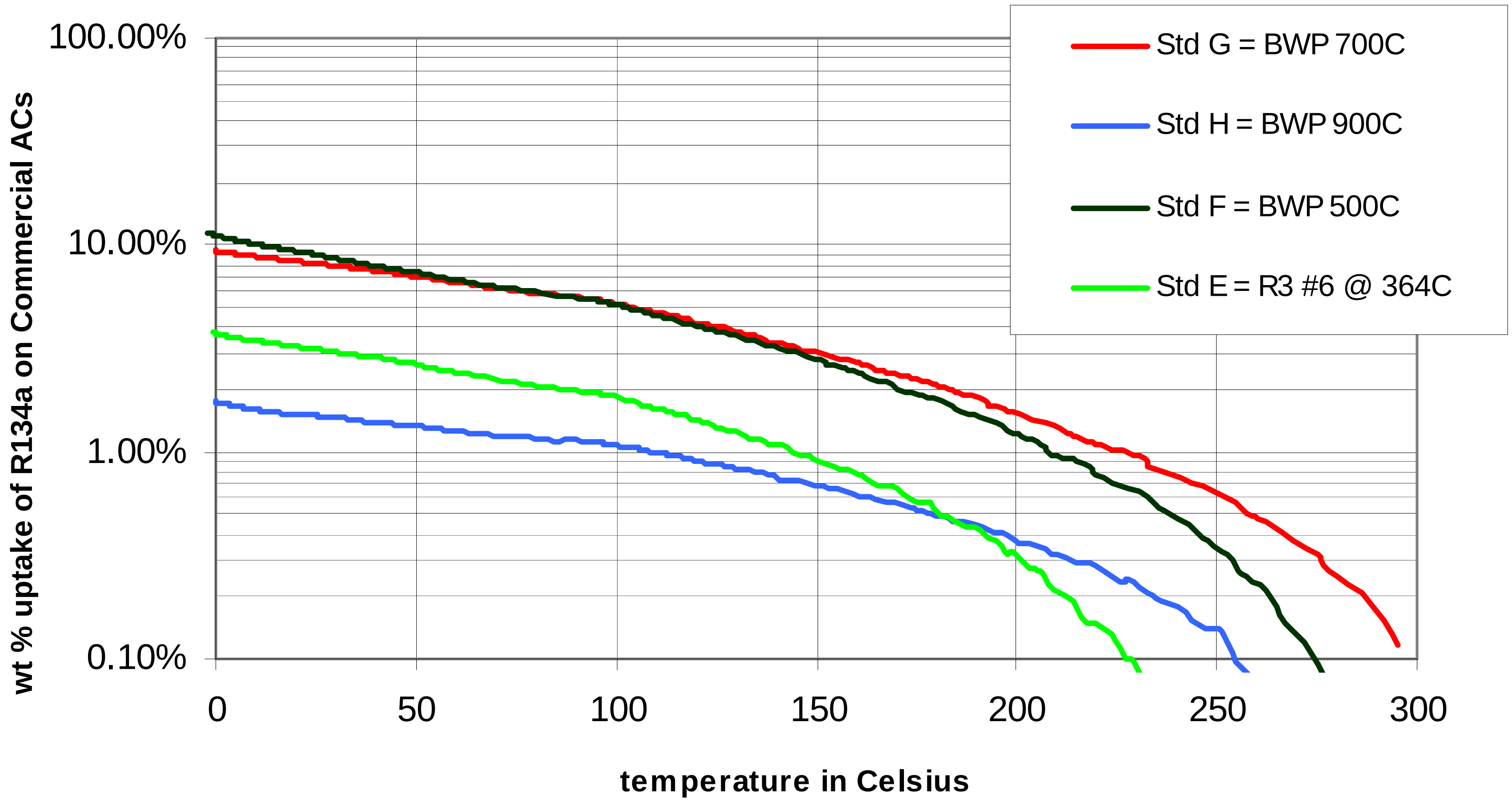
- Specialized test from Activated Carbon industry – measures actual adsorption over wide range of adsorption energies
- Adsorbate is R134a = 1,1,1,2 Tetra-Fluoro Ethane (Refrigerant in automobile AC systems)
- R134a is dense (heavy molecule), relatively large, and hard to adsorb compared to other probe molecules (N2, CO2, Butane)
- Assay adapted to biochars – less well behaved

GACS – R134a adsorption test



Well behaved over the entire range of temperatures for all TLUD chars

GACS – R134a adsorption test



Not as well behaved, Highest temperature char much lower capacity

Butane Working Capacity

- ASTM D5742 - 95(2010) Standard Test Method for Determination of Butane Activity of Activated Carbon (applied to biochar)
- Weight gain by bone-dry char sample after equilibration in pure butane at one atm.
- Essentially represents the total micropore volume of the porous adsorbent
- Low equipment cost and relatively fast
- Sample must be bone-dry – water interferes

Butane Working Capacity

	Butane
Sample A - TLUD 0V	3.77%
Sample B - TLUD 3V	5.85%
Sample C - TLUD 6V	7.99%
Sample D - TLUD 9V	11.28%
Sample E - Retort 364C	2.89%
Sample F - Retort 500C	4.47%
Sample G - Retort 700C	6.27%
Sample H - Retort 900C	3.07%

- TLUD chars
  - well behaved and saw an increase in butane adsorption with increased char temperature
- Retort chars
  - decrease in activity with the highest temperature Retort char, very similar to R134a GACS results

BET Surface Area

- Widely used in many industries including carbon, carbon black, activated carbon, etc
- Multiple ASTM and ISO methods available
  - IS0 9277
  - ASTM D6556, C1274, C1069, D3663, ….
- Calculation of the external surface area of a material from the volume of gas adsorbed at 0.05 to 0.3 relative pressures
  - Assumes multi-layer adsorption on non-porous surface
  - Pressure range modified to fit microporous materials

N2, BET results

	Initial BET result (m2/g)	Repeat BET result (m2/g)
Sample A TLUD 0V	216	182
Sample B TLUD 3V	361	333
Sample C TLUD 6V	403	386
Sample D TLUD 9V	472	472
Sample E Retort	2	3
Sample F Retort 500 C	9	4
Sample G Retort 700 C	389	370
Sample H Retort 900 C	80	3

- TLUD chars
  - Increase in BET surface area with an increase in activation energy
  - Reasonable repeatable
- Retort chars
  - Decrease in BET surface area with highest temperature
  - Poor repeatability
  - Likely due to the small pore sizes created during activation and the slow kinetics of N2 gas equilibrating in the small pores
- We have seen this many times in past with activated carbons and zeolites that have pores near 5 Angstrom
- Run time range from 5 to 24 hours

