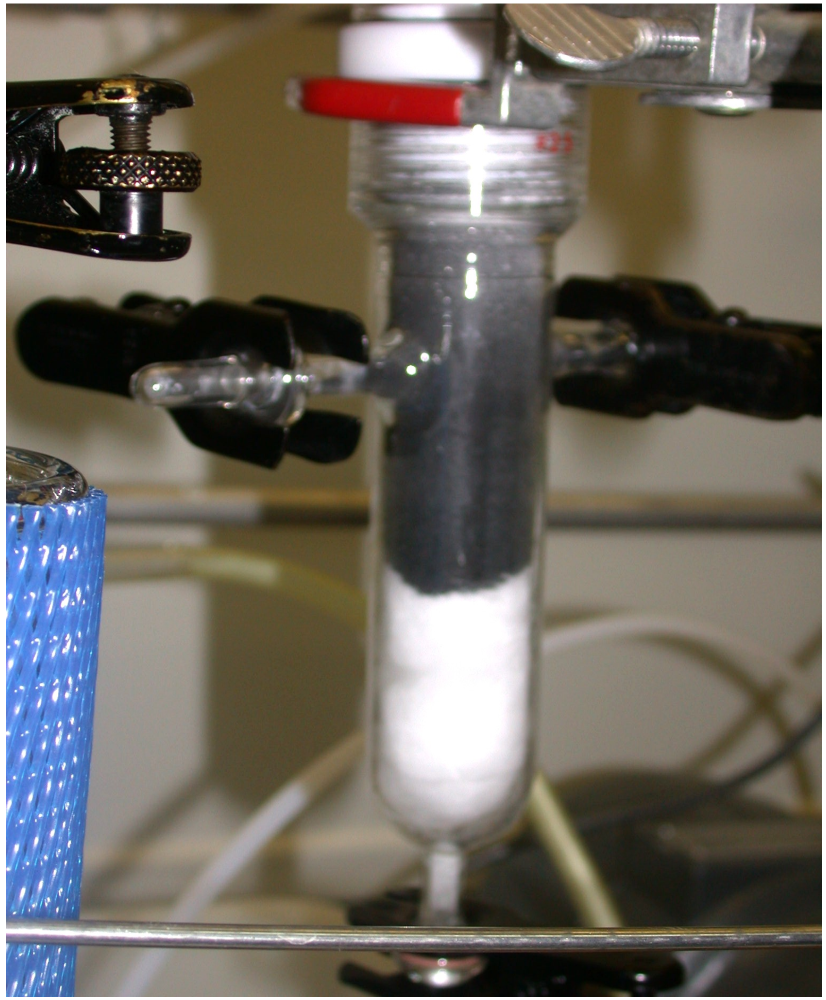
Biochar surface oxygenation through ozonization for dramatically enhancing cation exchange capacity

James W. Lee, PhD
Department of Chemistry and Biochemistry
Old Dominion University, Norfolk, VA 23529 USA
Email: jwlee@odu.edu

Lee's NH_3-CO_2-Biochar Experiment in Collaboration with Danny Day of Eprida at ORNL in 2002



Development of "Carbon-Negative" Energy Technology Concept for Global Carbon Sequestration: Some Paper Trails

[1] James W. Lee and Rongfu Li (1998) "Method for reducing CO2, CO, NOx, and SOx emissions," ORNL Invention Disclosure ERID 0631; 2002 Patent No. US 6,447,437 B1.

[2] James W. Lee and Rongfu Li (December 3-7, 2001) "Integration of coal-fired energy systems with CO2 sequestration," presented at the 18th Annual International Pittsburgh Coal Conference, Newcastle, Australia.

[3] J. W. Lee, D. Day, R. Evans, and R. Li (2002) "Integration of fertilizer production and biomass pyrolysis for carbon management," ORNL Invention Disclosure ID 1221, S-101,807.

[4] X. Li, E. Hagaman, C. Tsouris, and J. W. Lee (2003). "Removal of carbon dioxide from flue gas by ammonia carbonation in the gas phase," *Energy & Fuels*, 17:69-74.

[5] J. W. Lee and R. Li (2003). "Integration of fossil energy systems with CO2 sequestration through NH4HCO3 production," *Energy Conversion & Management*, 44(9): 1535-1546.

[6] J. W. Lee, D. Day, R. Evans, and R. Li. "Ammonia carbonation and biomass pyrolysis for carbon management," presented at the Second Annual Conference on Carbon Sequestration, May 5-8, 2003, Alexandria, Virginia.

[7] Day, Danny; Lee, James (2004) "The production and use of a soil amendment made by the combined production of hydrogen, sequestered carbon and utilizing off gases containing carbon dioxide." PCT Int. Appl. 58 pp. WO 2004037747 A2.

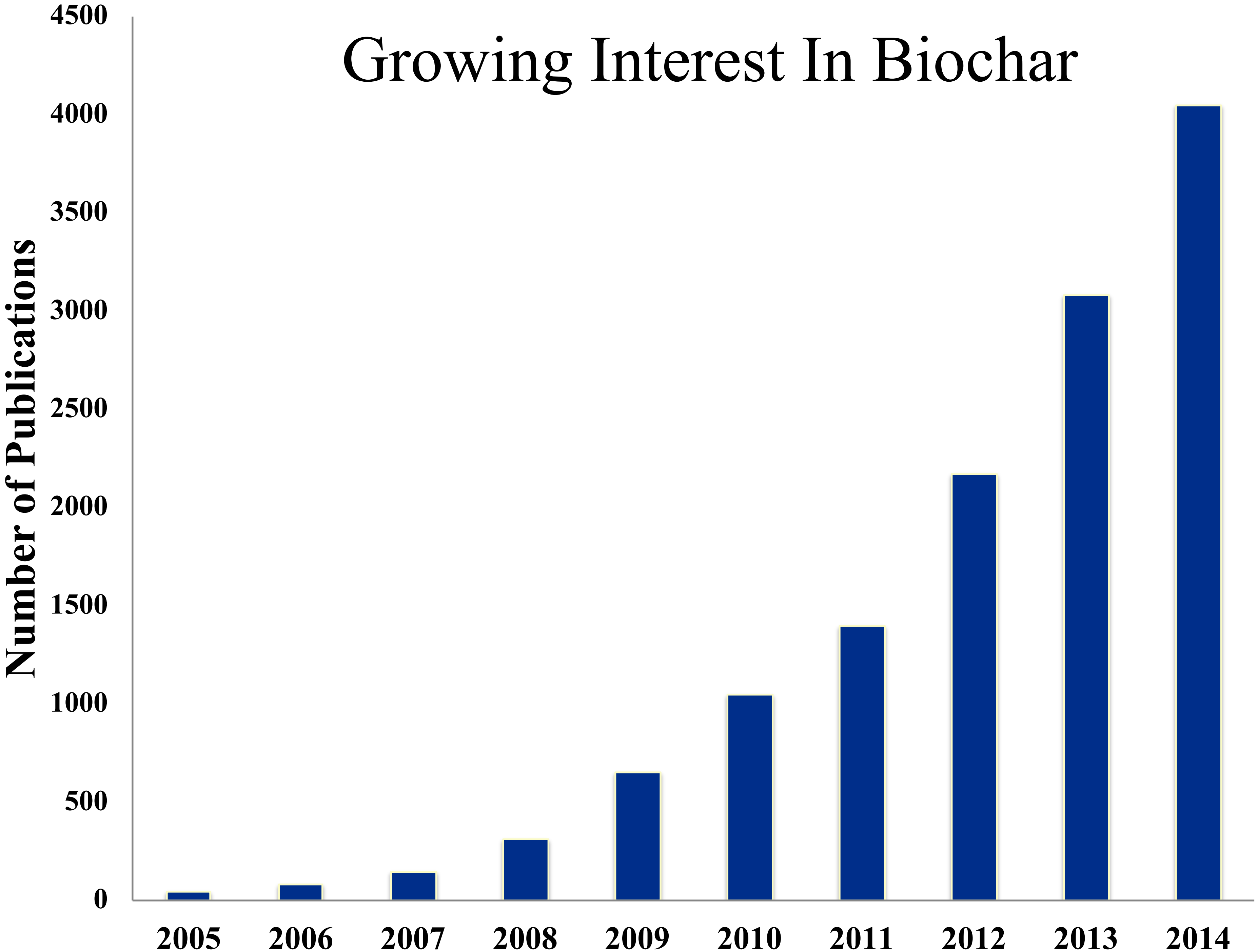
[8] J. W. Lee, D. Day, R. Evans, and R. Li (June 10-11, 2004). "Ammonia carbonation and biomass pyrolysis for carbon management," presented at the Energy with Agricultural Carbon Utilization Symposium, Athens, GA.

[9] J. W. Lee, B. Hawkins, D. M. Day, and D. C. Reicosky (2010) Sustainability: The capacity of smokeless biomass pyrolysis for energy production, global carbon capture and sequestration, *Energy Environ. Sci.*, 3 (11): 1609–1812;

[10] J. W. Lee, M. Kidder, B. R. Evans, S. Paik, A.C. Buchanan, C. Garten, and R. Brown (2010) Characterization of biochars produced from cornstover for soil amendment, *Environmental Science & Technology*, 44:7970–7974.

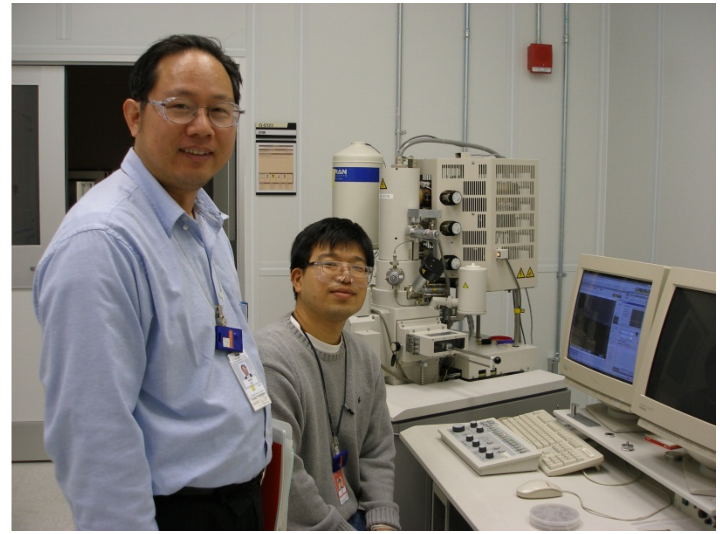
[11] Smith CR, Buzan EM, Lee JW (2013) Potential impact of biochar water-extractable substances on environmental sustainability, ACS Sustainable Chem. Eng. 2013, 1, 118−126; DOI: 10.1021/sc300063f.

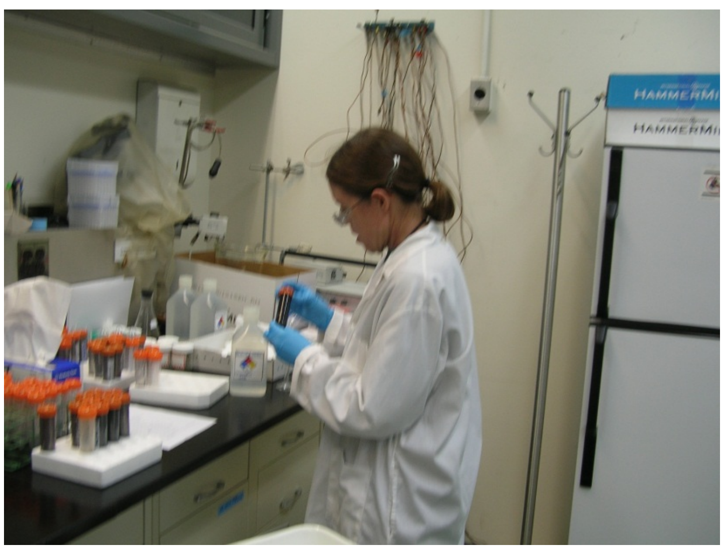
[12] Lee JW, Buchanan AC, Evans BR, Kidder MK (2013) Biochar production method and composition therefrom, US Patent No. 8398738 B2.

