

Biochar Characterization in Complex Soil Mixtures - High Resolution Nitrogen Pore Distribution Analysis (HRPDA)

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Introduction

- Experimental technique used for catalysts and sorbents
- Results for 'state-of-art' Cabot carbon black
- Results for Cabot carbon black mixed with soil
- Results for commercial charcoal subjected to freeze-thaw cycles
- Future application potential for biochar samples



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Analytical Technique

- Volumetric dosing N₂ adsorption at liquid nitrogen temperature gives accurate 'map', or 'blue print', of both size and amount of voids in materials < 3000 Å diameter
- When combined with Hg porosimetry detailed structure of porous materials produced from 500 micrometer diameter to about 5 Å or 0.5 nm
- Two techniques are complimentary and provide complete detail of void structure in porous materials
- Total analysis time per sample: 16 hours



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Cabot 'Unique' Carbon Black

- Cabot Black Pearl 2000 developed for fuel cells

Sample	BET Surface Area (m ² /g)	Total Pore Volume (cc/g)	t-plot Micro-pore Area (m ² /g)
Black Pearl 2000	1500	3.0	1123

- Black Pearl 2000 represents an apparently unique carbon black development with combination of high surface area and high pore volume with wide pore distribution between 10 and 100 nm diameter



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BP 2000 mixed with Mississippi Loess

Sample	BET Surface Area (m ² /g)	Total Pore Volume (cc/g)	t-plot Micro-pore Area (m ² /g)
Loess	20	0.02	7
1 wt. % Black Pearl 2000/Loess	40	0.07	28
3 wt. % Black Pearl 2000/Loess	70	0.13	50

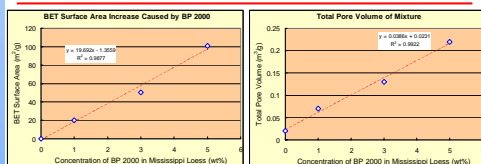
- Calculated BET surface areas of 35 and 65 m²/g and total pore volume of 0.05 and 0.11 cc/g for two samples agree with experimental results



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BP 2000 mixed with Mississippi Loess



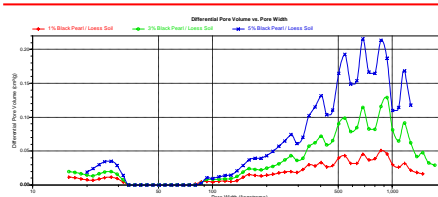
- Surface area variation tracks well with amount of Black Pearl 2000 in mixture
- Pore volume variation tracks well with amount of Black Pearl 2000 in mixture



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"Blue-Print" of BP 2000 in Loess Soil



- Complex and detailed pattern of void spaces related to "bunch-of-grapes" structure about 800 nm size made from strings of primary particles



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Commercial Charcoal Results

Sample	BET Surface Area (m ² /g)	Total Pore Volume (cc/g)
Charcoal	2.9	0.006
Charcoal with 8-cycles 'freeze-thaw-cycles'	5.5	0.009

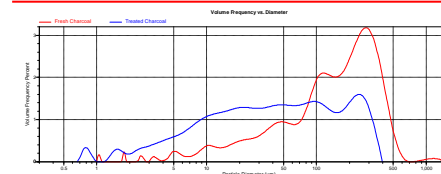
- N₂ porosimetry provides information < 3000 Å diameter
- Hg porosimetry provides information on particles < 360 micrometer diameter and explains 2 cc/g water uptake



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Charcoal Sample: Fresh and After Aging



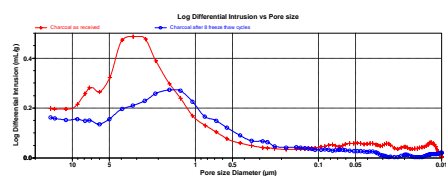
- Hg porosimetry shows eight cycles of freeze-thaw-freeze treatment shifts particle distribution to smaller particle
- Smaller particle size will lead to higher BET surface area
- We are probably missing the fresh charcoal interstitial volume because it is too large to be seen (>360 micrometers)



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Charcoal Sample: Fresh and After Aging



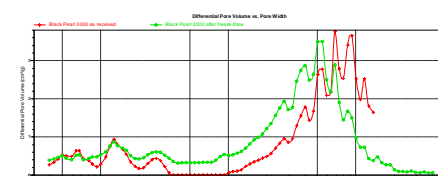
- As received charcoal (red) and following eight freeze-thaw cycles (blue)
- Large 3-7 micron size particle are being fractured into smaller size particles following freeze-thaw cycles



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BP 2000 Transformed by Freeze-Thaw Cycles



- As received BP 2000 (red) and following eight freeze-thaw cycles (green)
- note especially the decrease in the pores at the largest size



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Conclusions

- Micromeritics analysis proves mixture of carbon black with soil can be analyzed by HRPDA
- Commercial charcoal has low surface area and low pore volume and is shown to be unstable to 'freeze-thaw-freeze' cycles
- Hg porosimetry (combined) with HRPDA give complete 'blue print' of micro-, meso-, and macropores
- Biochar analysis possible for moderate surface area samples



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Future Direction

- Prove applicability to biochar samples aged in soils
- Find partners with Micromeritics to apply HRPDA technique to historic biochar beds in Amazon Basin
 - Soil samples
 - Ceramic green ware in these soils
- Use technique to aid development of structure-function relationships for understanding biochar crop yield improvements
- Application of techniques to synthetic soils



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