CO_2 Adsorption Isotherms at 0 C

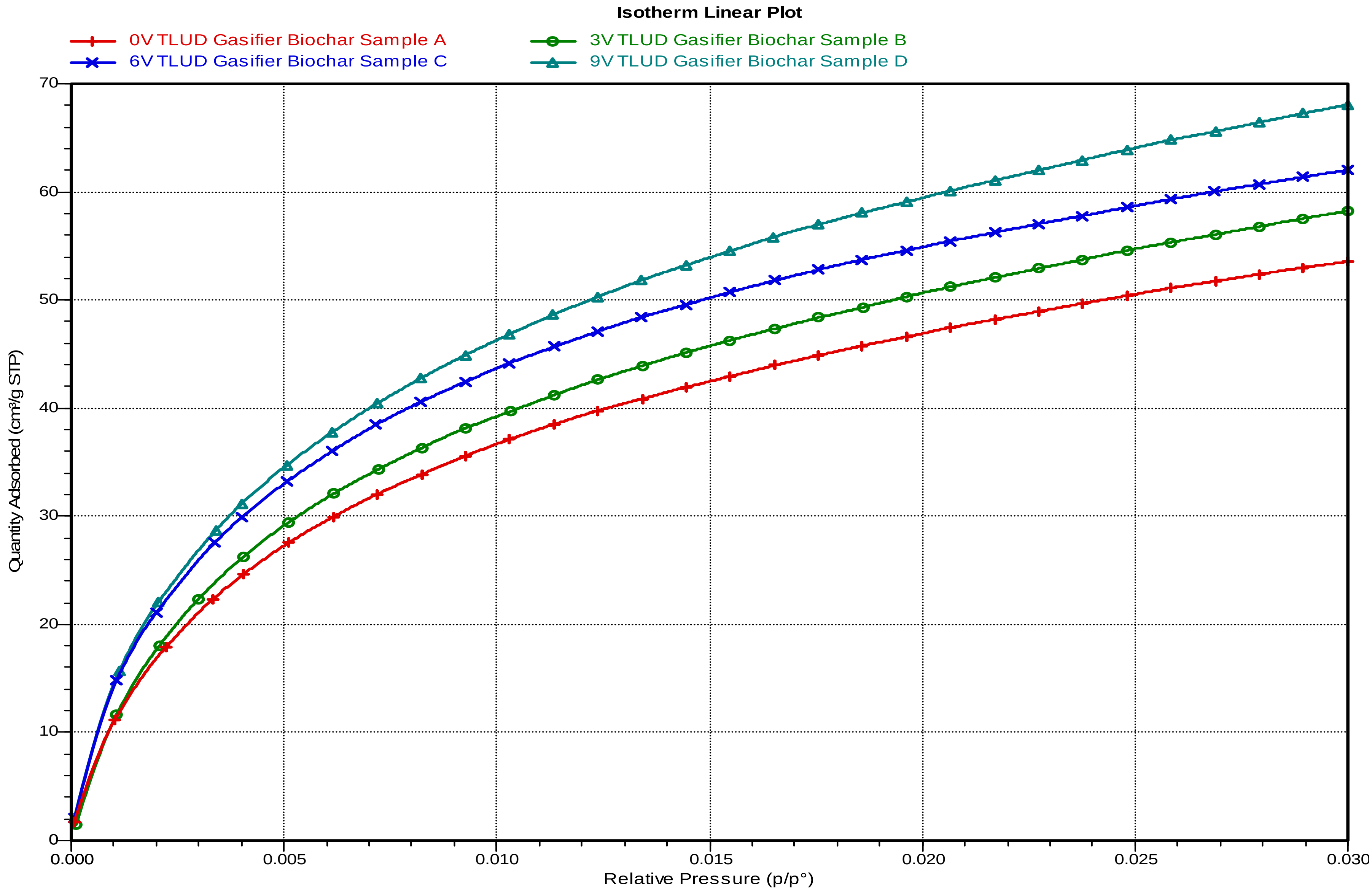
- Originally used by carbon industry to calculate pore size of microporous materials before high-quality vacuum systems and low pressure transducers became widely available and affordable
- Not as popular today with automated instruments, but still used as an adsorbent probe for extremely small pore carbons
- Fast, Easy
- Use some unique modeling and fitting algorithms
  - Dubinin and DFT for micropore volume and area