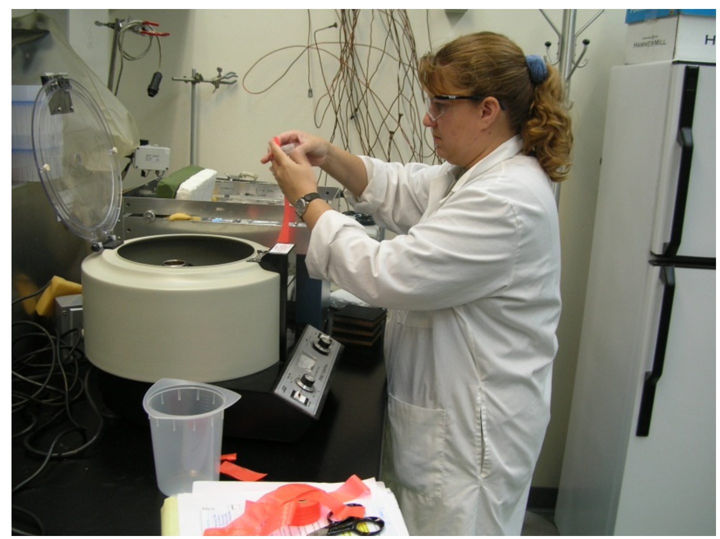


Growing Interest In Biochar
Number of Publications
4500
4000
3500
3000
2500
2000
1500
1000
500
0
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014

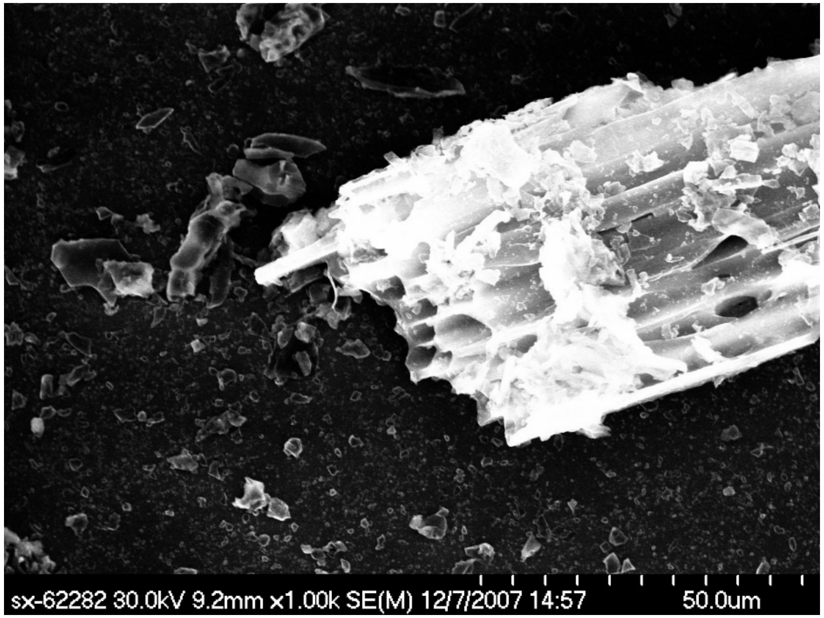
Lee started working on biochar for soil amendment and carbon sequestration since 2002 at ORNL

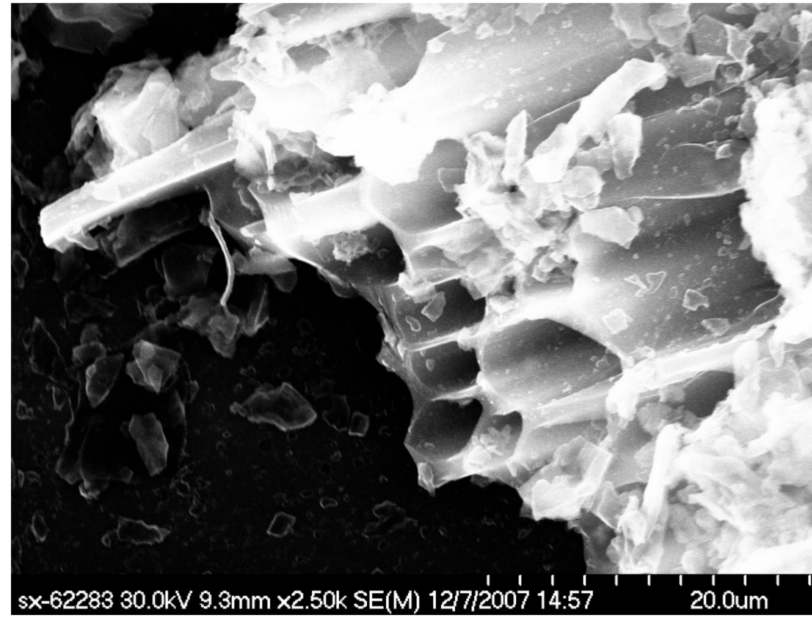


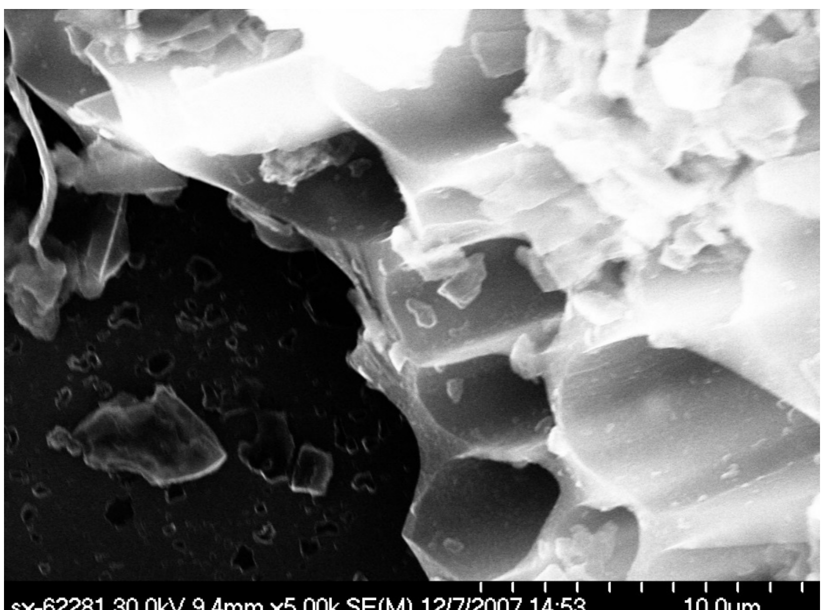


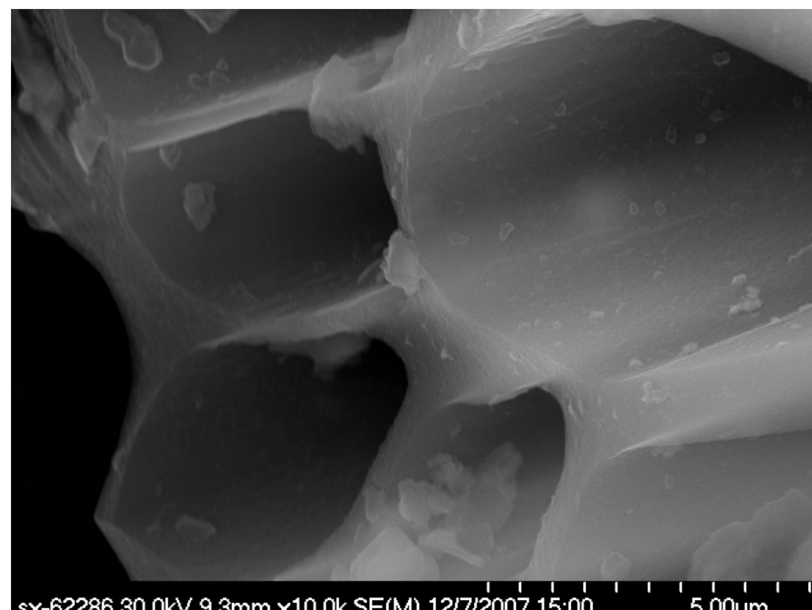


SEM Images of Cornstover Fast Pyrolitic Char-450C (ORNL 2002-2007)









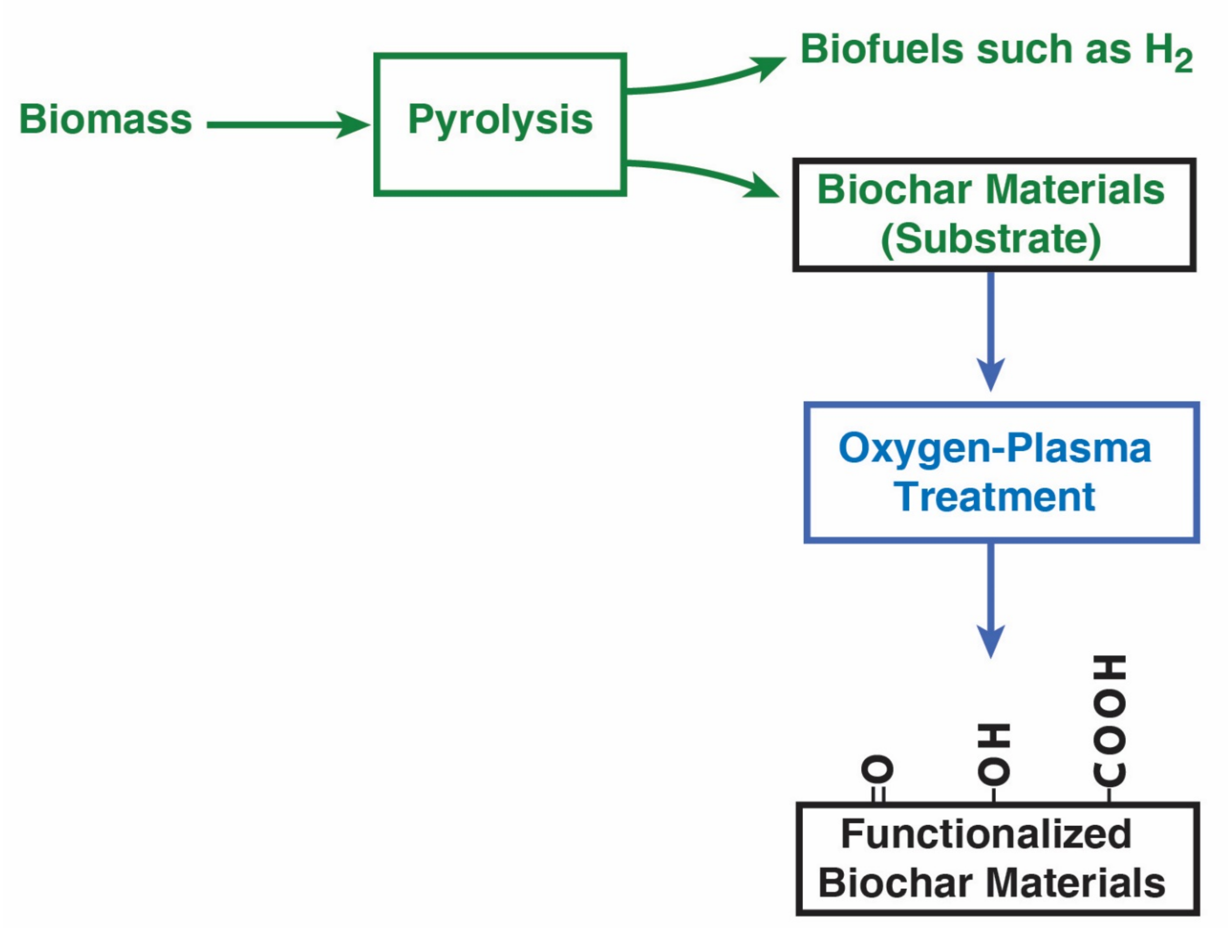
Correlation between Biochar O:C Ratio and Cation Exchange Capacity Measured in USDA Funded Project at ORNL

Sample	O:C (mol ratio)	Cation Exchange Capacity: cmol (+)/kg
Cornstover Gasification Char-700 C	0.11	10.28 ± 2.91
Cornstover Fast Pyrolitic Char-450 C	0.20	26.36 ± 0.17

Application of oxygen-plasma treatment to create biochar product with higher cation-exchange capacity and wettability

Lee JW, Buchanan AC, Evans BR, Kidder MK (2011) **Biochar production method and composition therefrom**, US Patent Application Publication No. 2011/0172092 A1

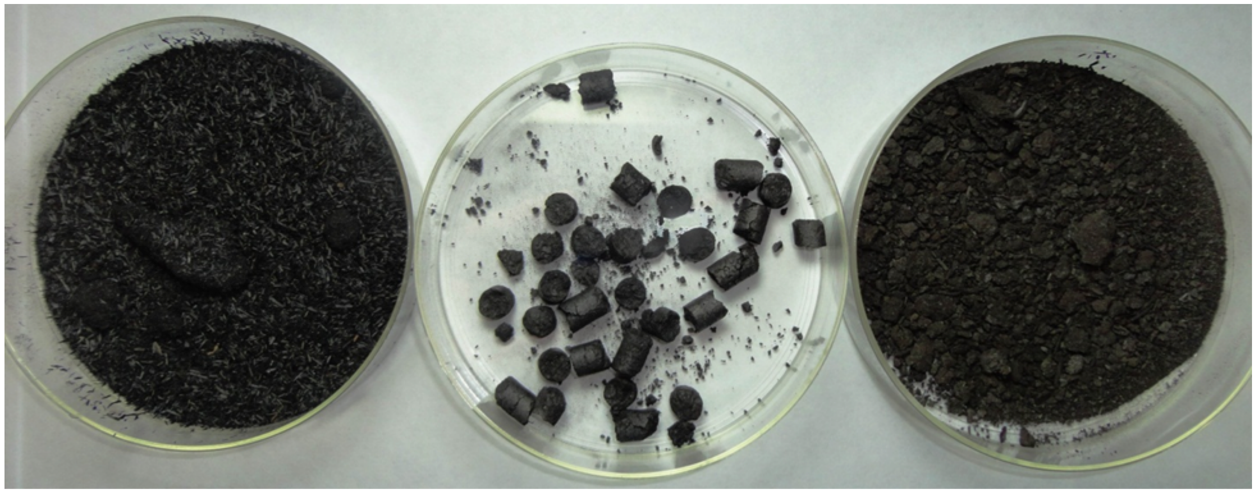
(US Patent No. US 8709122 B2 and US Patent No. 8398738 B2)



Lee ODU Lab Biochar Research:

Chemical Analyses and Bioassays of Water-Extractable Substances of Biochars Produced from Pinewood, Peanut Shell, and Chicken Litter

Pinewood | Peanut Shell | Chicken Litter

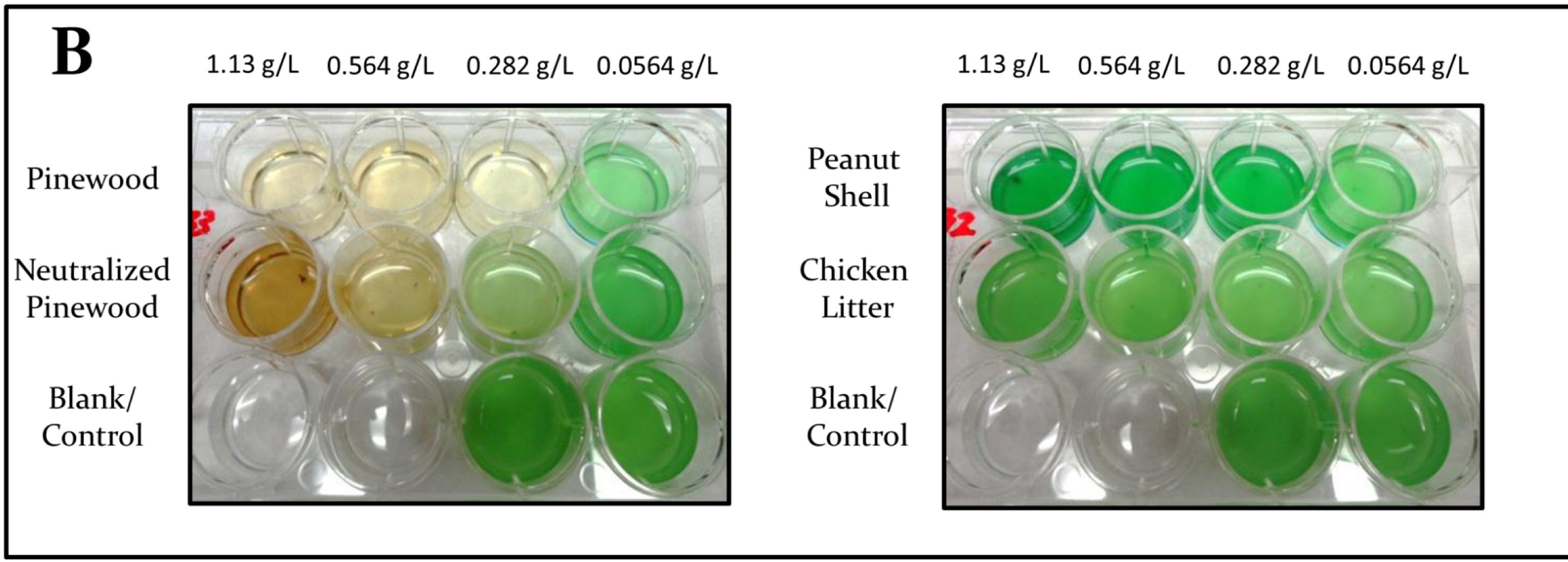


Evaluate the Potential impact of Biochar Water Extractable Substances on agriculture environmental sustainability

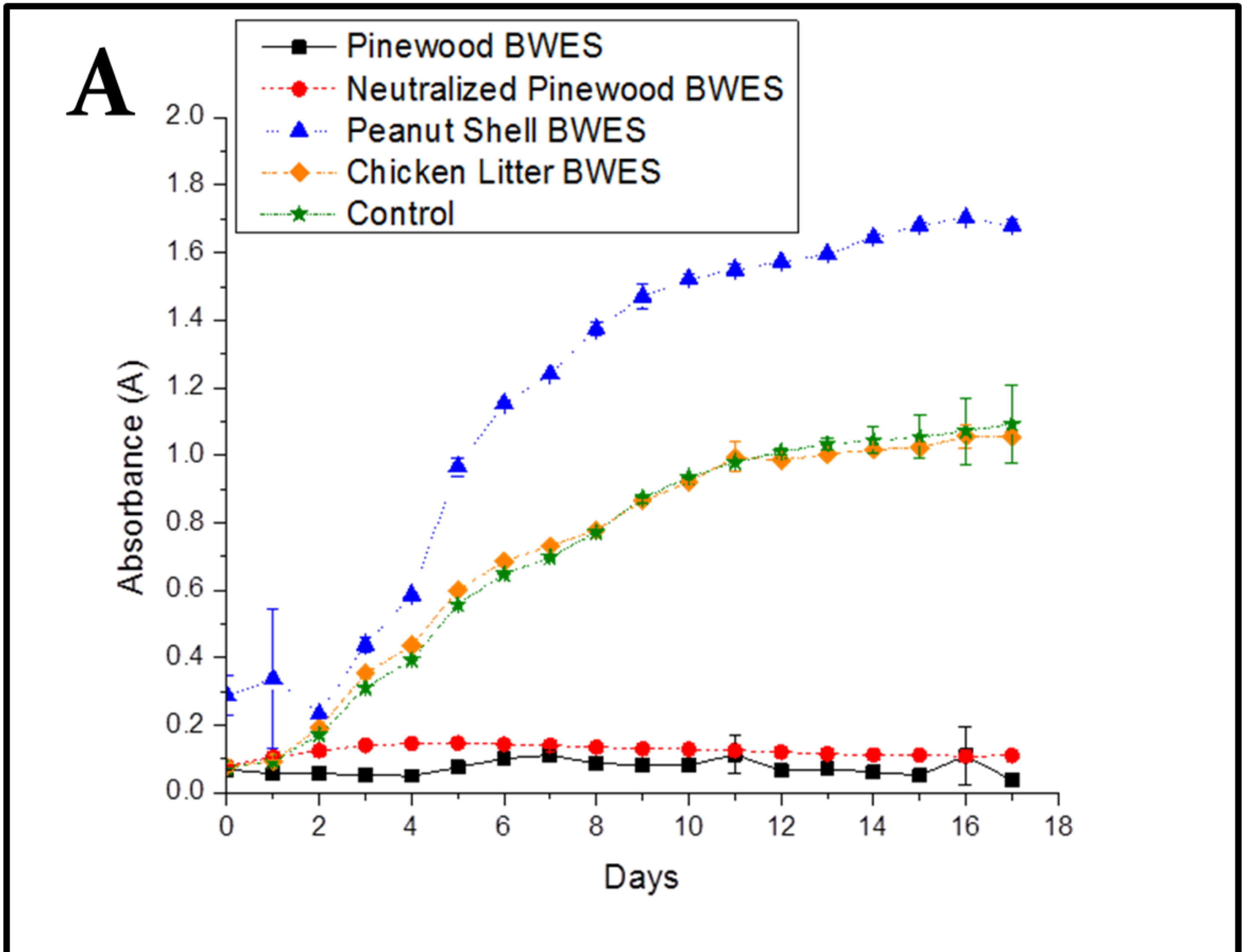
Goal:

High-Tech Biochar with higher cation exchange capacity and free of undesirable substances (toxins)

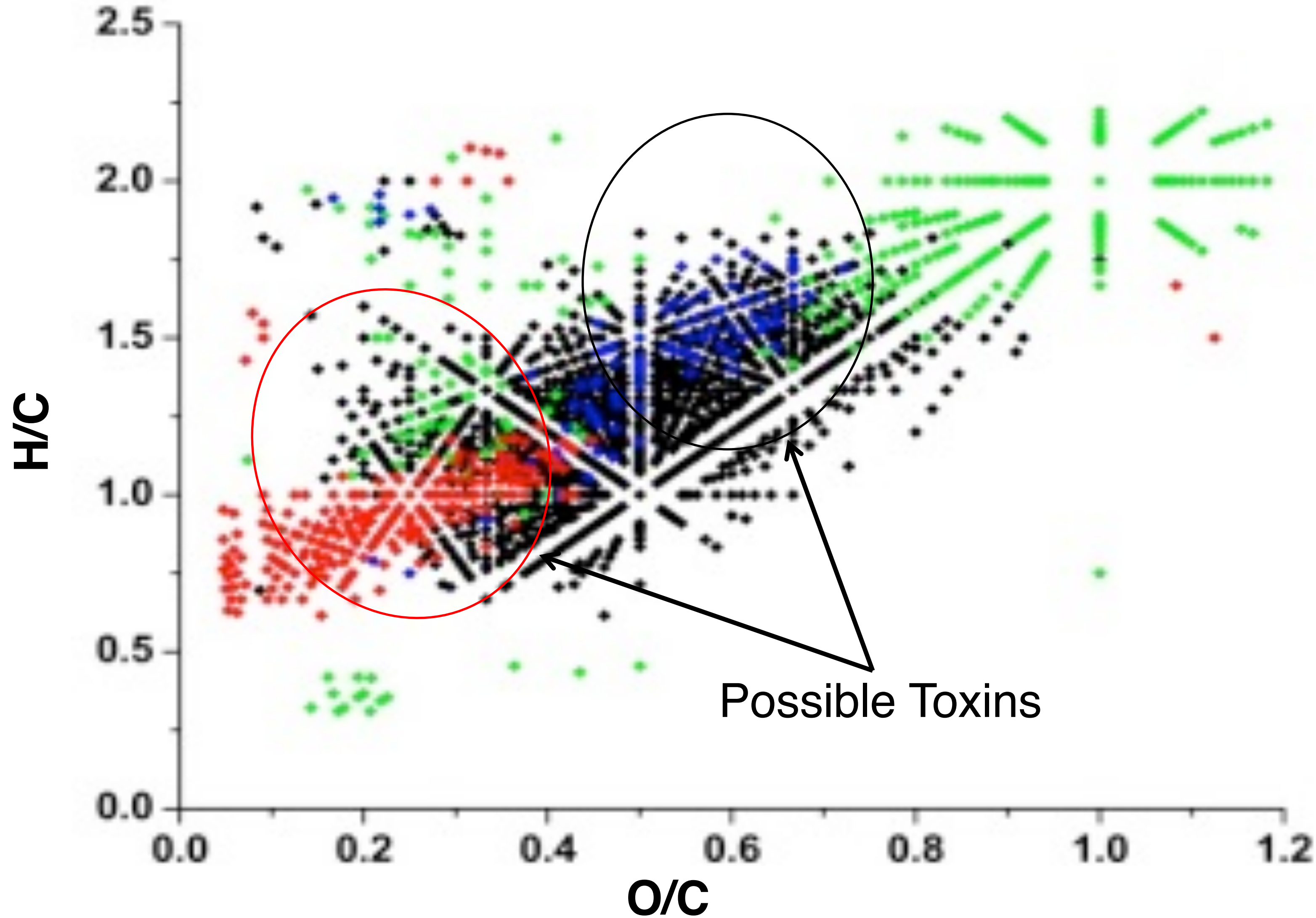
Bioassay: Tests of Biochar Substances with Blue-Green Algae



Discovered: some of the biochar water extractable substances are toxic to algal growth

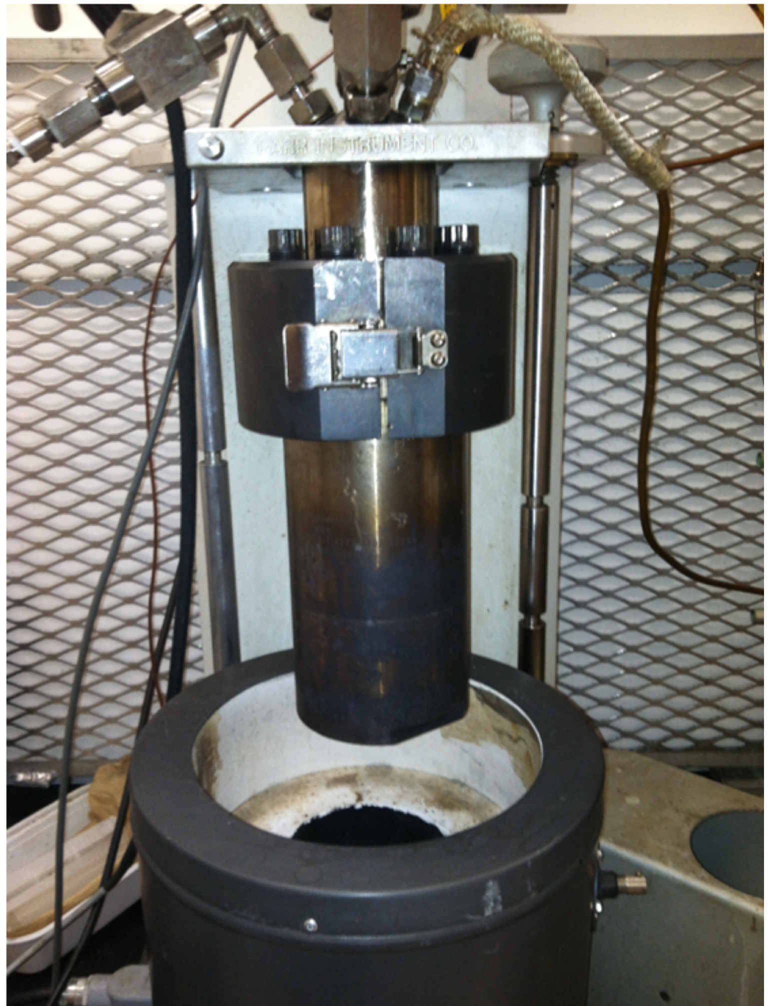


Application of electrospray ionization (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) for identification of biochar toxins