CO2 adsorption results

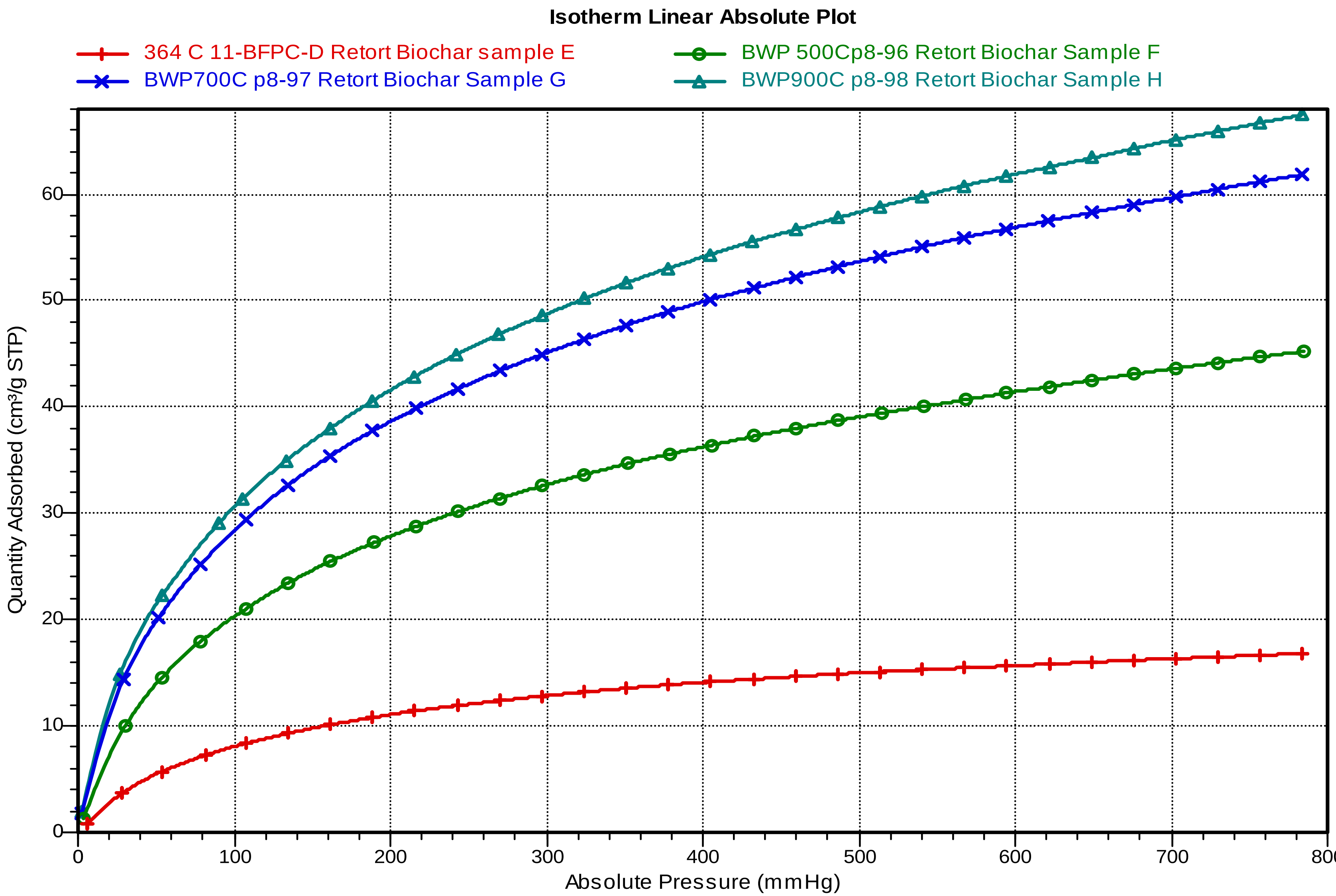
	DFT Surface Area - Run1 (m2/g)	DFT Surface Area - Run2 (m2/g)	Dubinin Micropore volume (cc/g)
Sample A TLUD 0V	300	287	0.166
Sample B TLUD 3V	330	319	0.182
Sample C TLUD 6V	349	345	0.186
Sample D TLUD 9V	365	360	0.21
Sample E Retort	103	NA	0.05
Sample F Retort 500 C	251	NA	0.139
Sample G Retort 700 C	348	NA	0.188
Sample H Retort 900 C	375	NA	0.207

- Both TLUD and Retort samples see an increase in DFT surface area and micropore volume with an increase in activation energy
- The repeatability is much better than we experienced with N2 adsorption
- CO2 adsorption is performed at 0 C and at much higher relative pressures, so it equilibrates more quickly than N2
- Run time on the order of 3-5 hours, but could be reduced to 1-2 hours if needed