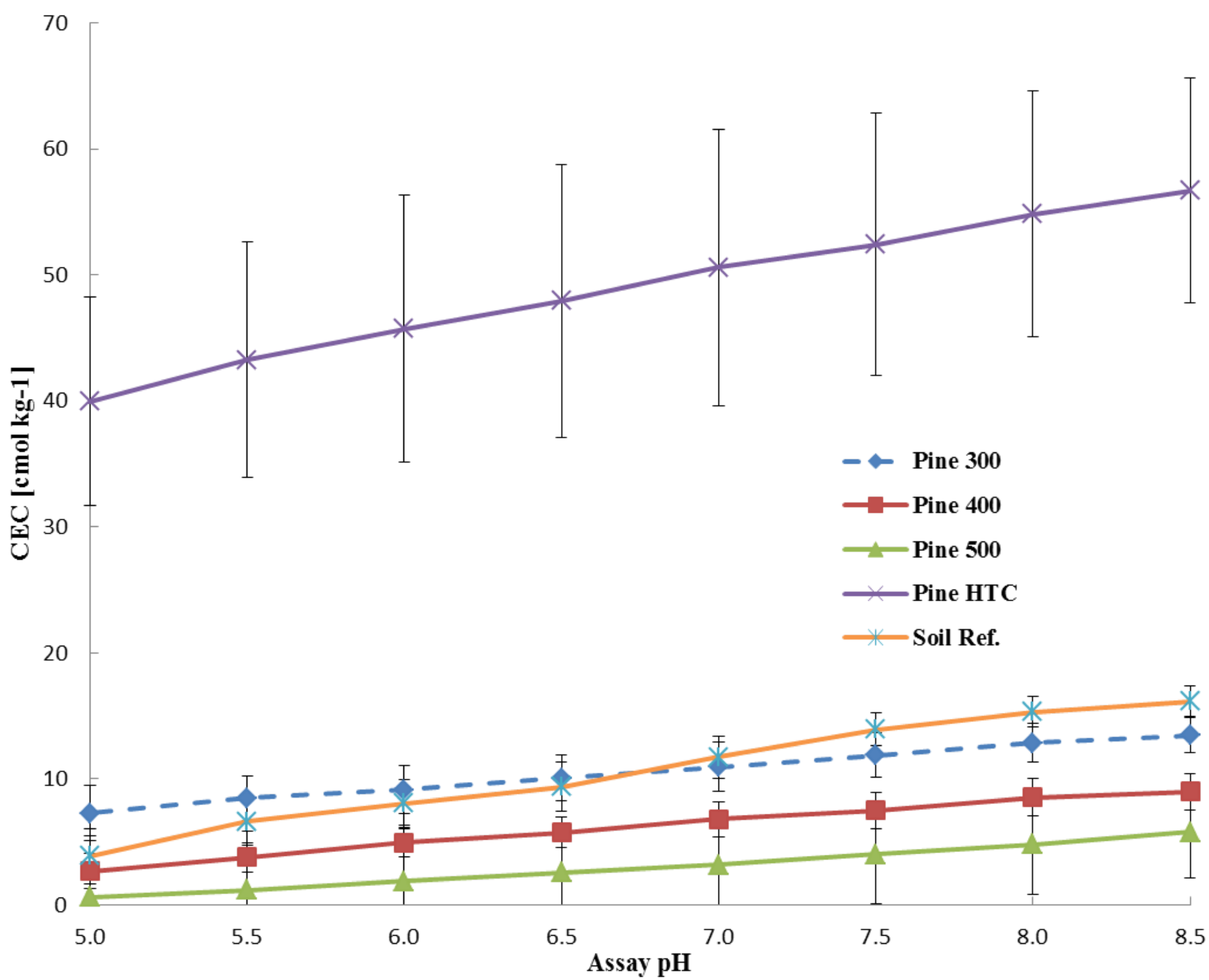
Testing of Biochar Production at ODU

Biochars Produced Through Different Thermoconversion Processes Were Comparatively Studied: Slow (30 min) Pyrolysis and Hydrothermal Conversion using a reactor at Dr. Kumar's lab



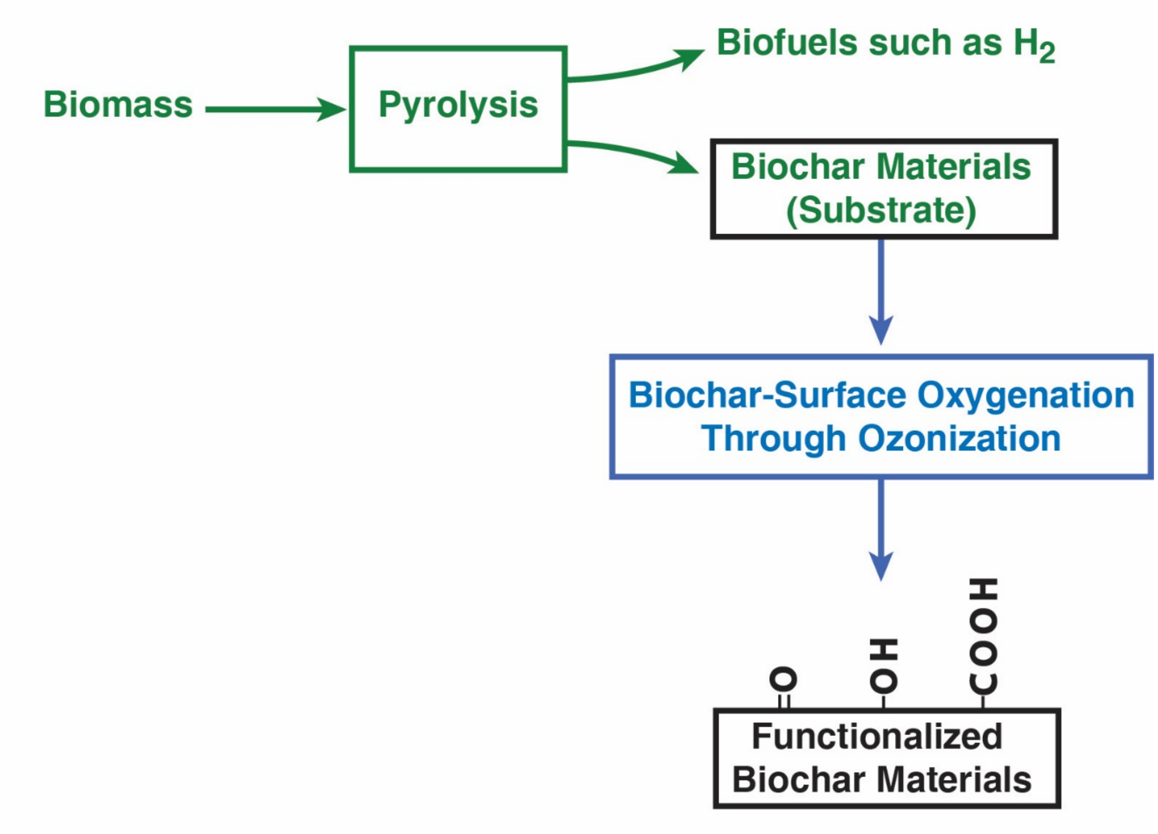
Comparative Analysis of Biochars Produced at ODU

Cation exchange capacity of biochars and soil reference sample



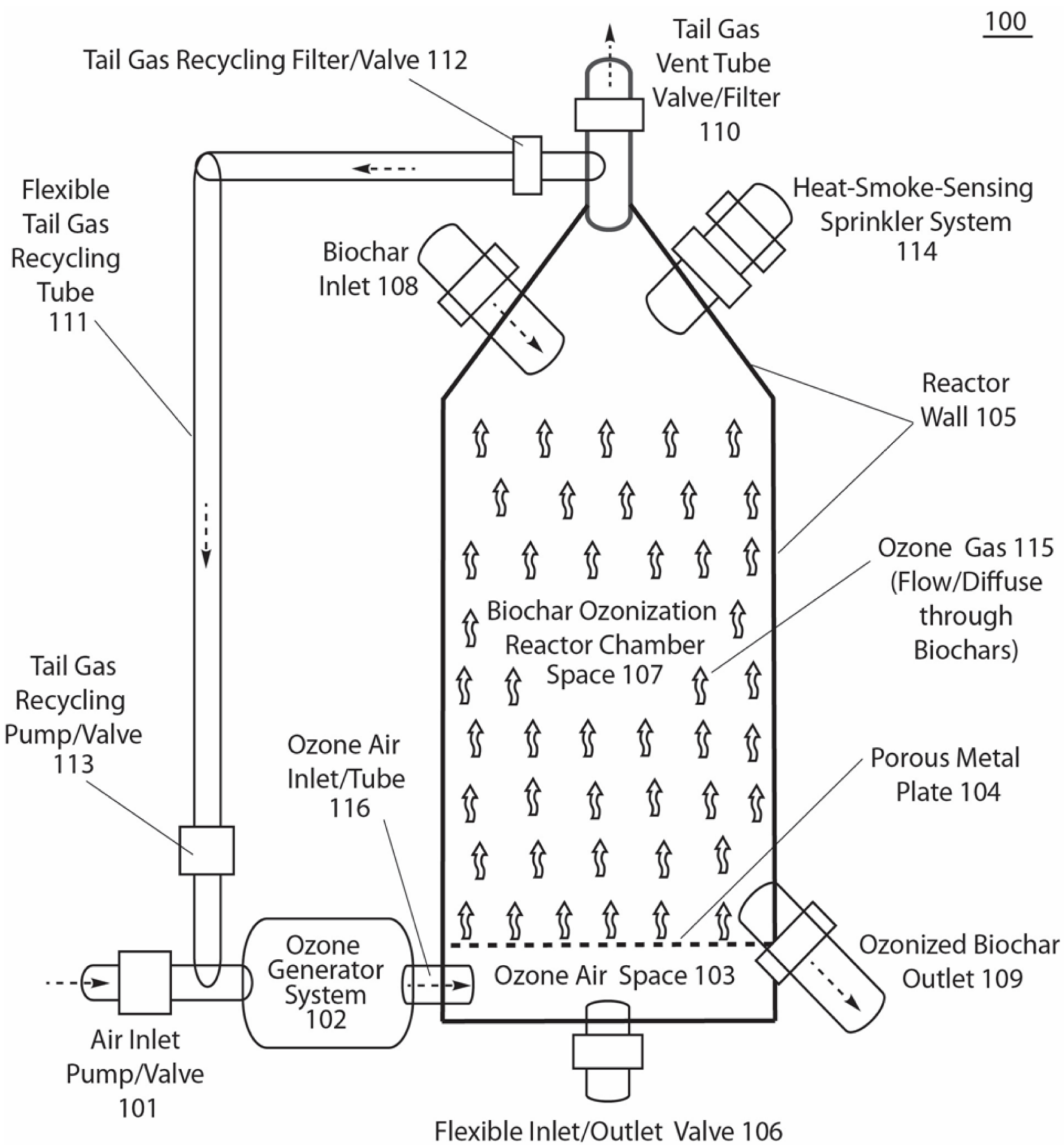
Developing surface-oxygenated biochar through ozonization

Lee JW (2015) Ozonized biochar compositions and methods of making and using the same, Patent Application pending

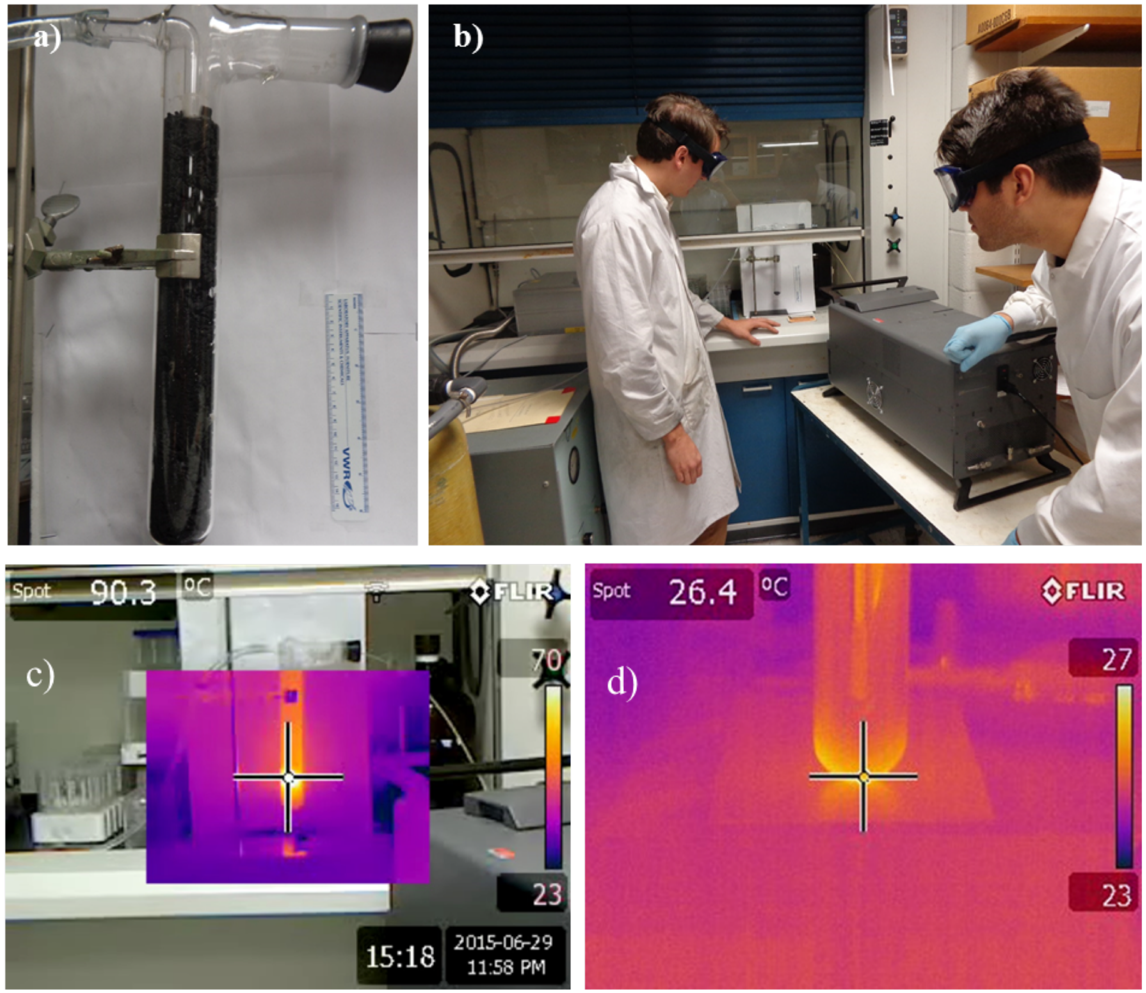


Developing surface-oxygenated biochar through ozonization

Biochar ozonization treatment reactor system



Biochar Surface Oxygenation with plasma-based O_3 treatments



Ozone Treatment Reducing Biochar pH and Improving Cation Exchange Capacity

Table 1. Summary data for pH, CEC, and Methylene blue adsorption.

Sample	pH	CEC mmol/kg	Methylene Blue Adsorption mg/g
Untreated	7.30 ± 0.39	153.9 ± 15.9	1.79 ± 0.18
30 Min O_3	5.46 ± 0.40	302.6 ± 32.3	9.22 ± 0.18
60 Min O_3	5.33 ± 0.28	310.3 ± 24.4	9.45 ± 0.07
90 Min O_3	5.28 ± 0.33	326.9 ± 25.1	9.35 ± 0.04
Ref. Soil	N/A	131.8 ± 9.6	N/A

The Possible Chemistry of Biochar-Surface-Oxygenation With Ozonization Improving Cation Exchange Capacity

According to our preliminary understanding, the most significant reactions of O_3 with organic matter are likely based on the cleavage of the carbon double bond, which acts as a nucleophile having excess electrons. For example, the injected O_3 air stream may, to some extent, lead to the formation of carbonyl and carboxyl groups on biochar surfaces, by reacting with certain C=C double bonds of biochar materials at ambient pressure and temperature:

$$\text{Biochar-CH=CH-Biochar} + O_3 \rightarrow \text{Biochar-COH} + \text{Biochar-COOH}$$

In this aspect, the ozonized biochar product will: 1) become more hydrophilic since both carbonyl and carboxyl groups can attract water molecules; and 2) have higher CEC since the carboxyl groups readily deprotonate in water and result in more negative charge on the biochar surfaces:

$$\text{Biochar-COOH} \rightarrow \text{Biochar-COO}^- + H^+$$

Latest Result: Use of this ozonization technology improved the CEC value of Oregon Biochar Solutions' "Rogue Biochar" by a factor of 5 from 14 to 84 cmol/kg

Solubilize Phosphate from "Insoluble" Phosphate Materials Using Ozonized Biochar

Phosphorus sustainability has recently been identified by both USDA and NSF as one of the major issues for long-term agricultural and environmental sustainability on Earth

$$Ca_{10}(PO_4)_6(OH)_2 + \text{Biochar-COOH} \rightarrow HPO_4^{2-} + Ca_9(PO_4)_5(OH)_2^{+} + \text{Biochar-(COOCa)}^{+}$$

Preliminary experimental results on phosphate solubilization of Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ with ozonized biochar

Solubilizing Treatment (for 2 Days)	Solubilized Phosphate Concentration
Hydroxyapatite (0.5 g) in 20 ml water with 1 g of ozonized biochar	272±9 mg/L
Hydroxyapatite (0.5 g) in 20 ml water (Control)	25±1 mg/L
Hydroxyapatite (0.5 g) in 20 ml water with 1 g of conventional biochar	42±9 mg/L

Summary

1. Biochar cation exchange capacity (CEC) is a key property central to help retain soil nutrients and reduce fertilizer runoff protecting agroecosystem water quality;

2. Biochar with higher CEC value would be highly desirable for industrial applications including the use of biochar as water filtration material and/or soil amendment;

3. We have now experimentally demonstrated that biochar surface oxygenation with inexpensive ozonization can dramatically improve biochar CEC value by a factor of nearly 2; improved the CEC value of Oregon Biochar Solutions "Rogue Biochar" by a factor of 5 from 14 to 84 cmol/kg.

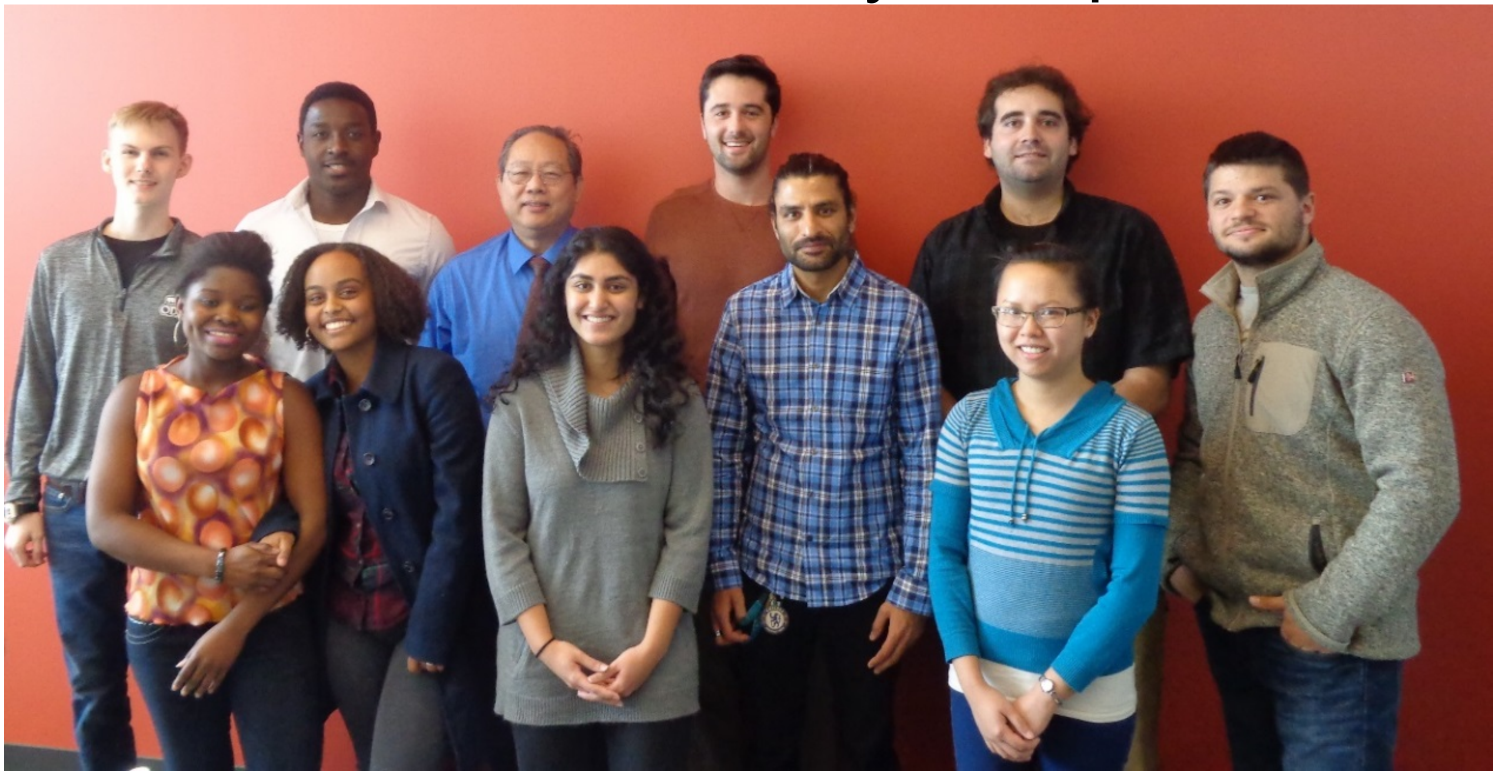
4. Possible biochar ozonization chemistry: the injected O_3 may lead to the formation of carbonyl and carboxyl groups on biochar surfaces, by reacting with certain C=C double bonds of biochar materials at ambient pressure and temperature:

$$\text{Biochar-CH=CH-Biochar} + O_3 \rightarrow \text{Biochar-COH} + \text{Biochar-COOH}$$

5. Surface-oxygenated biochar may be used to solubilize phosphate from "insoluble" phosphate materials including phosphate rock materials such as hydroxyapatite for phosphorus sustainability.

Acknowledgements

Lee Laboratory Group



Thanks for Funding Support:

1) ODU Multidisciplinary Seed Funding Program

2) Lee Laboratory start-up funds

Preliminary Economic Estimate For Doubling Biochar CEC Value from 150 to 300 mmol/kg through Ozone-Enabled Biochar Surface Oxygenation

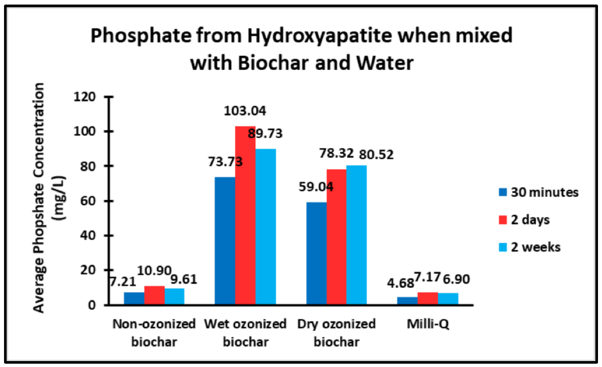
Amount of O_3 required	**7200 g per ton biochar**
Amount of electricity to generate O_3	158.4 kW per ton biochar*
Cost of electricity to generate O_3	$10.50 per ton biochar
Assuming 50% for other processing costs	$10.50 per ton biochar
Total biochar ozonization processing cost	$21 per ton biochar

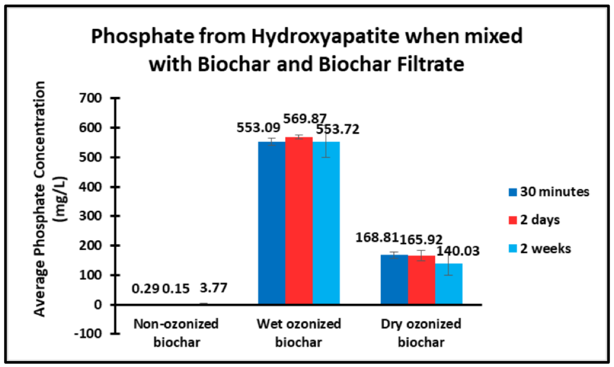
*Using a Primozone Model GM-18 Ozone Generator that generates 900 g of O_3 per hour with energy power consumption at 19.8 kW with industrial electricity price of 6.63 cents per kWh.