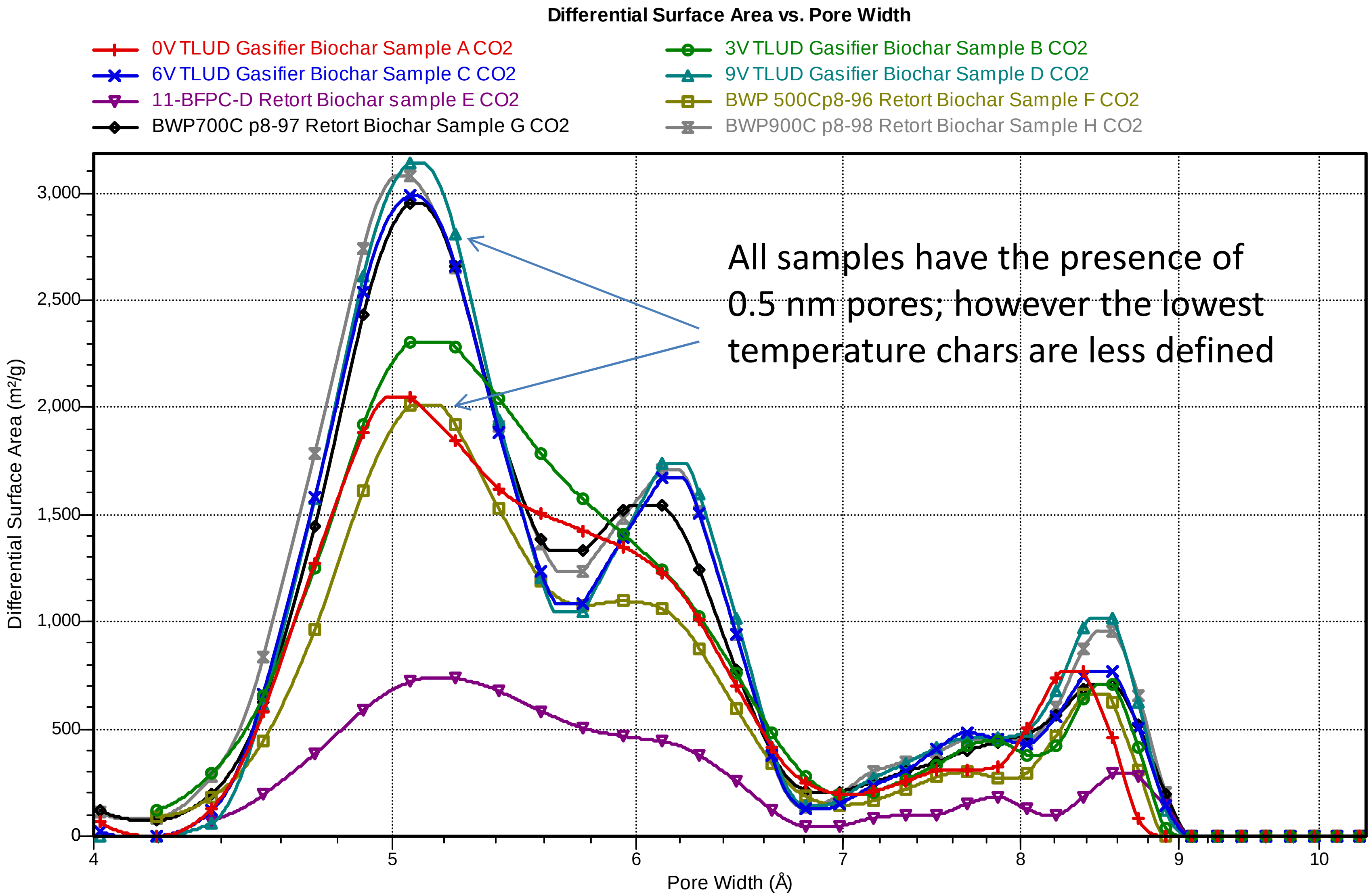
CO2 adsorption results – TLUD Chars



CO_2 adsorption results – Retort Chars



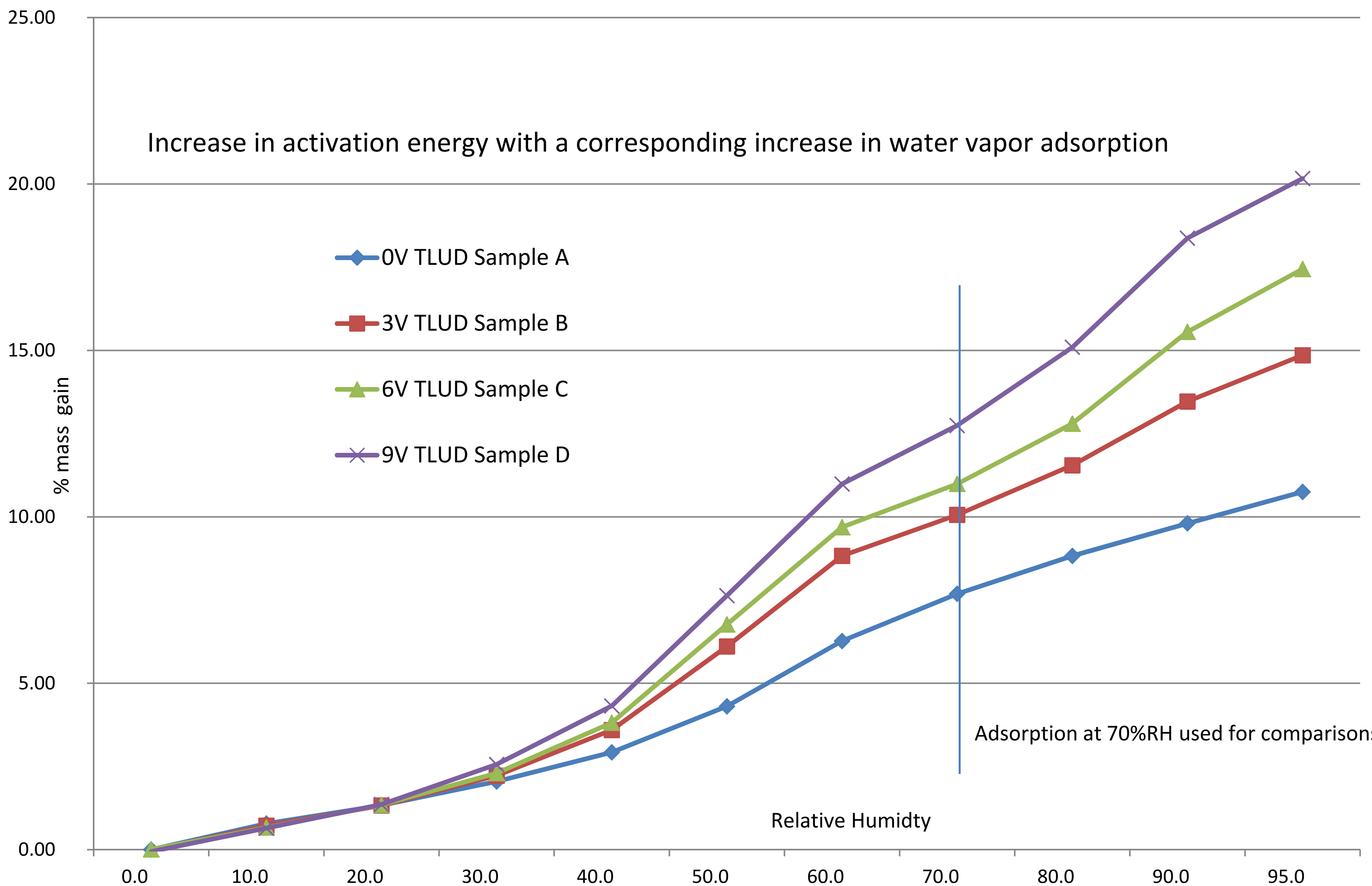
CO_2 adsorption results



Water Vapor Adsorption Isotherms at 25 C

- Measures the uptake and loss of water vapor gravimetrically using an ultra-microbalance
- Mimics behavior of biochar in soils – water uptake & release versus relative humidity
- May measure critical biochar dynamic in soil - need research guidance