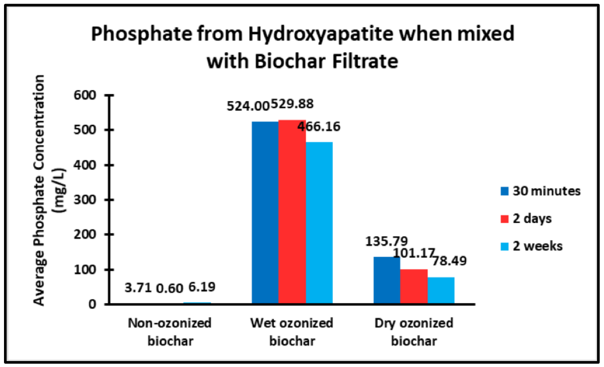
	Biochar for industrial application	**Biochar for industrial application**
Conventional biochar price	$2000 per ton	$500 per ton
Ozonized biochar value	$4000 per ton	$1000 per ton
Biochar value improvement by ozonization	$2000 per ton	$500 per ton
Biochar ozonization cost (Investment)	$21 per ton	$21 per ton
Return (profit)/Investment	$94.2/$1	$22.8/$1

Hydroxyapatite Phosphate Solubilization Assays with Ozonized Biochar

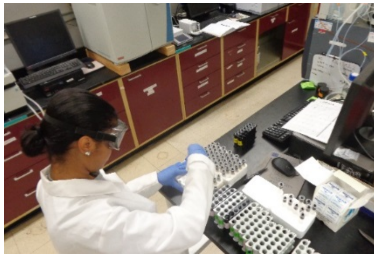
- **Measured the phosphate concentration of all of the samples using the Ion Chromatography System in Dr. Kumar's Lab (Kaufman Hall)**



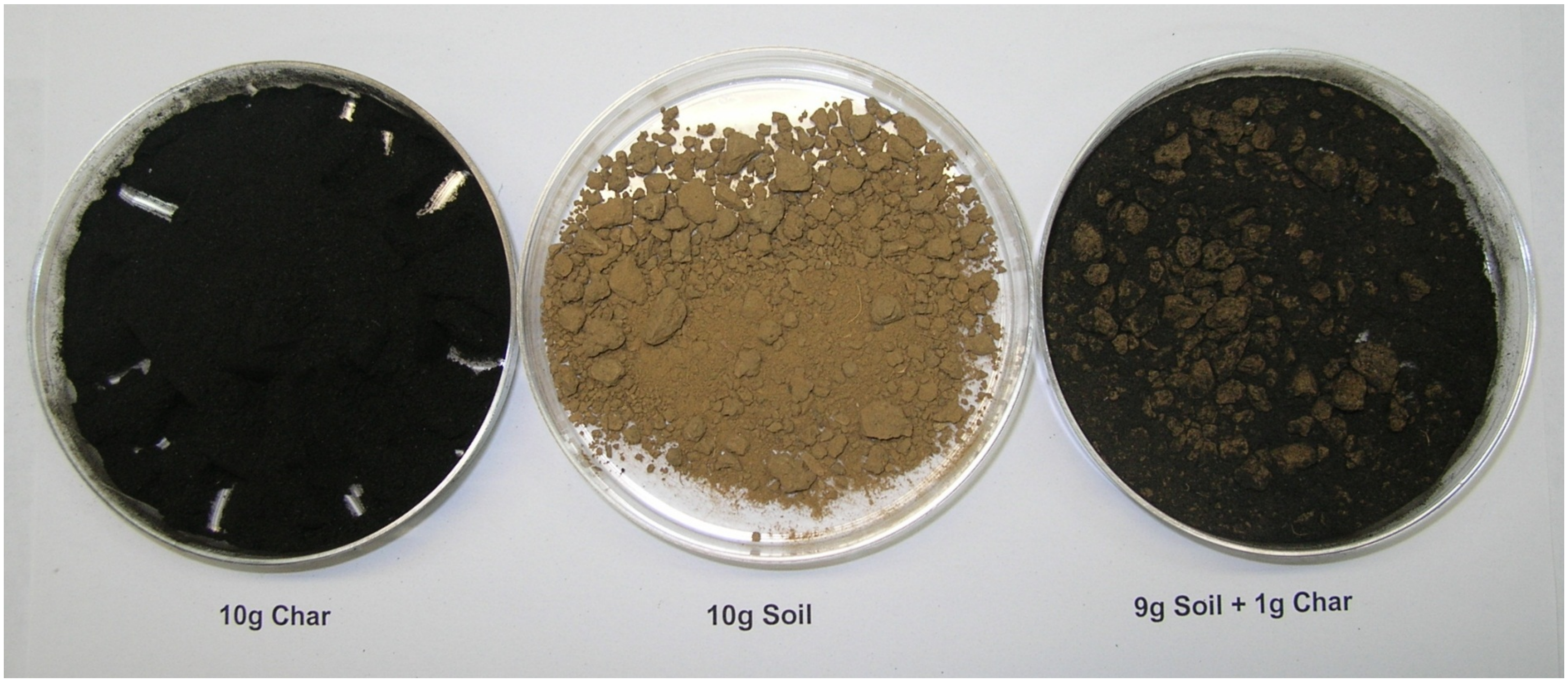




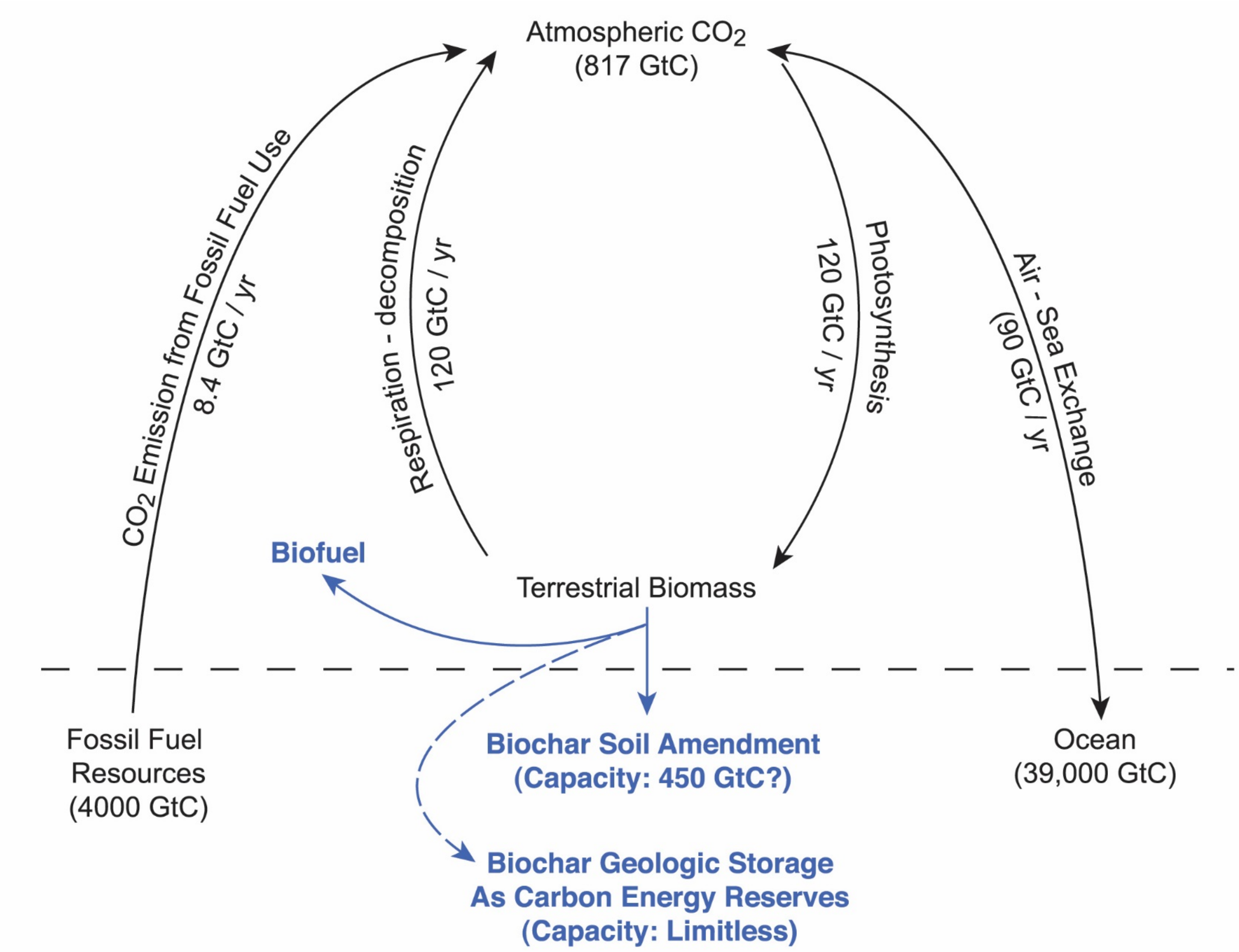
- Highest phosphate concentration came from the wet ozonized biochar for all of the conditions
- Wet ozonized biochar phosphate concentration increased and then decreased



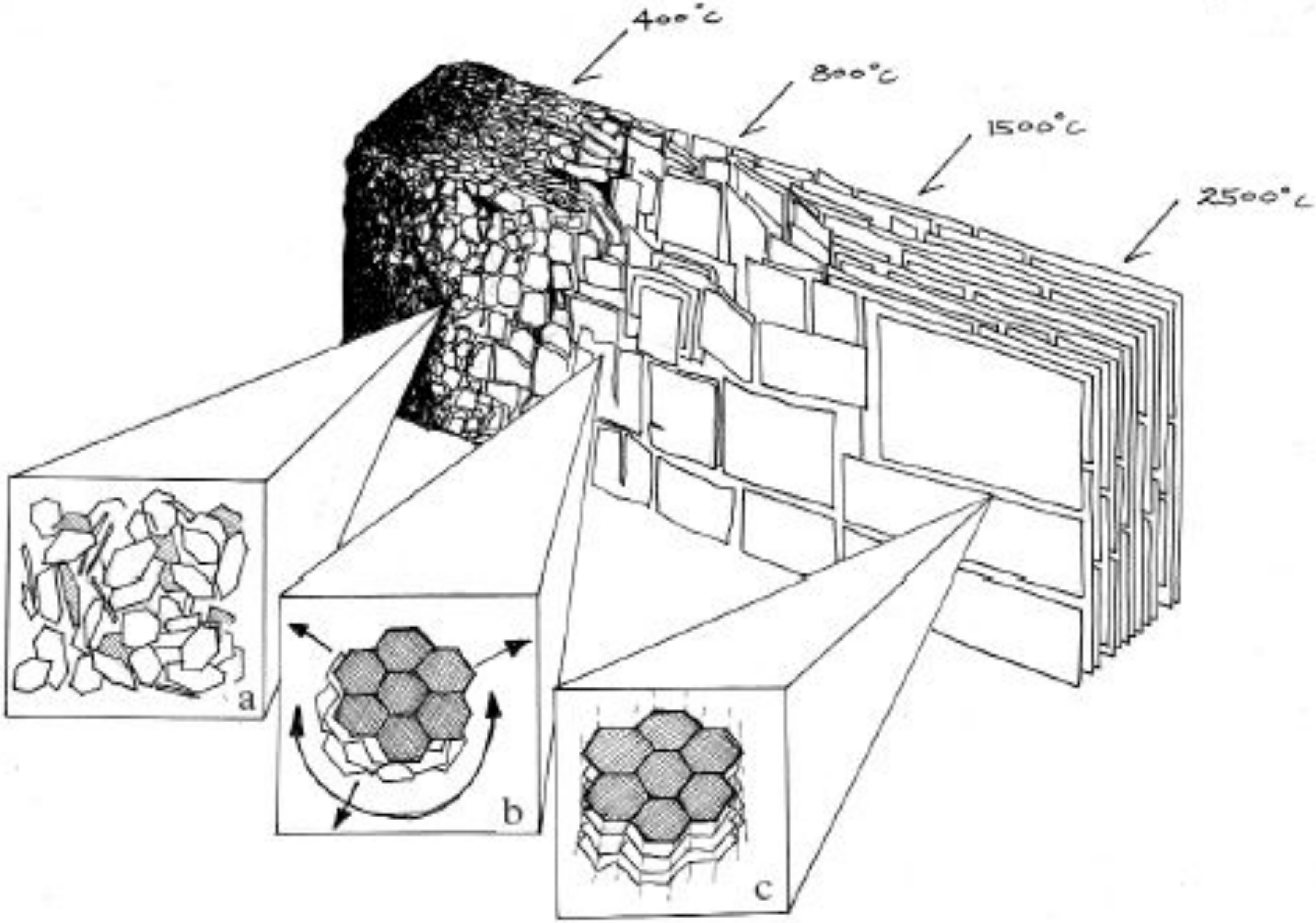
The possibility of using biochar material as a soil amendment and carbon sequestration agent