Water Vapor adsorption results



Water Vapor adsorption results

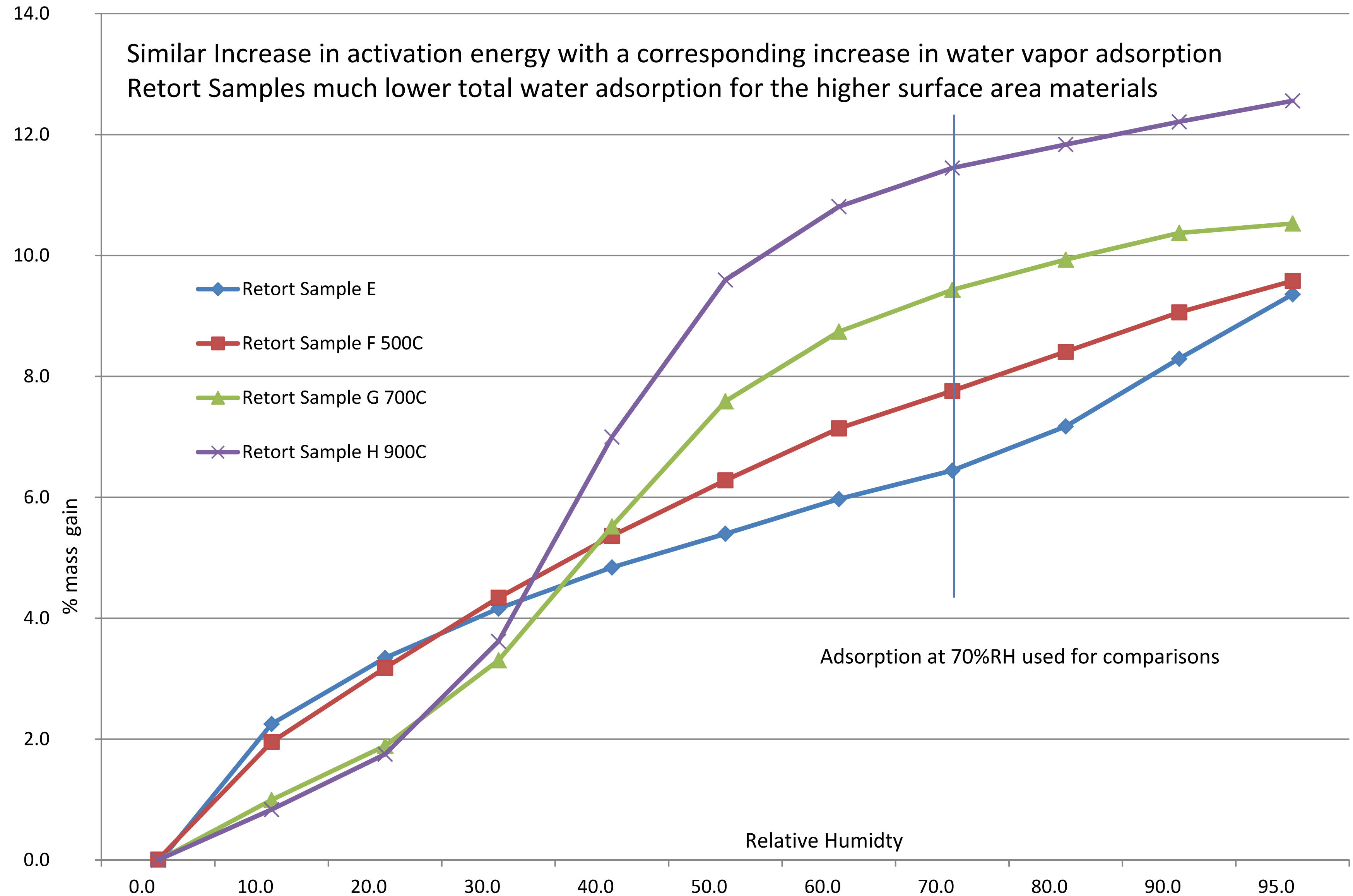
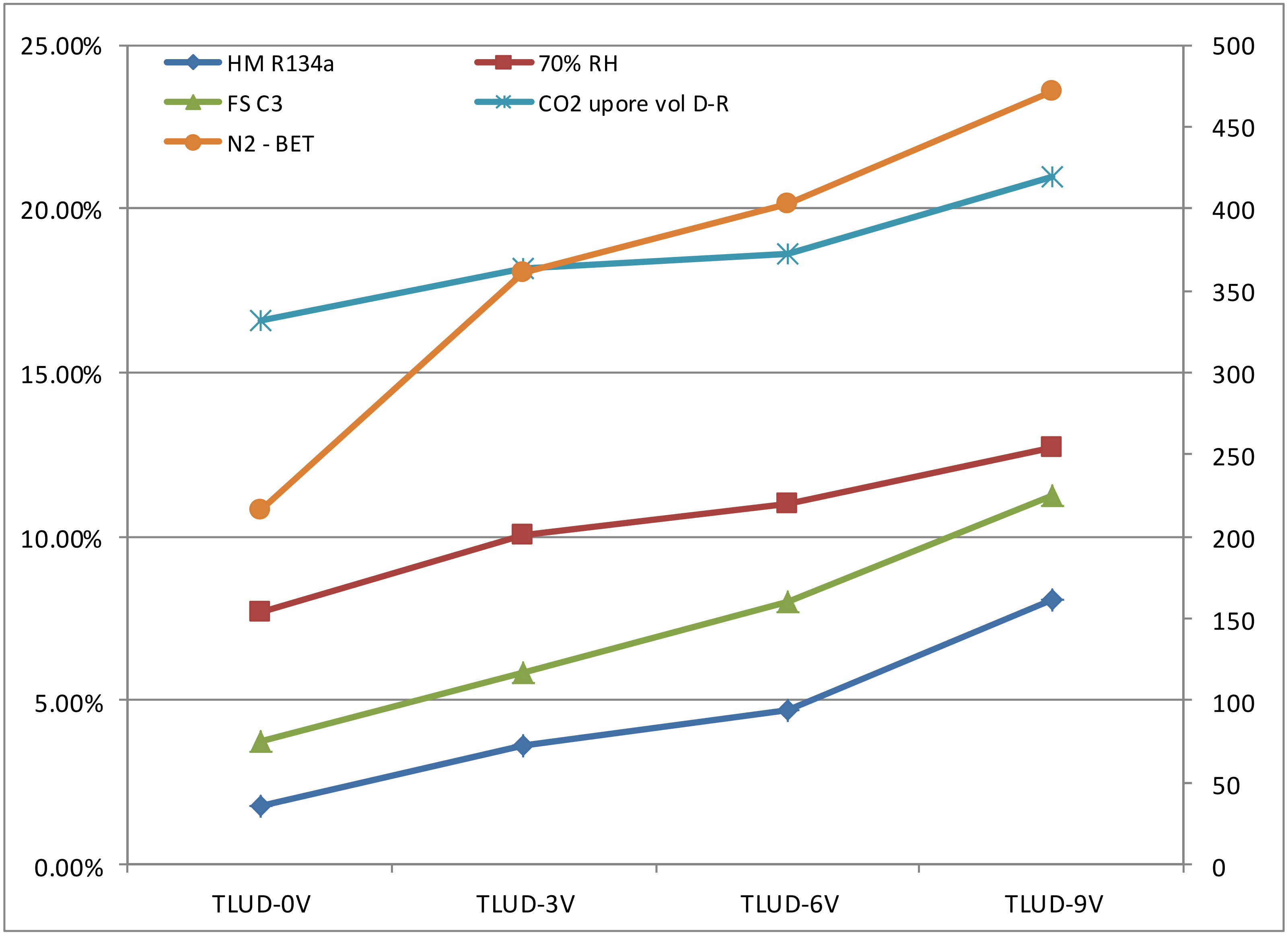


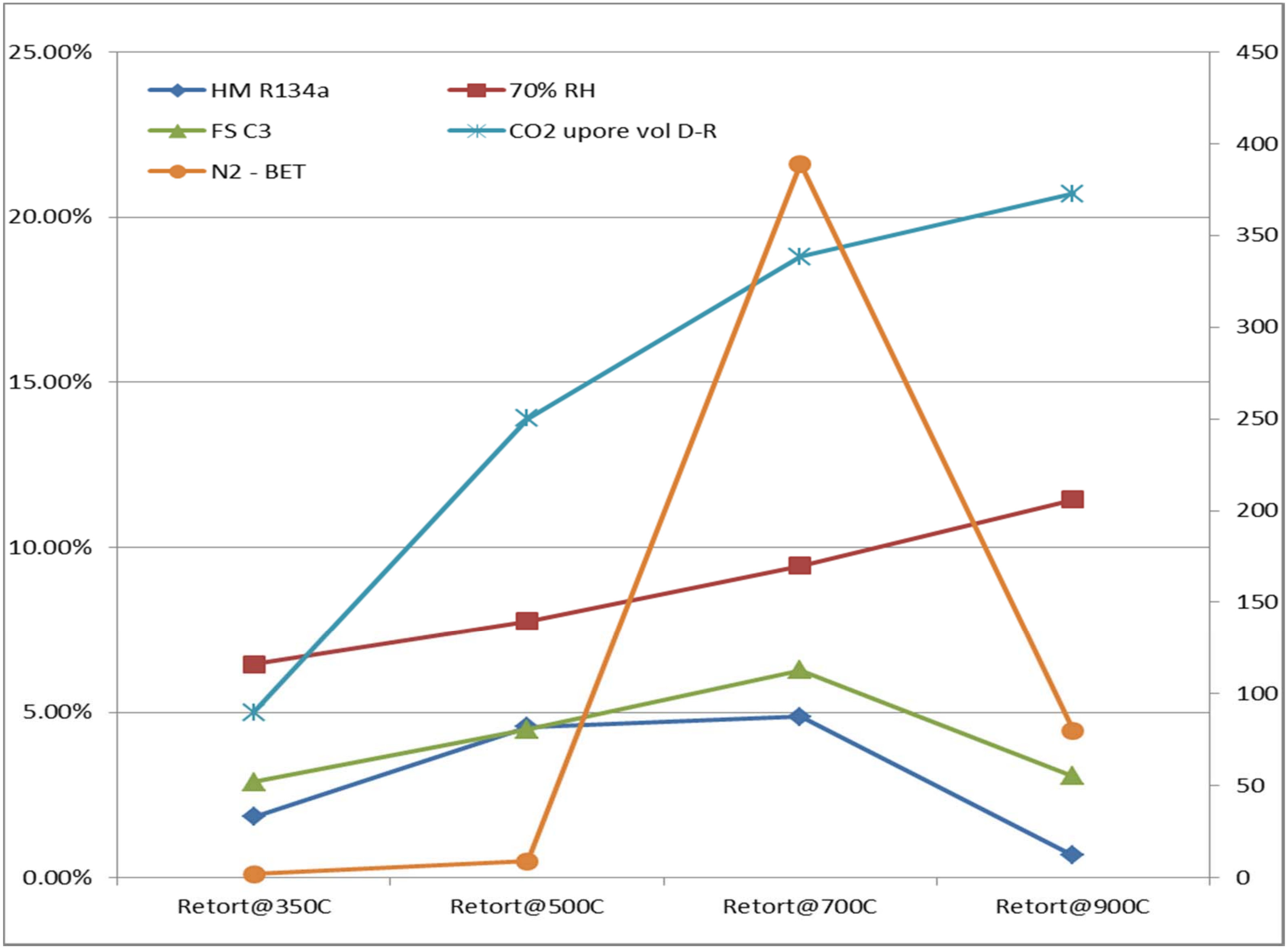
Table of results

	A	B	C	D		E	F	G	H
	TLUD-0V	TLUD-3V	TLUD-6V	TLUD-9V		Retort @350C	Retort @500C	Retort @700C	Retort @900C
HM R134a	**1.79%**	**3.64%**	**4.74%**	**8.05%**		1.84%	4.56%	4.86%	0.68%
FS C3	**3.77%**	**5.85%**	**7.99%**	**11.28%**		2.89%	4.47%	6.27%	3.07%
N2 – BET (m2/g)	**216**	**361**	**403**	**472**		2	9	389	80
70% RH	**7.69%**	**10.06%**	**10.99%**	**12.74%**		**6.44%**	**7.76%**	**9.43%**	**11.45%**
CO2 – DFT (m2/g)	**300**	**330**	**349**	**365**		**103**	**251**	**348**	**375**
CO2 vol ads (cc/g)	**53**	**58**	**62**	**68**		**17**	**45**	**62**	**67**
CO2 Micropore volume (cc/g)	**0.166**	**0.182**	**0.186**	**0.21**		**0.05**	**0.139**	**0.188**	**0.207**