Global carbon cycle and the envisioned "carbon-negative" biomass-pyrolysis biochar approach for carbon capture/sequestration

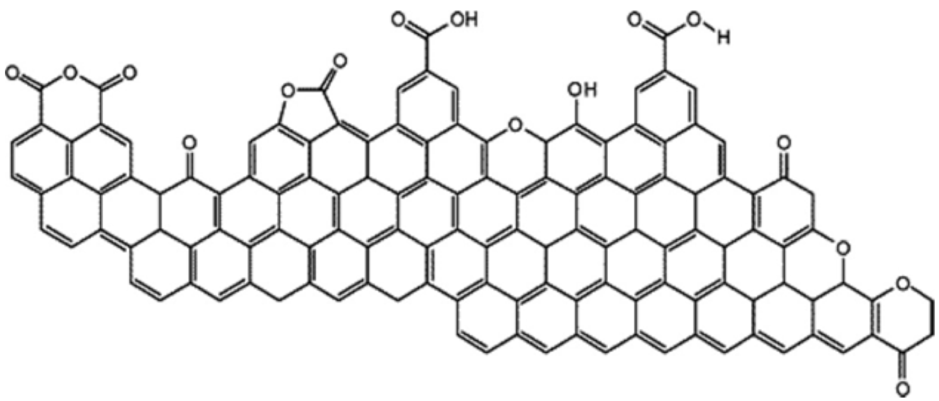


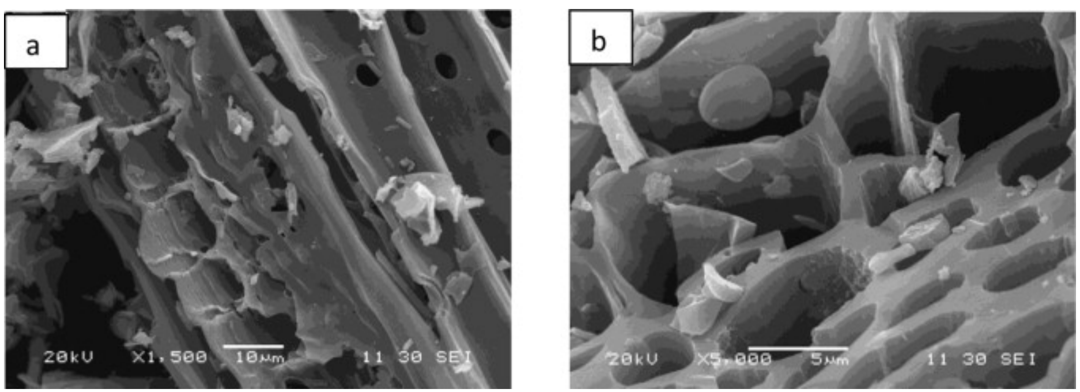
Highest Treatment Temperature (HTT)

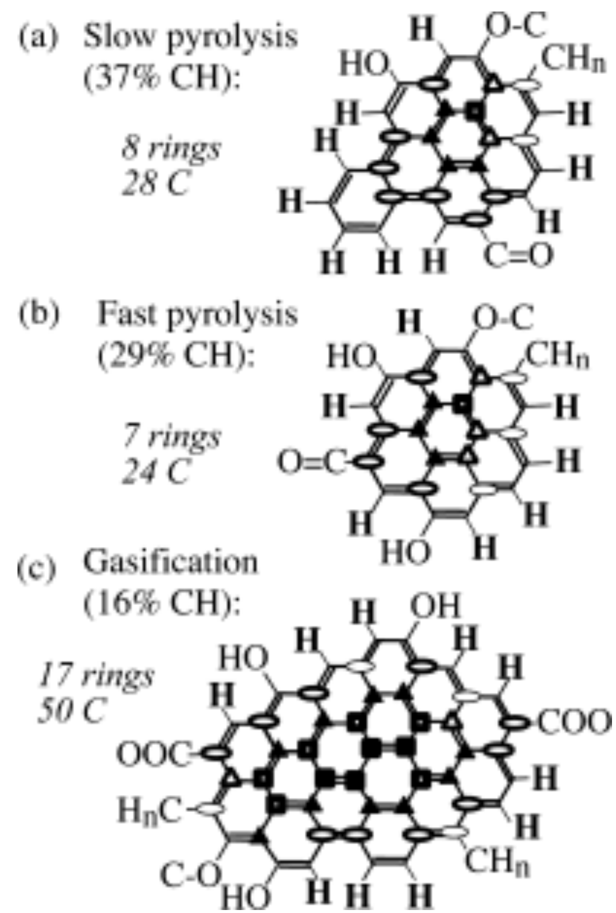


Joseph, Stephen; Lehmann, Johannes (2012-05-16). Biochar for Environmental Management: Science and Technology

Biochar Structures







Environmental Progress & Sustainable Energy Volume 28, Issue 3, pages 386-396, (2009)

Abdel-Fattah, Tarek M., et al. "Biochar from woody biomass for removing metal contaminants and carbon sequestration." *Journal of Industrial and Engineering Chemistry* (2014).

Developing surface-oxygenated biochar through ozonization

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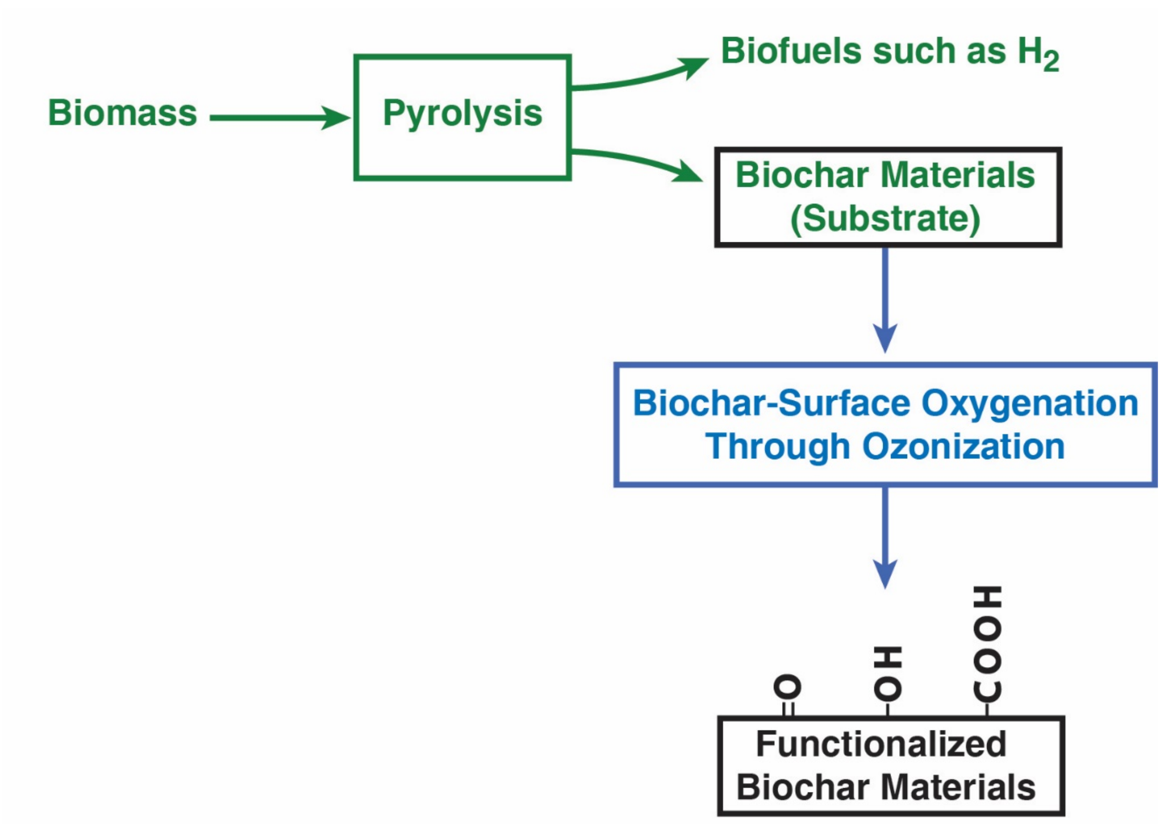
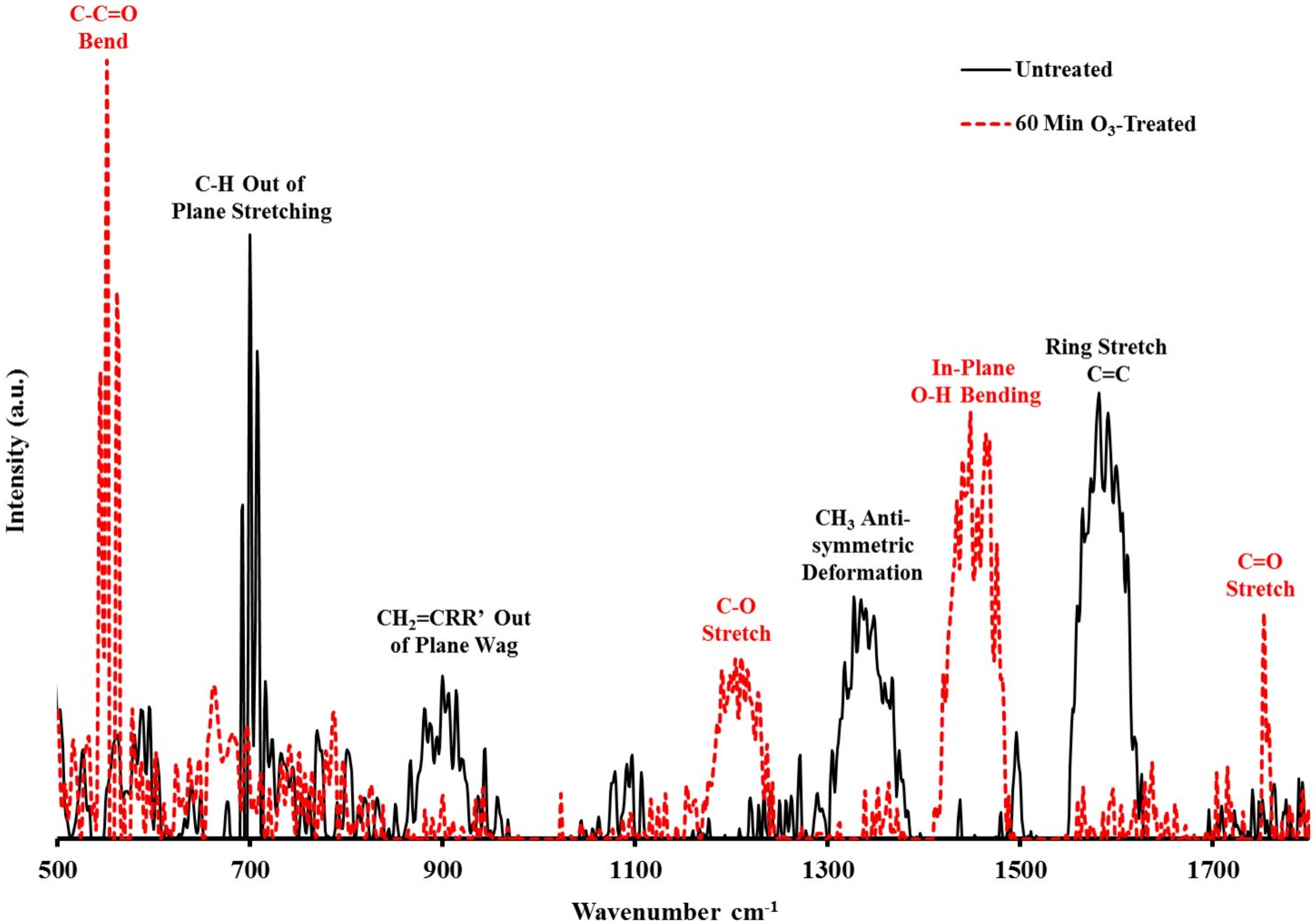
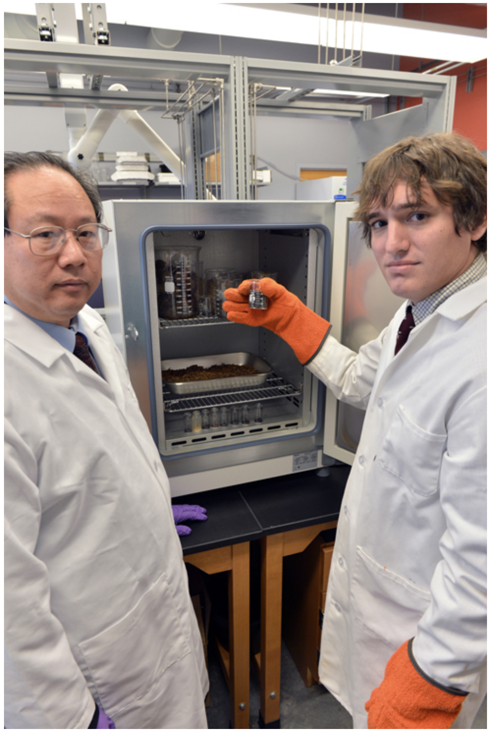