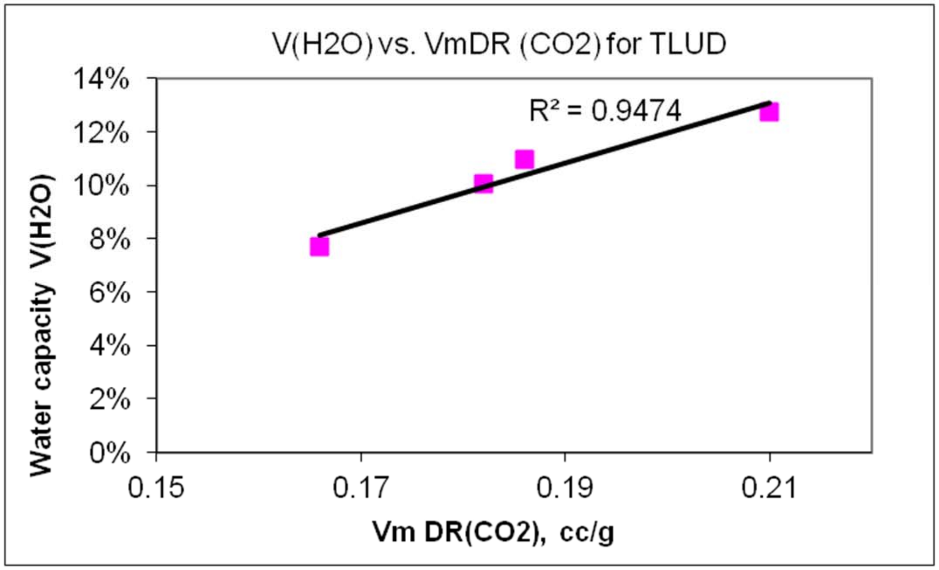
Summary of all TLUD results

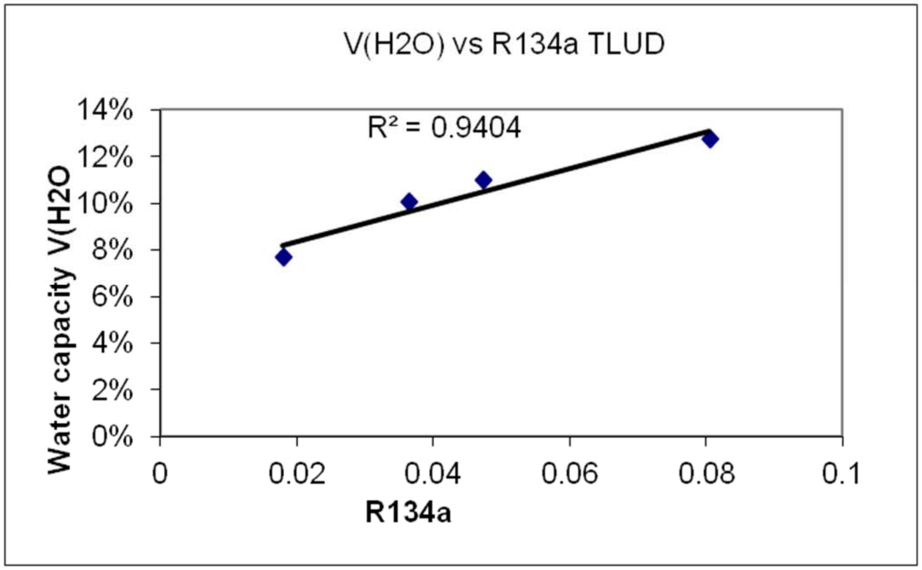


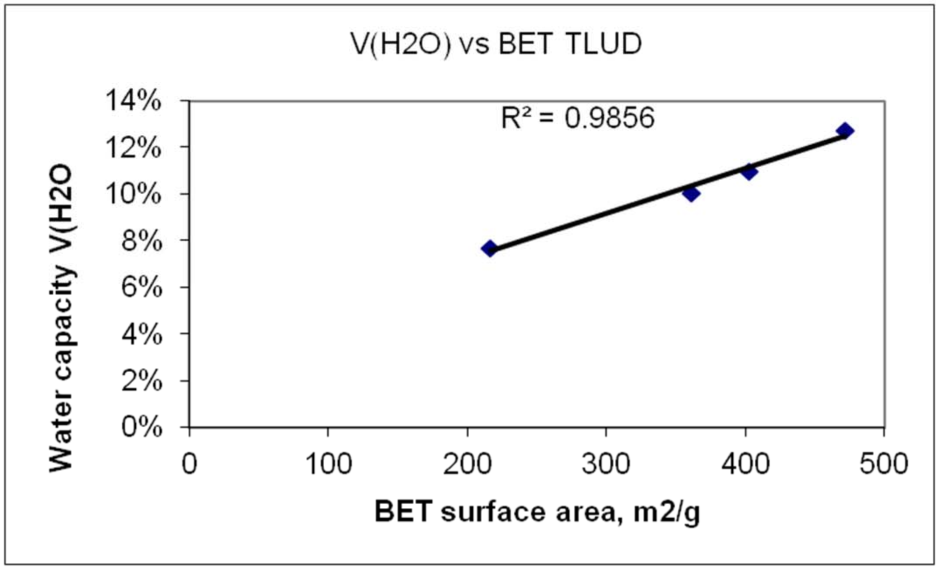
Summary of all Retort results

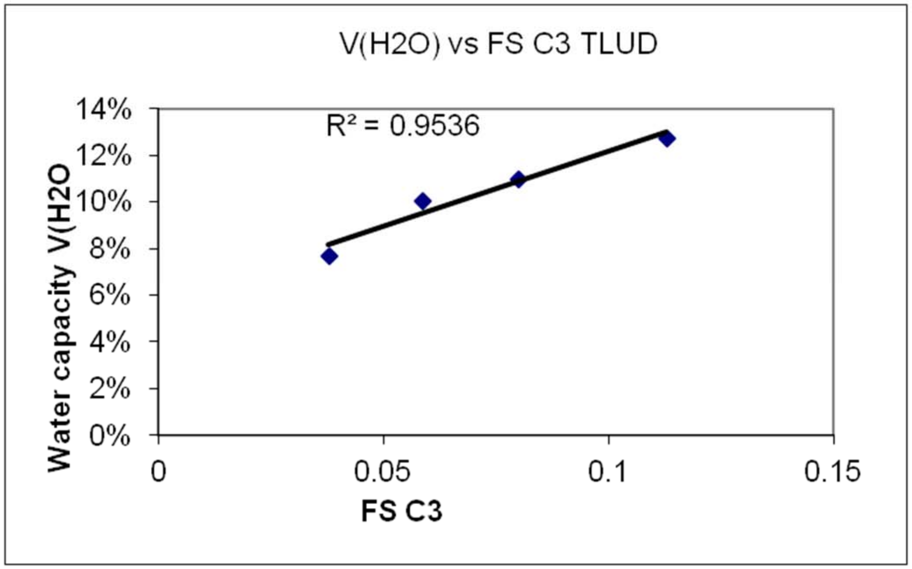


Correlation to 70% RH adsorption (TLUD Chars)

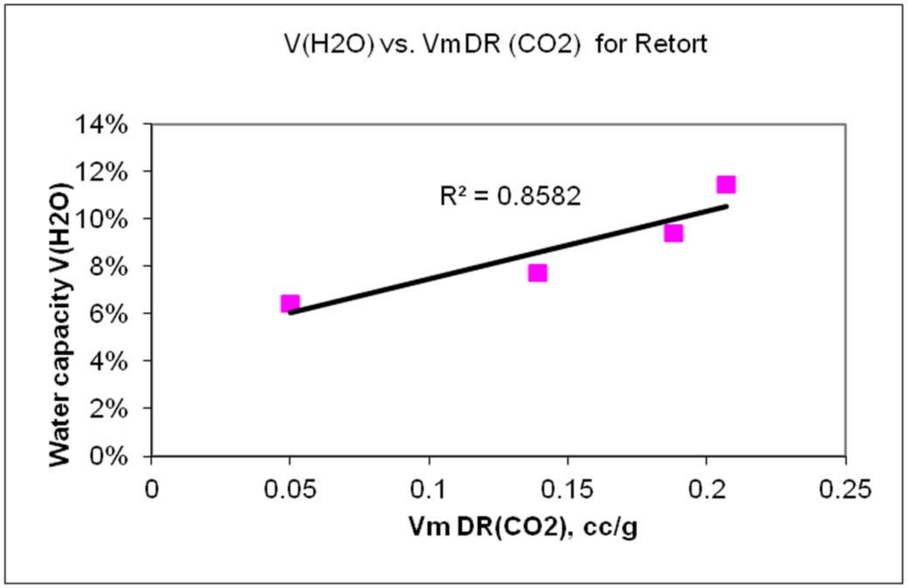


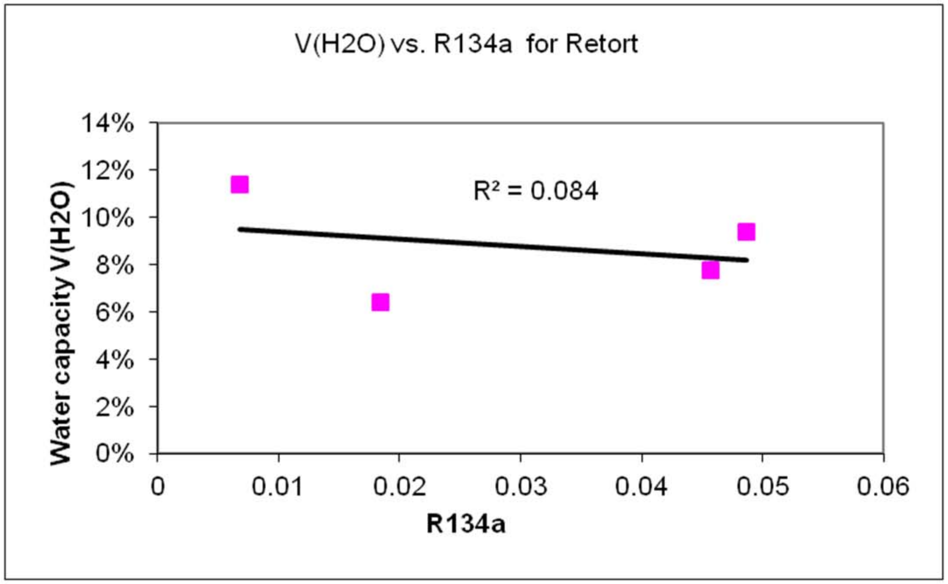


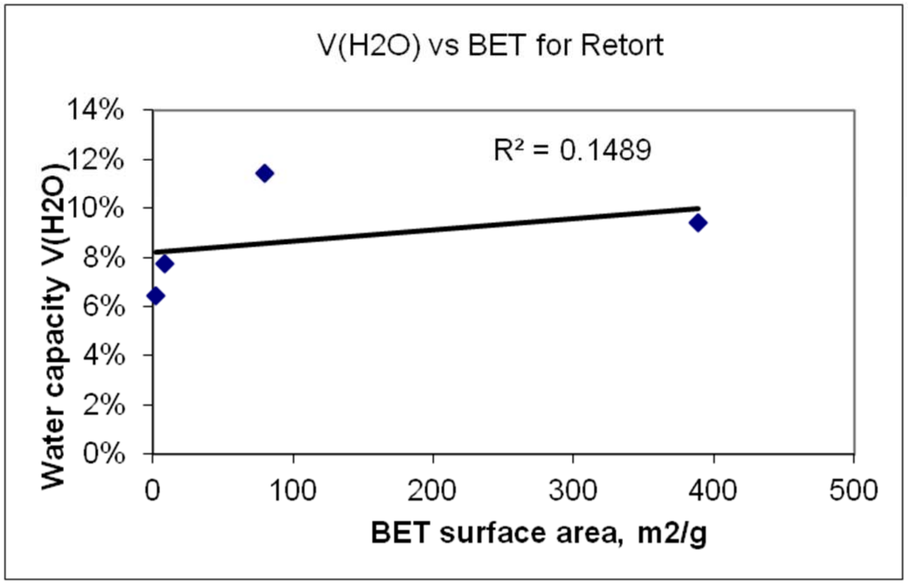


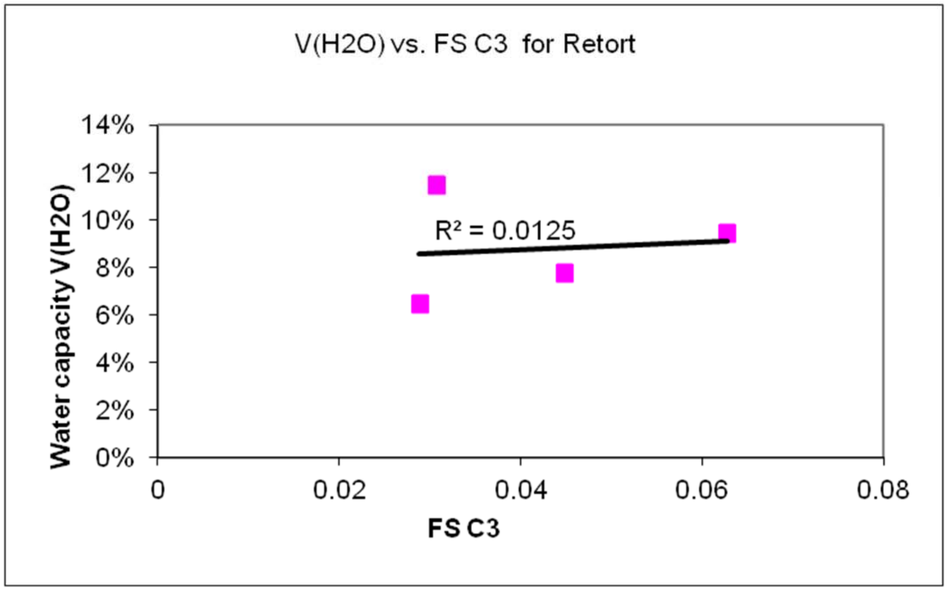


Correlation to 70% RH adsorption (Retort Chars)









Summary Characterization Results

- All techniques and probes did a nice job of measuring increased capacity, surface area, or activity for the TLUD chars
- CO_2 and Water were the only probes which measured increased capacity with high temperature Retort chars
  - Potentially due to kinetics for N_2, and size of adsorbate molecule for Butane and R134a
- R134a, Butane, and BET reported similar decreases in activity for the highest temperature Retort char
  - Pores in high temp Retort chars may collapse and exclude adsorbate
- CO_2 provides a faster, more repeatable adsorption isotherm and allows calculation of micropore distribution and micropore volume
- Further studies and **soil application research** is needed to determine which technique truly provides the best prediction of performance

Thank You

- Thanks to Dan Burnett of Surface Measurement Systems for the water vapor adsorption data and input
- Thanks to Hugh McLaughlin for organizing and leading this research
- Thanks to Frank Shields from Control Labs
- Thanks to Dr. Jacek Jagiello, colleague from Micromeritics for his input and expertise with activated carbons