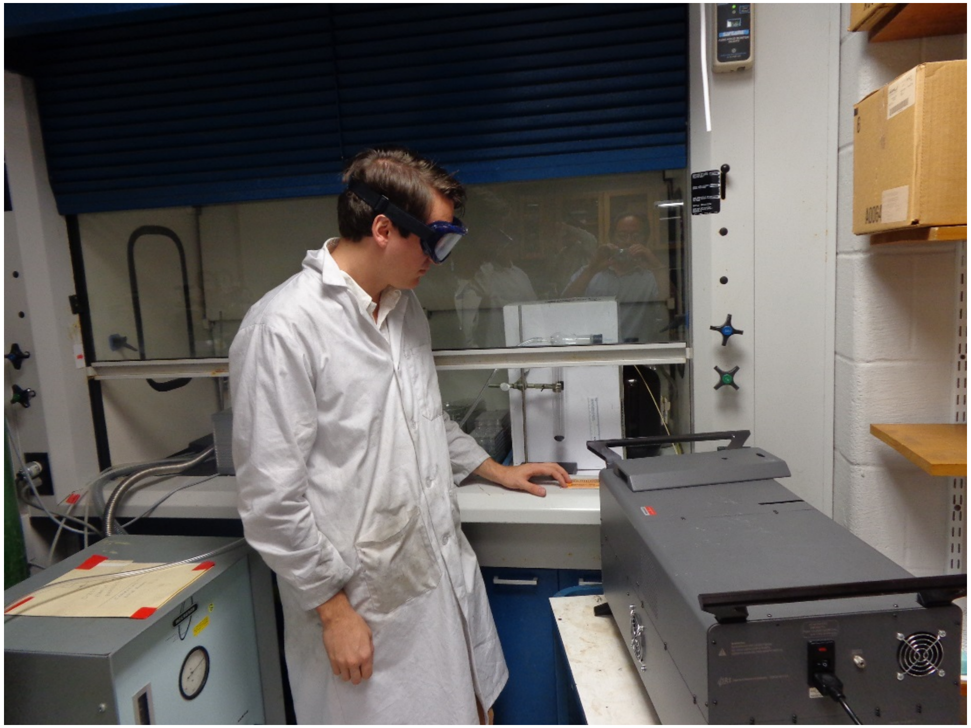
Biochar Raman Spectroscopy Showing Ozone-Enabled Biochar-Surface Oxygenation



Developing High-Tech Biochar with higher cation exchange capacity and free of toxins

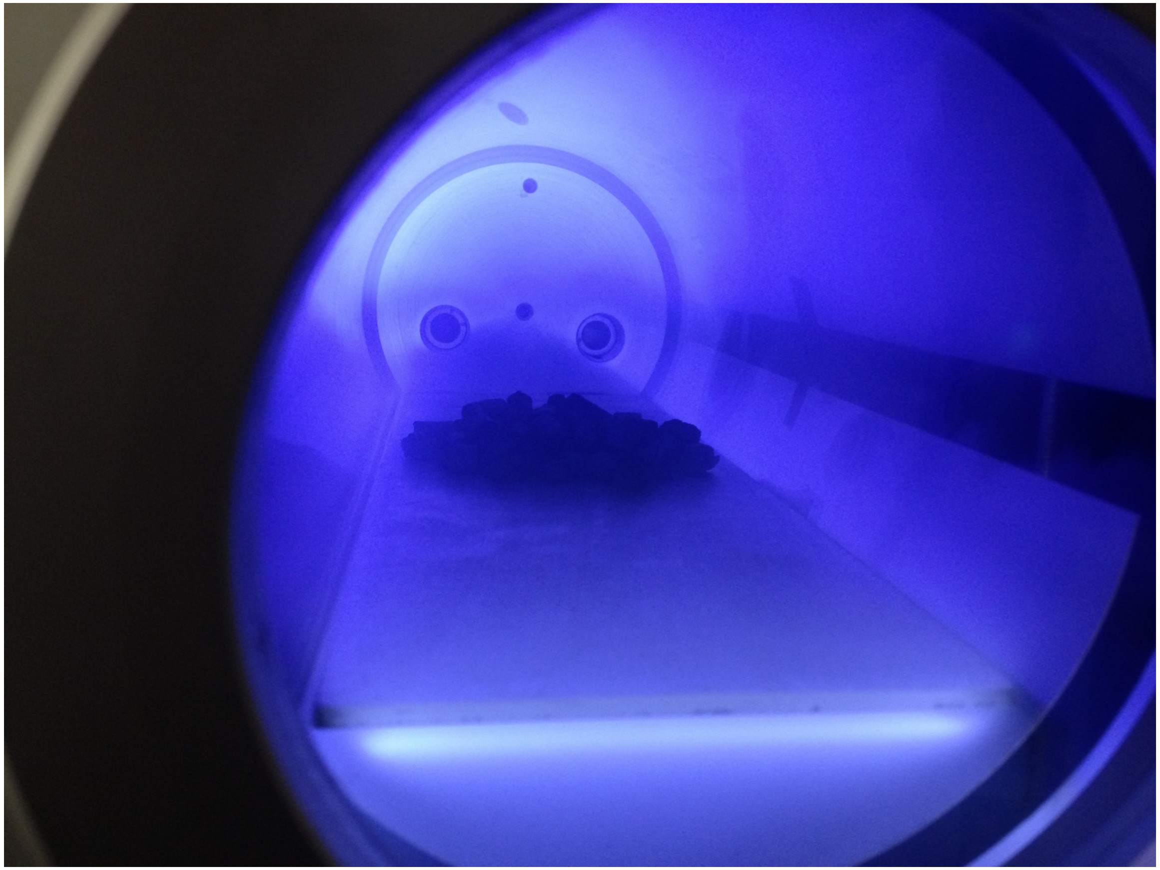
Approach: Carboxylation of biochar materials through innovative application of $O_3/O_2/CO_2$ plasma treatments (Lee Lab)



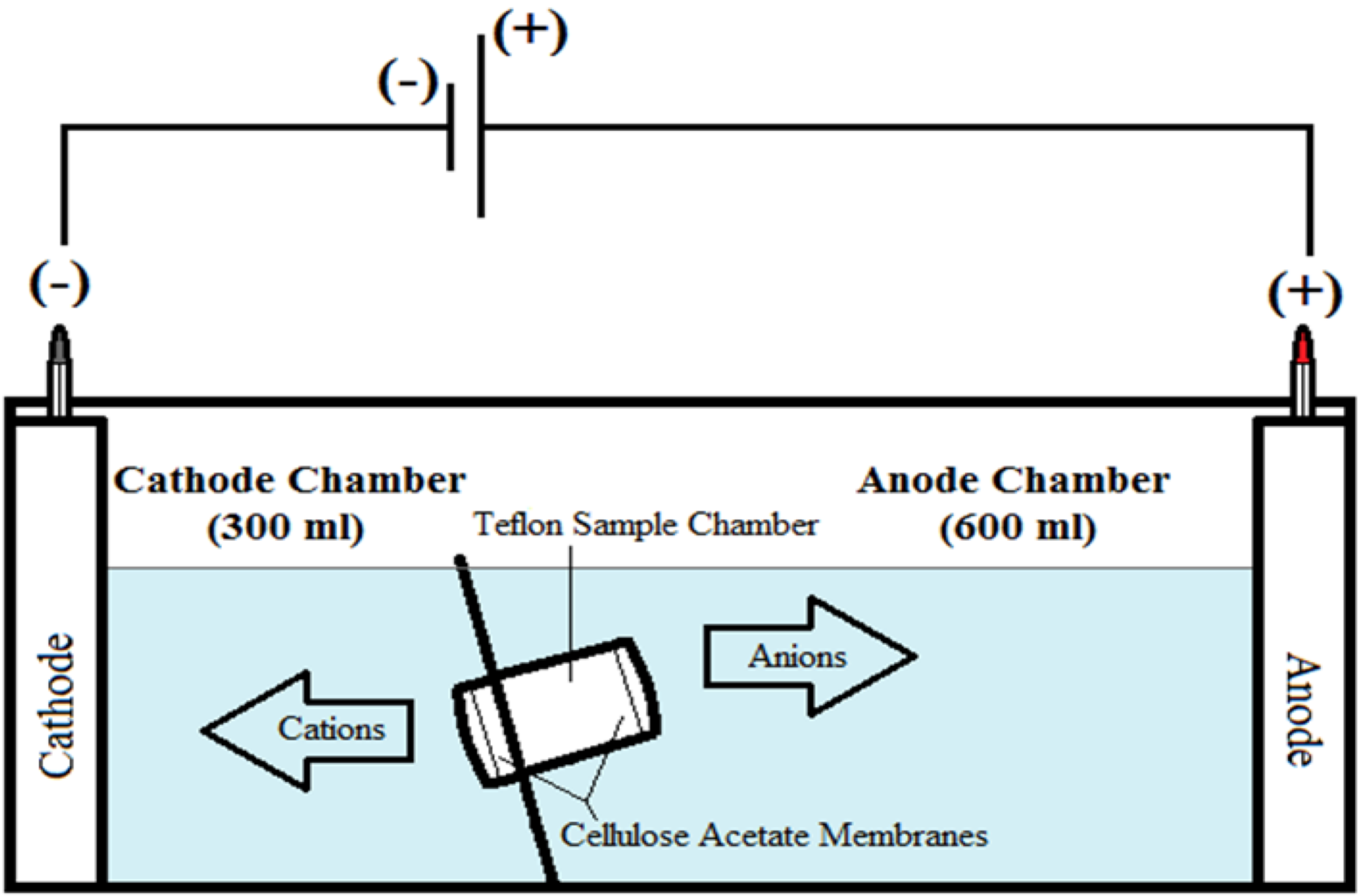


Developing High-Tech Biochar with higher cation exchange capacity and free of toxins

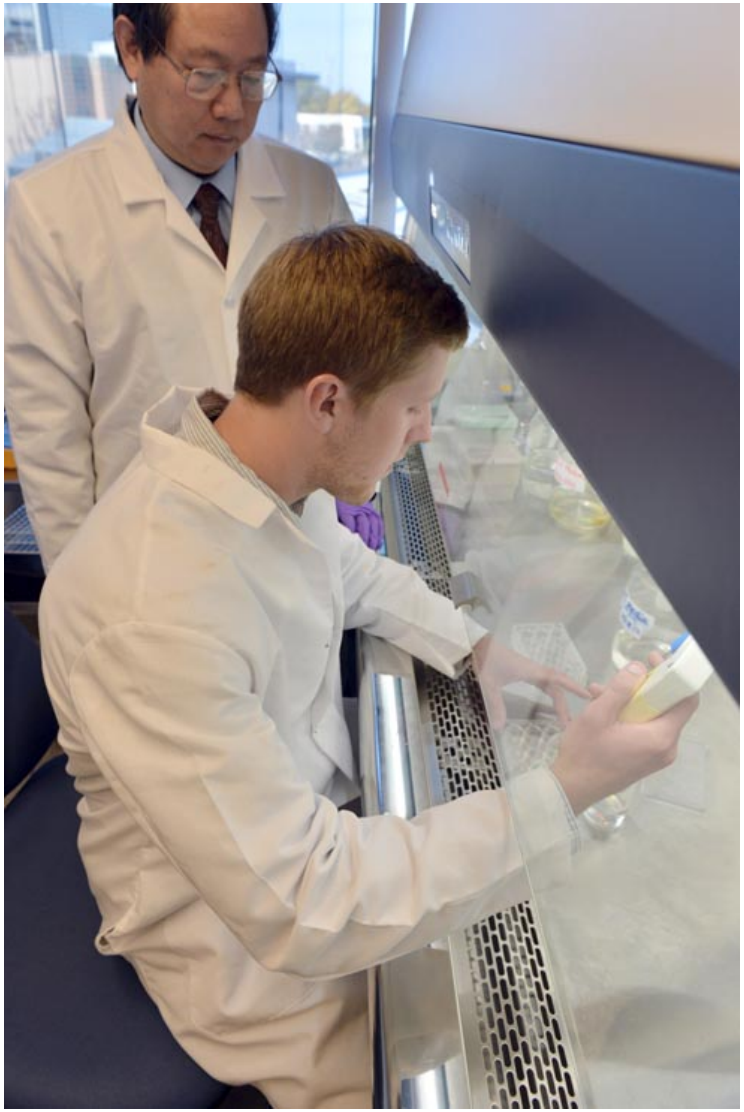
Approach: Carboxylation of biochar materials through innovative application of CO_2 plasma treatments (Lee Lab)



Separation of biochar toxins from water-extracted substances through electrodialysis



Discovered: some of the biochar water extractable substances are toxic to algal growth



Smokeless Biomass Pyrolysis for Producing Advanced Liquid Biofuels and Biochar